Russian Chemical Reviews **77** (11) 995 – 1016 (2008) © 2008 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2008v077n11ABEH003787

Catalytic production of hydrogen from methanol for mobile, stationary and portable fuel-cell power plants

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Abstract. Main catalytic processes for hydrogen production from methanol are considered. Various schemes of fuel processors for hydrogen production in stationary, mobile and portable power plants based on fuel cells are analysed. The attention is focussed on the design of catalytic reactors of fuel processors and on the state-of-the-art in the design of catalysts for methanol conversion, carbon monoxide steam conversion and carbon monoxide selective oxidation. Prospects for the use of methanol in on-board fuel processors are discussed. The bibliography includes 198 references.

I. Introduction

Catalytic production of hydrogen from methanol is promising for fuel-cell based power generation.[1] The density of the energy stored in modern fuel cells is 20 times higher compared with the best Li-ion cells. The energy efficiency of solid oxide fuel cells (including utilisation of heat) exceeds 70% and even 80% (*cf.* 30% – 37% for fuel combustion), being as high as 40% – 50% for proton-exchange membrane (PEM) fuel cell vehicles (*cf.* 20% – 35% for internal combustion engines). Interest in methanol as source of hydrogen for power generation is due to its advantages over pure hydrogen and other fuels, namely, higher energy density and hydrogen production rate, convenience for transportation and storage, economic benefits and safety. As to hydrogen, its transportation and storage are difficult. Liquid hydrogen can only be stored at low temperatures and high pressures. The use of hydrides is inefficient because of low hydrogen concentration (at most 8%), high storage medium unit weight, low energy density, passive mechanism of H_2 recovery and high cost.[2–4] Hydrogen storage in nanostructured carbon is still far from practical implementation.[5] A compromise is provided by compressed hydrogen, which has been used in some automotive vehicles. The difficulties related to gas storage gave an impetus to intensive research aimed at producing hydrogen from more easy-to-handle liquid fuels. Hydrogen production by electrolysis of water is very costly and its percentage is only 4% worldwide. Chemical production of hydrogen by, *e.g.*, oxidation of natural gas to synthesis gas is four times cheaper. Other chemical compounds can also act as sources of hydrogen. For instance, a portable technique developed by the QinetiQ research company (UK) uses aminoborane NH_3BH_3. But methanol remains the best candidate because hydrogen production from MeOH occurs at lower temperatures compared to processes involving other organic compounds. Methanol reforming requires temperatures in the range 250 – 300 °C in contrast to 800 – 900 °C needed for petrol reforming. Methanol is characterised by high H : C ratio, which provides the lowest level of carbon black formation compared to other compounds. Methanol contains no sulfur and can be obtained from renewable sources. It is readily oxidised. Note that methanol reforming processes have been best studied to date.

Hydrogen production from methanol for automotive PEM fuel cells or stationary power plants involves the use of fuel processors. Of course, this leads to complication of the design of automotive vehicles, so some warm-up time is needed. To ensure immediate start of such vehicles, the energy stored in an accumulator is spent for a few minutes. On-board hydrogen production is performed using methanol reforming in fuel processors. This process is not a direct methanol oxidation in fuel cells. At present, the idea of using methanol without reforming is practically implemented in direct methanol fuel cells. In this case, hydrogen and CO_2 are produced from methanol and water immediately at the fuel cell electrode. This technology has been intensively commercialised on the portable personal electronics market. To this end, methanol is produced in small cartridges and, *e.g.*, a cell phone equipped with such a cartridge can operate for a period of a month.

Intensive research and development of reactors and catalysts for methanol reforming for stationary, mobile and portable power plants and fuel cell based devices has been carried out. The aim of this review is to discuss the

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Received 28 February 2008
Uspekhi Khimii **77** (11) 1065 – 1087 (2008); translated by A M Raevskyi

state-of-the-art in this field and to critically analyse the prospects for using methanol in hydrogen energetics.

II. Catalytic processes of hydrogen production and methanol reforming reactors

1. General principles

Hydrogen can be extracted from methanol using the following four different processes.[6–10]

1. Methanol decomposition to carbon monoxide and hydrogen in the absence of water and oxygen

$$CH_3OH \rightleftharpoons CO + 2H_2;\ \Delta H^\circ_{298} = 92.0\ kJ\ mol^{-1}$$

followed by direct reaction of CO steam reforming

$$CO + H_2O \rightleftharpoons CO_2 + H_2;\ \Delta H^\circ_{298} = -41.2\ kJ\ mol^{-1}.$$

2. Partial oxidation of methanol in the presence of oxygen only

$$CH_3OH + 0.5\,O_2 \rightleftharpoons CO_2 + 2H_2;$$

$$\Delta H^\circ_{298} = -192.2\ kJ\ mol^{-1}.$$

3. Steam reforming of methanol in the presence of water vapour only

$$CH_3OH + H_2O \rightleftharpoons CO_2 + 3H_2;$$

$$\Delta H^\circ_{298} = 49.4\ kJ\ mol^{-1}$$

followed by a reaction, which is the reverse of CO steam reforming, until attainment of equilibrium

$$CO_2 + H_2 \rightleftharpoons CO + H_2O;\ \Delta H^\circ_{298} = 41.2\ kJ\ mol^{-1}.$$

4. Autothermal reforming of methanol in the presence of water vapour and oxygen (oxygen-steam, or combined, reforming)

$$4CH_3OH + 3H_2O + 0.5\,O_2 \rightleftharpoons 4CO_2 + 11H_2;$$

$$\Delta H^\circ_{298} = 0.0\ kJ\ mol^{-1}.$$

The decomposition and steam reforming of methanol are endothermic processes, CO steam reforming and partial oxidation of methanol are exothermic ones and autothermal reforming of methanol is characterised by zero enthalpy. The decomposition of methanol to CO and H_2 has been intensively studied by many researchers, because syngas obtained from methanol is more efficient than petrol and conventional methanol (by about 60% and 34%, respectively).[11] The choice of the process of hydrogen production from methanol is the key step in the design of reforming reactors and catalysts. For instance, steam reforming of methanol seems to be the most appropriate for implementation in power plants for automotive vehicles. Indeed, stoichiometrically this process is characterised by the largest amount of hydrogen produced (3 moles of H_2 from 1 mole of MeOH), which exceeds the amount of hydrogen in methanol itself (2 moles). However, owing to its exothermicity, partial oxidation of methanol appears to be more energetically favourable than steam reforming of methanol, although being less efficient stoichiometrically (2 moles of H_2 from 1 mole of MeOH).[12] Autothermal reforming of methanol is the most convenient method of on-board production of hydrogen.[6,7,9,13] In this case a mixture of methanol, water and air passes through a catalytic layer. The reactant ratio can be chosen in such a manner that the overall reaction be thermally neutral or weakly exothermic. The advantages of autothermal reforming of methanol are as follows: 1) the reaction occurs at a lower temperature compared to steam reforming of methanol; 2) there is no need for heat transfer from the outside because it is supplied *in situ* due to exothermic reaction of partial oxidation of methanol; 3) fast start of fuel processor; 4) weak exothermicity of the reaction allows one to avoid the 'hot point' typical of partial oxidation of methanol; 5) the reaction results in H_2 containing very low CO concentrations as compared to steam reforming of methanol; 6) production of about 3 moles of H_2 from 1 mole of MeOH under optimal conditions; and 7) potentially, the cheapest fuel processors.

Carbon monoxide, a side product of methanol decomposition and steam reforming of methanol, causes poisoning of platinum anode of a fuel cell. In the case of of steam reforming of methanol, steam reforming of carbon monoxide provides a CO concentration of about 0.5 vol.% (5000 ppm) in the output gas; however, the target for PEM fuel cells is 10 ppm. This requires additional stages of reformate purification using preferential oxidation of CO or methanation:

$$CO + 0.5\,O_2 \longrightarrow CO_2;\ \Delta H^\circ_{298} = -283.6\ kJ\ mol^{-1},$$

$$CO + 3H_2 \longrightarrow CH_4 + H_2O;\ \Delta H^\circ_{298} = -206.2\ kJ\ mol^{-1}.$$

Preferential oxidation of CO is accompanied by partial oxidation of hydrogen produced

$$H_2 + 0.5\,O_2 \longrightarrow H_2O;\ \Delta H^\circ_{298} = -243.5\ kJ\ mol^{-1}.$$

The equilibrium gas compositions for the processes mentioned above in the preferred temperature interval 200–300 °C at different pressure and optimal H_2O : MeOH and O_2 : MeOH ratios have been quite reliably calculated and confirmed experimentally using various catalysts. For instance, the calculated composition of the final mixture for steam reforming of methanol with allowance for CO steam reforming and preferential oxidation of CO at 0.3 MPa and 223 °C is as follows (vol.%): H_2 61.8, CO_2 21.1, H_2O 14.1 and N_2 3.0 (Ref. 14).

2. Methanol fuel processors: flow diagrams and apparatuses

a. Direct oxidation of methanol in fuel cell

Up to date, direct methanol fuel cells (DMFC) have been a single type of power supplies for portable devices; however, recently they have been actively used for mobile and stationary power plants. Direct reforming of methanol accompanied by generation of electricity occurs at temperatures below 150 °C. Replacement of Li-ion cells by DMFC seems to be the most promising application of this type of fuel cells. The advantages in the field of design and improvement of DMFC have been summarised in reviews;[15,16] therefore, here we leave them out of consideration.

b. Indirect methanol oxidation in fuel cell

Fuel processors are designed to produce hydrogen from hydrocarbon fuel for further use in fuel cells. The type and operation of fuel processors depend on the type and particular application of the fuel cell. We will restrict ourselves to consideration of the fuel processors for low-

temperature PEM fuel cells operating at temperatures of at most 100 °C.

Among low-temperature methanol fuel processors, on-board fuel processors for automotive vehicles have been best elaborated.[17–19] Their designs are almost identical to those of fuel processors for power plants and high-temperature petrol fuel processors. The differences consist in physical dimensions and the start time of apparatuses, namely, reactors for transport should be as compact as possible and have short start times, whereas fuel processors for stationary power plants can have any dimensions and reduced transient characteristics. Yet another distinctive feature of the design of fuel processor for transport is the method of fuel reforming, the autothermal reforming being the most preferable. Despite the fact that the yield of H_2 in steam reforming of methanol can be as high as about 70 vol.% – 80 vol.% *vs.* ~35 vol.% – 45 vol.% for partial oxidation of methanol (this reduces the fuel cell efficiency), low response of the former process to transition regimes dictates the use of autothermal reforming of methanol.[18] The key components of a fuel processor are shown in Fig. 1.

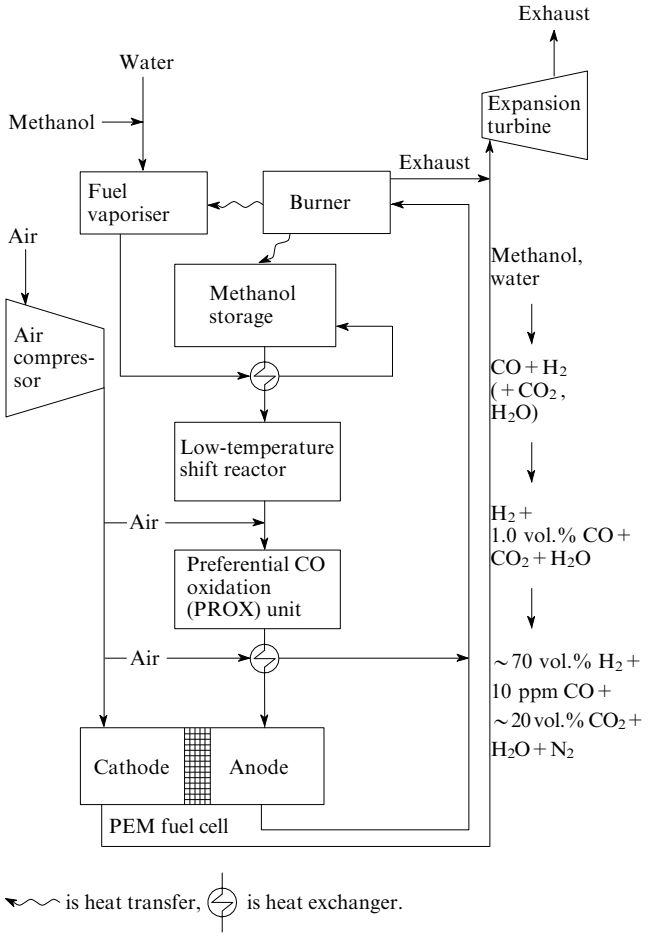


Figure 1. On-board methanol steam reformer/PEM fuel cell system.[17]

The fuel mixture package includes a methanol tank; a methanol/water mixture is fed to a vaporiser and then heated with gases transfered from afterburner, which serves for afterburning of hydrogen-containing anode off-gases. The afterburner also supplies heat for the methanol steam reforming reactor. The water vapour/methanol mixture is passed from the vaporiser to a recuperative counter-flow heat exchanger placed after the steam reforming reactor and is then fed to the steam reforming reactor. Steam reforming of methanol produces syngas, which passes to a low-temperature CO shift reactor through a recuperative heat exchanger. Then, the hydrogen-containing gas (reformate) is mixed with air for oxidation reforming of CO to occur in a preferential CO oxidation unit. The low-temperature CO shift reactors and the preferred CO oxidation reactors are designed to reduce the CO concentration in the hydrogen-containing gas to 10 ppm, which is necessary for operation of PEM fuel cells. In some cases the preferential CO oxidation units are replaced by pressure swing absorbers. In the flow diagram shown in Fig. 1, compressed air is fed to the preferential CO oxidation unit (PROX), to the cathodic cell of the PEM fuel cell and to the afterburner; then, a mixture of exhaust gases is fed to the expansion turbine and is released into atmosphere.

From the aforesaid it follows a multistage design of the methanol fuel processor. It includes reactors for various chemical reactions with different catalysts to occur in different temperature regimes. This process train characterises the early stage of the development of fuel processors; it was designed for a particular type of fuel. Using this flow diagram a 75-kW methanol autothermal fuel processor has been recently developed in China; the device comprised a reactor for autothermal reforming of methanol, a CO shift reactor and a preferential CO oxidation unit.[20] The next step involves the development of multifuel processors which can flexibly be tuned for operation using any type of hydrocarbon materials from methane to light gas oil. Recently, there has been a trend towards transition from multi-apparatus fuel processors to compact single-unit ones. This avenue of research is associated with the use of membrane technology, which allows fuel reforming and (one-step) extraction of hydrogen to proceed simultaneously in the same reactor. In this case the reactor can be called a fuel processor. Such reactors-processors have been most intensively developed for transport.[21] Figure 2 presents the schemes of traditional and membrane fuel processors.

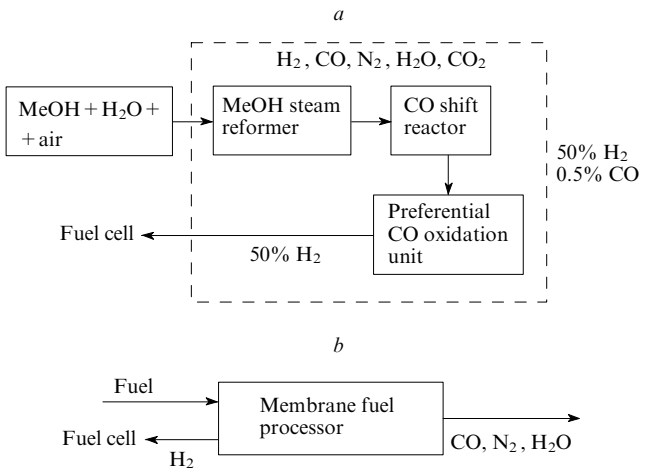


Figure 2. Block schemes of traditional (*a*) and membrane (*b*) fuel processors for production hydrogen for fuel cells.
Dashed line frames the apparatuses in the traditional fuel processor, which are replaced by a single reactor in the membrane fuel processor.

A single-modulus, micro-scale second-generation fuel processor (power plant) for microelectronic devices with a thermal efficiency of 33% was reported.[22] The methanol fuel processor (volume 0.2 cm^3, mass less than 1 g) comprises a catalytic combustion unit (volume 5 mm^3), a reactor (volume 50 mm^3), methanation reactor for CO extraction and has a performance of 3.55 cm^3 of H_2 per minute. The power density of methanol ($\sim$5.6 kW kg^{-1}) is about 47 times higher than that of Li-ion cells ($\sim$0.12 kW kg^{-1}). Therefore, this power plant is more favourable than Li-ion cells even at low efficiency of methanol conversion to electricity (up to 5%) .

A single-module autothermal microchannel methanol fuel processor consisting of a fuel vaporiser, heat exchanger, reactor and catalytic combustion unit was proposed.[23] This device will be considered in more detail in Section II.3.d.

The flow diagrams of fuel processors considered above include all catalytic stages of hydrogen generation from methanol. In the last two decades they remained almost unchanged, although recently practical implementation of integrated fuel processor with no CO extraction in the CO shift reactor (POX reactor) has been reported.[24] A compact integrated fuel processor comprised a plate-fin reactor and a multistage reactor of preferential CO oxidation (PROX-reactor). A microstructured fuel processor including a catalytic combustion unit, heat exchangers, a methanol steam reforming reactor and a PROX reactor (also without the POX reactor) was reported in another study.[25] This type of fuel processors makes the hydrogen generation process much cheaper. In the case of steam reforming of methanol the flow diagram of fuel processor remains unchanged at elevated pressures of up to 4.5 MPa, although the problem of the 'cold point' in the beginning of the catalytic layer in the reactor still should be solved.[26] Since the weight and dimensions of fuel processor components determine the fields of practical application, their technical characteristics should be determined in advance. This problem can be solved by modelling fuel processors.[27–29]

3. Methanol reforming reactors

a. Traditional reactors of steam reforming of methanol with fixed-bed catalyst layer

Traditionally, reactors for reforming of hydrocarbon fuel are made as fixed-bed reactors. The key components of fuel processors, that is, the methanol reforming reactors, have been intensively developed since 1990, mainly for low-temperature fuel cell vehicles. A review of patent information revealed a general trend towards producton of compact and light methanol reforming reactors with good dynamic properties and rather long operating life. Since complete characterisation of all patented reactors is too cumbersome, we present here a list of references to relevant patents since 1999.

Reactor	Ref.
Reactor for partial oxidation of methanol	30
Compact multifuel reactor	31
Catalytic reactor for steam reforming of methanol	32
Membrane reactor for steam reforming of methanol	33
Monolithic reactor for autothermal reforming of methanol	34
Combined pressure and temperature swing reactor for steam reforming of methanol	35
Reactor for autothermal reforming of methanol	36
Reactors for catalytic pyrolysis of MeOH and CO shift	37
Reactor for steam reforming of methanol with through-the-wall heat integration with CO oxidation reactor	38
Heat-integrated two-stage reactor for steam reforming of methanol	39
Reactor for reforming of MeOH and Me_2O with a thin porous strip coated with Cu – Zn catalyst and a CO oxidation unit with a strip coated with Pt – Ru catalyst with folded fins separating catalytic strips	40
Reactor for steam reforming of methanol, reactors for CO oxidation, catalytic combustion unit	41
Pressure swing reactor for steam reforming of methanol with catalytic combustion unit	42
Catalytic reactors for partial oxidation of MeOH (Fe_2O_3 or SnO_2 on MoO_3) decomposition of MeOH (noble metals on porous metal oxides) steam reforming of formaldehyde (Cu – ZnO on porous metal oxides)	43
Reactor for steam reforming of methanol, heat-integrated with a CO shift reactor with counter-flow of the methanol steam reformer and catalytic burner flows	44
Reactor for steam reforming of methanol using Cu catalyst (thin metal filaments, specific surface area of 10 $m^2 g^{-1}$; or with foil 20 – 50 mm thick) and heater in the reforming zone	45
Reactor for steam reforming of methanol with electrical start using the conducting catalyst layer	46
Reactor for autothermal reforming of methanol	47
Reactor for steam reforming of methanol, heat-integrated with a PEM reactor with bilayer catalyst	48
Reactor for steam reforming of methanol with heat supply from catalytic combustion unit surrounded by the reforming catalyst	49
Reactor for steam reforming of methanol with membrane extraction of hydrogen	50
Compact reactor for steam reforming of methanol with internal cylindrical heater and membrane extraction of hydrogen	51
Compact, light-weight reactor for autothermal reforming of methanol with cylindrical monolithic foam catalyst	52
Reactor for steam reforming of methanol with heat supply from catalytic burner	53
Reactor for autothermal reforming of methanol with inlet of oxygen-containing gas into catalytic layer through porous tubes	54

From this list of the patented apparatuses it follows that reactors with heat integration with the reactors for partial oxidation of methanol or CO shift are most widely used.

A compact methanol reactor (CoMR; power 50 kW with respect to the lower heat value of H_2) for a utility truck was tested.[55–58] To test the CoMR (steam reformer of MeOH on $Cu-Zn/Al_2O_3$ catalyst), a catalytic burner in the form of six hollow ceramic cylinders (diameter 80 mm, height 212 mm) was made.[57] Methanol was mixed with air inside the cylinders. The mixture was fed to the outer side of the cylinder where a metal grid coated with an active layer of catalyst (40 g Pt m^{-2}, thickness 0.52 mm) was placed. The burner was placed under the CoMR and provided a nominal heat power of 16 kW. Calculations and tests showed that the necessary temperature of the 130-kg CoMR was

attained after 22 min. The CoMR tested (separate reaction tube of length 25 cm and diameter 12.2 mm; $Cu-Zn/Al_2O_3$ catalyst load of 35.5 g)[56] showed a specific performance with respect to hydrogen of 7.87 $Nm^3\ kg_{cat}^{-1}\ h^{-1}$ and a methanol conversion of 95% at 280 °C. When operated at increased pressure (up to 2.1 MPa) using a Pd-membrane for extraction of hydrogen, the CoMR showed a MeOH conversion of 86%, which is lower than the theoretical value (99.2%). An identical CoMR having four catalytic tubes was tested at different catalyst loads (10%, 17%, 25% or 50% of the reactor volume).[58] Life-cycle tests carried out over a period of more that 700 h revealed a considerable decrease in the catalyst activity at a load of 10%, which was explained by the loss of 3.5–6.5 mg of the active component per hour. At higher loads, the catalyst activity decreased to a lesser extent and remained unchanged at a load of 50%. This made it possible to determine the amount of catalyst necessary for operation of the CoMR over a period of 6000 h. In addition, the tests showed that a PEM fuel cell based transport system (electric power 400 W, efficiency of the system 42%, theoretical performance with respect to hydrogen 5.2 $Nm^3\ kg_{cat}^{-1}\ h^{-1}$) requires a total of 63 g of the catalyst of methanol reforming.

A 5-kW compact, modular fixed-bed methanol reactor comprising four units (catalytic combustion unit, vaporiser, reactor for steam reforming of methanol and CO shift reactor) was reported.[59] Heat was supplied from the reaction of catalytic oxidation of liquid MeOH pre-sprayed at the inlet of the catalyst layer. To a MeOH/water mixture prepared in a separate unit, oxygen was added (O_2 : MeOH = 0.15) and the mixture was subjected to autothermal reforming. The reactor start time was 4–6 min; shortening of the start time by increasing the O_2 : MeOH ratio led to abrupt increase in the concentration of carbon monoxide.

A fixed-bed reactor for autothermal reforming of methanol with longitudinal air distribution in the catalytic layer using porous ceramic membranes was reported.[60] This method of introduction of the oxidising agent (Fig. 3) made it possible to reduce the temperature in the catalytic layer to at most 300 °C, which is important for retention of the catalytic activity and operating life of the $Cu-ZnO$ catalyst. Stability of autothermal reforming of methanol at pressures in the range 0.18–0.5 MPa and a CO concentration of 0.4 vol.% over more than 50 h was demonstrated. Experimental data were correctly described using a known kinetic model [26,27] assuming that the rates of the oxidation reactions are limited by the oxygen supply.

A 6-kW compact reactor for methanol fuel processor (Hot Spot Methanol Processor, HS; volume 6 litres, total weight 8.8 kg) was proposed.[61,62] Methanol reforming in this device is achieved by combining exothermic partial oxidation and endothermic steam reforming. The reactor comprises a collector and eight reactors for autothermal reforming of methanol attached in parallel to the top and bottom of the collector (Fig. 4). The reactor operates as follows. At start-up, liquid methanol and air (taken in 20% excess) were injected into the collector. Methanol was oxidised by air on the catalyst with heat release; after 25 s the collector was heated to 600 °C and the excess air was removed after 100 s. Then, a methanol/water/air mixture was injected into the collector at a specified flow rate and uniformly distributed over the volume of each reactor where

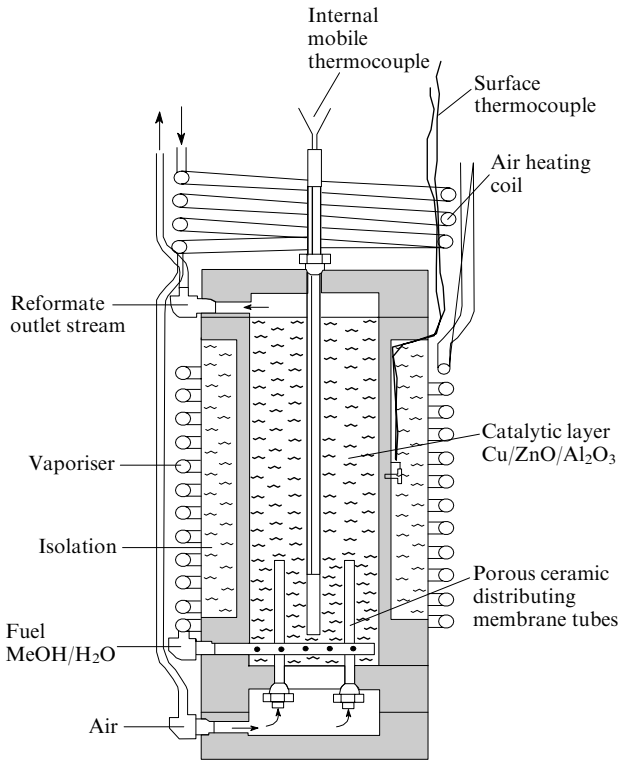


Figure 3. Scheme of adiabatic reactor for autothermal reforming of methanol.[60]

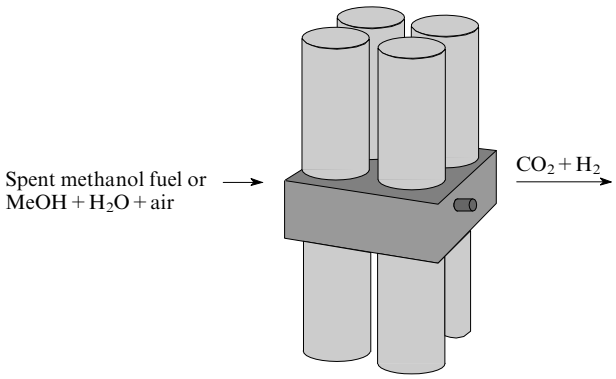


Figure 4. Hot Spot fuel processor (8 reactors, total performance with respect to hydrogen 6000 litre h^{-1}, see Ref. 62).

autothermal reforming occurred on a multicomponent noble-metal catalyst supported on a metal oxide. The temperature in the collector was maintained using heat released in the oxidation of hydrogen-containing anode gas in the afterburner and blowing it through the collector. The key feature of the reactor is its modular design. Each reactor (power 0.75 kW, volume 245 cm^3) showed a performance with respect to H_2 of 750 litre h^{-1} and the power density was 3 kW $litre^{-1}$. The HS-processor included a 18-kW CO cleaning reactor (CO concentration reduced from 2 vol.% to 10 ppm), which consumed up to 6% of hydrogen produced. The volume of the last-mentioned reactor was ~20% of the total volume of the fuel processor.

b. Plate-fin and folded-sheet reactors

A prototype of a plate-fin methanol reactor (PFMR) with heat integration through aluminium fins was proposed.[63] Plate-type $Cu-Zn/Al_2O_3/Al$ catalyst was used in the reactor for autothermal reforming of methanol, and plate-type $Pt/Al_2O_3/Al$ catalyst was used for catalytic oxidation. Tests of this reactor (P1) and a comparison with a fixed-bed (bulk) catalyst reactor (P2) gave the following results:[64]

Start time /min		Catalyst volume /cm^3		Overall heat transfer coefficient /W m^{-2} K^{-1}	
P1	P2	P1	P2	P1	P2
12	42	42	375	20.2	1.3

From the data presented it follows that the plate-fin methanol reactor has some advantages (reduced size, mass and start time) over the traditional apparatus. An improved design of PFMR has also been reported.[24, 64]

A particular PFMR unit comprising a reforming chamber, two vaporisation units and two catalytic oxidation units is shown in Fig. 5. Hydrogen is fed to the combustion units *via* two distributors. This provides a uniform gas distribution and makes it possible to avoid heating at the inlet. The reforming unit is filled with $Cu-ZnO/Al_2O_3$ industrial catalyst (grain diameter 0.44–0.68 mm). The combustion unit was filled with Pt/Al_2O_3 catalyst (grain diameter 1 mm). The reforming catalyst was reduced with the reducing gas (3 vol.% H_2+N_2); the temperature was raised from 25 to 300 °C at a rate of 4 deg min^{-1}. This reformer was augmented with four reactors for preferential CO oxidation (*i.e.*, the fuel processor contained no CO shift reactor, which is the largest and heaviest component), which made it possible to reduce the CO concentration to 50 ppm. The reformer provided a stable methanol conversion of ~95% over a period of 1000 h at a CO concentration of 1.2 vol.%–1.5 vol.% with a heat efficiency (ratio of the lowest heat of combustion of hydrogen produced to that of fuel) of 75%. The dimensions of the fuel processor with PFMR were 680 × 500 × 400 mm; the desired power can be reached by increasing the linear size and number of units.

A compact folded-sheet reactor[65] with a common zone for (i) vaporisation and steam reforming of methanol and (ii) steam reforming of CO and through-the-wall heat integration with the combustion zone of hydrogen-containing anode gas of PEM fuel cells is shown in Fig. 6. In this reactor, vaporisation of methanol/water mixture with overheating of their vapours on inert glassware occurs on the reforming side. Then, steam reforming of methanol on the reforming catalyst and then CO shift on another catalyst is performed downstream. Heat necessary for reforming of methanol is released in the oxidation of hydrogen (hydrogen-containing anode gas of PEM fuel cells) and transferred from the combustion zone through the reactor wall. Hydrogen is supplied to a number of points along the reactor length in the oxidation zone where the walls are coated with the combustion catalyst. Air is fed to the oxidation zone counterwise with respect to the methanol and water flows in the reforming zone. This makes it possible not only to enable heat transfer for endothermic reforming of methanol, but also to transfer the heat of CO shift, which is used for pre-heating of the air–hydrogen mixture. The reactor (thermal power 10 kW, length 0.6 m) contained 16 reforming channels, 17 oxidation channels and provided a meth-

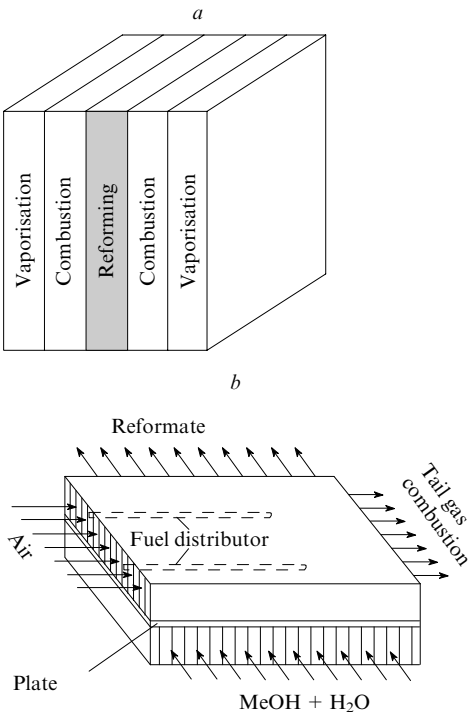


Figure 5. Design of plate-fin methanol reactor with heat integration through aluminium fins.[63]
A module with two vaporiser units and heat intergation of the MeOH steam reforming unit with two catalytic combustion units (*a*) and scheme cross-flows in reactor unit (*b*).

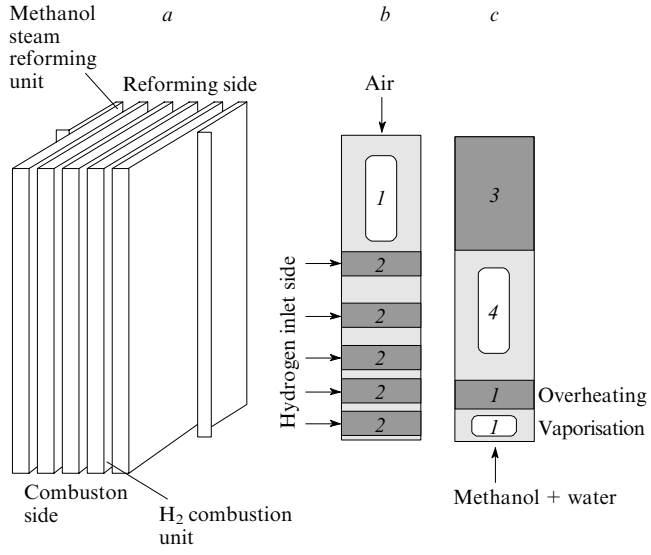


Figure 6. A compact folded-sheet reactor with a common zone for vaporisation and steam reforming of methanol and steam conversion of CO and with through-the-wall heat integration with the combustion zone.[65]
Arrangement of units (*a*) and catalyst arrangement in the H_2 combustion unit (*b*) and in the methanol steam reforming unit (*c*); inert distributor (*1*), catalyst (*2*), catalyst of CO steam conversion (*3*) and catalyst of reforming (*4*).

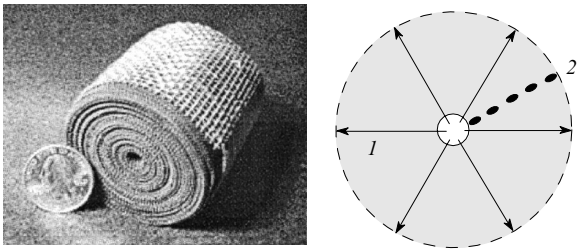


Figure 7. A radial microreactor.[66]
Radial gas flow (*1*) and mutual position of thermocouples and the sampling point (*2*).

anol conversion of 90% at a CO concentration of about 3 vol.% and a hydrogen yield of 72.1%. Thermal control of the reactor through the specified distribution of the oxidation catalyst, efficient through-the-wall integration and compact arrangement of reaction zones (reforming zone and CO shift zone) belong to undoubtful advantages of this reactor. To reduce the CO concentration to less than 10 ppm, the reactor should be equipped with an apparatus for preferential CO oxidation.

A novel radial catalytic reactor for autothermal reforming of methanol (Microlith) was studied.[66] The reactor has a form of a catalytic sheet (length 5 cm, external diameter 5 cm, volume ~ 100 cm^3) sandwiched between two flanges at the ends to ensure good packing and extraction of the flow passed around the sheet (Fig. 7). A $MeOH + O_2 + H_2O$ mixture ($MeOH : O_2 = 0.27$; $MeOH : H_2O = 0.5$; MeOH flow rate of 16 g min^{-1}) was introduced *via* a narrow tube into the central part of the reactor (Pt/Al_2O_3 catalyst). Based on the performance with respect to H_2, the reactor could provide a power density of 425 kW litre^{-1}, but at high CO concentration. Having reduced the H_2 concentration in the reformate to 50 vol.%, the CO concentration was reduced to 1.2 vol.%, which is admissible for the PROX reactor; however, the power density decreased to 4.6 kW litre^{-1}. The thermal efficiency of the process exceeded 80%. The reactor operated in this regime over a period of 50 h with no reduction of catalyst activity.

c. Reactors with membrane extraction of hydrogen

Recently, reactors with membrane extraction of hydrogen have been a subject of the most intensive research and development among fuel processor reactors.[67] A catalytic membrane reactor (CMEMR) is a membrane reactor in which the membrane has no catalytic function and only serves for extraction of hydrogen from the reformate. Reforming occurs on the catalyst in the reaction zone and the target product (hydrogen) is removed by passing through the membrane to the permeability zone. Hydrogen produced *in situ* in the reforming of hydrocarbon fuels in CMEMR is used in the fuel cell. The membrane module can either be combined with the reforming zone or be arranged outside the reactor. In the former case the degree of conversion of the initial fuel can be higher than the thermodynamically allowed value owing to shift of the equilibrium in the target reaction to the right. In the latter case, the degree of conversion is no higher than the equilibrium value. Due to low temperature of the reforming processes, methanol reactors are very convenient for the use of metallic membranes with a thermal limit of about 500 °C. Using the CMEMCR concept, a traditional multi-unit fuel processor can be replaced by a single module which combines the reaction and separation. Compactness of the CMEMR is most attractive for the designers of hydrogen fuel cell powered electric vehicles .

A 50-kW autothermal CMEMR (Fig. 8) was reported.[68] The authors compared the volumes of conventional fixed-bed reactors for steam reforming and autothermal reforming. They were equal to ~ 29 and ~ 22 litres, respectively. The key advantage of the membrane reactor for autothermal reforming consisted in much smaller volume (13 litres). With counterflow of purge gas and reformate the degree of hydrogen extraction was as high as 91% at an average pressure in the reactor of 0.5 MPa; the overall efficiency of the CMEMR – fuel cell system was $\sim 84\%$.

A ten-module, 30-kW catalytic membrane reactor was developed[69] for transport (Fig. 9). The module (volume 3.9 litres, weight 5.7 kg with no flanges) had the performance with respect to hydrogen of 2.3 Nm^3 h^{-1} (Fig. 10). The reactor for steam reforming was integrated with the membrane extractor of hydrogen from reformate. The membrane was made of Pd – Cu alloy (thickness 25 μm), although Pd – Ag alloys and palladium-coated V – Ni – Cr alloy were tested. The specific flow rate of hydrogen

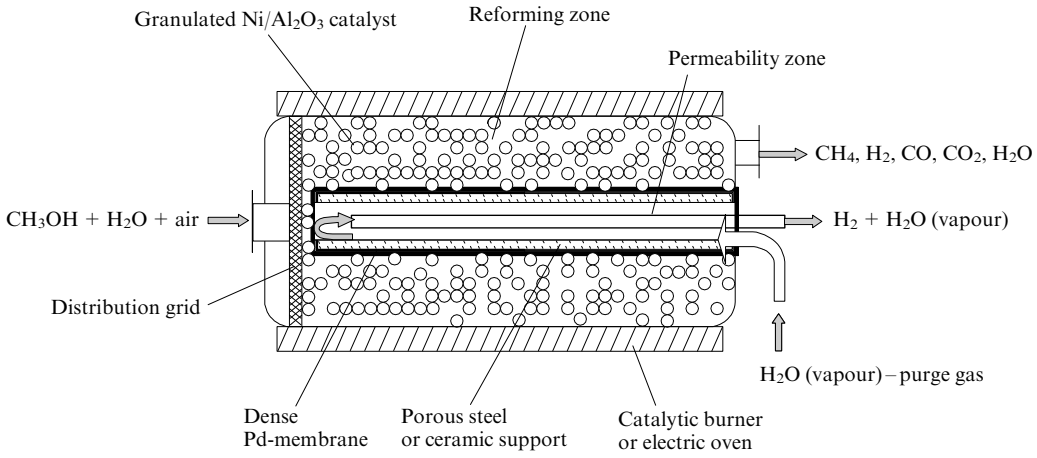


Figure 8. Membrane reactor for autothermal reforming of methanol with counterflow of purge gas.[68]

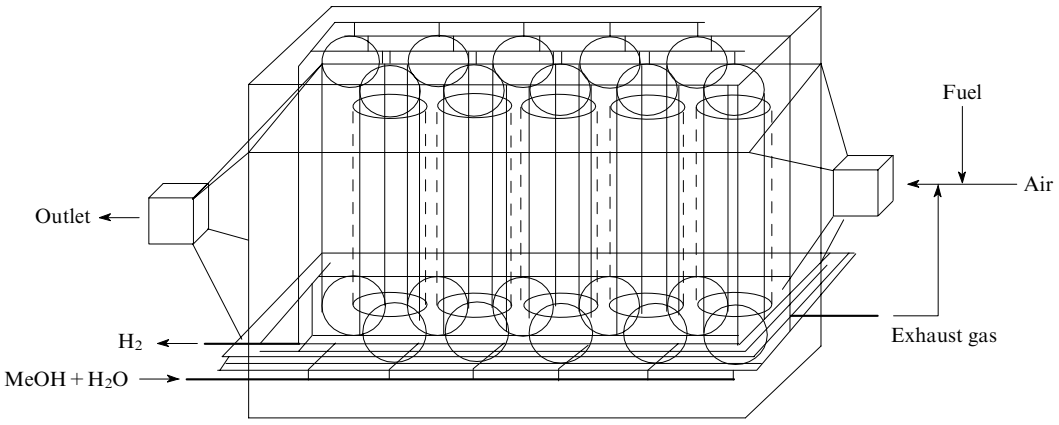


Figure 9. Scheme of 30-kW methanol fuel processor comprising ten 3-kW modules.[69]

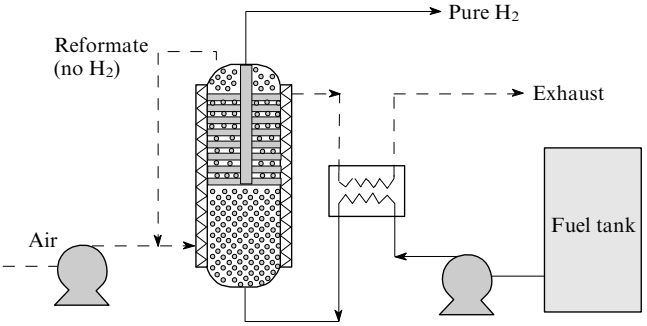


Figure 10. Module for methanol reforming to produce pure hydrogen.[69]
The lower part of the reactor is filled with Pt catalyst coated on metal grid, the upper part of the reactor is filled with Pd–Cu-membrane tubes.

through the membrane increased with temperature and pressure, being equal to 30 $cm^3\ min^{-1}\ cm^{-2}$ at 300 °C and a partial pressure of H_2 of 0.414 MPa. The presence of CO in the reformate caused a nearly 25% decrease in the hydrogen flow rate because irreversible adsorption of CO blocked the hydrogen adsorption (dissociation) sites. The reforming catalysts tested included $CuO/ZnO/Al_2O_3$, $CuO/ZnO/TiO_2$ and $CuO/Cr_2O_3/TiO_2$. The residual gas containing non-extracted hydrogen was fed to the catalytic burner surrounding the modules. The combustion heat was used for steam reforming of methanol. Cold system was heated using liquid methanol, which was sprayed and injected into the burning zone through a nozzle and then burnt up. At a temperature of about 45 °C, the catalytic burning scheme switched on. Platinum on Al_2O_3 coated on a steel grid served as burning catalyst. Five minutes after cold start the flow temperature at the outlet of the housing was ~350 °C; one minute later, hydrogen production began in the unit heated to a temperature of 100 °C. After 12 min of heating the temperature of the heating flow reached 500 °C. At 20th minute, the reformate temperature at the outlet of the module was 300–320 °C and each module reached a maximum performance with respect to hydrogen (2.3 $Nm^3\ h^{-1}$, purity 99.9999%, CO concentration less than 1 ppm). The specific characteristics of the fuel processor are as follows: the power density for processor 1 kW $litre^{-1}$ (0.84 kW g^{-1}), the total volume 40 litres and the weight 50 kg. The degree of methanol conversion was 95%, the degree of hydrogen extraction by metallic membrane was 75%, 25% of non-extracted hydrogen and the residual MeOH were oxidised on the combustion catalyst. The total thermal efficiency of the system was 89%. The fuel processor system transient period (response time) from a 100% load to restart after short-term break was about two minutes.

A 25-kW catalytic membrane reactor with two metallic membrane modules arranged outside of the reactor was designed for automotive vehicles.[70] The membrane modules contained tailor-made metallic frames with flat membranes (Pd–Cu alloy, 25 μm thick) assembled in multimodules (Fig. 11).[71] The membrane reactor loaded with industrial catalyst ICI 33–5 M (7 kg), produced 25 $Nm^3\ h^{-1}$ of hydrogen (purity 99.9995%, CO concentration less than 1 ppm). The operating conditions of the reactor and the membrane modules were maintained at 300–350 °C and a pressure of 0.9 MPa. The reactor was used for steam reforming of methanol (methanol 63 vol.% + water 37 vol.%). Excess water ensured completion of the CO shift reaction. The system was switched on by heating the reactor by combustion of injected methanol in the vaporiser. Air was also fed in 30% excess to ensure complete combustion of MeOH. As stable temperature and pressure

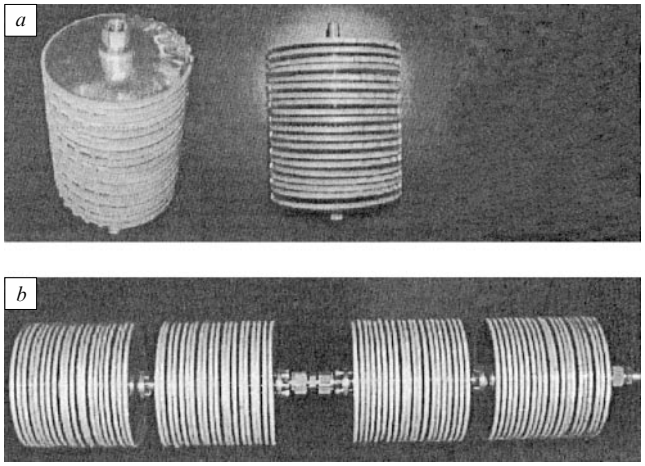


Figure 11. Single membrane module with flat membranes (Pd–Cu alloy, 25 μm thick) (*a*) and a multimodule (*b*).[71]

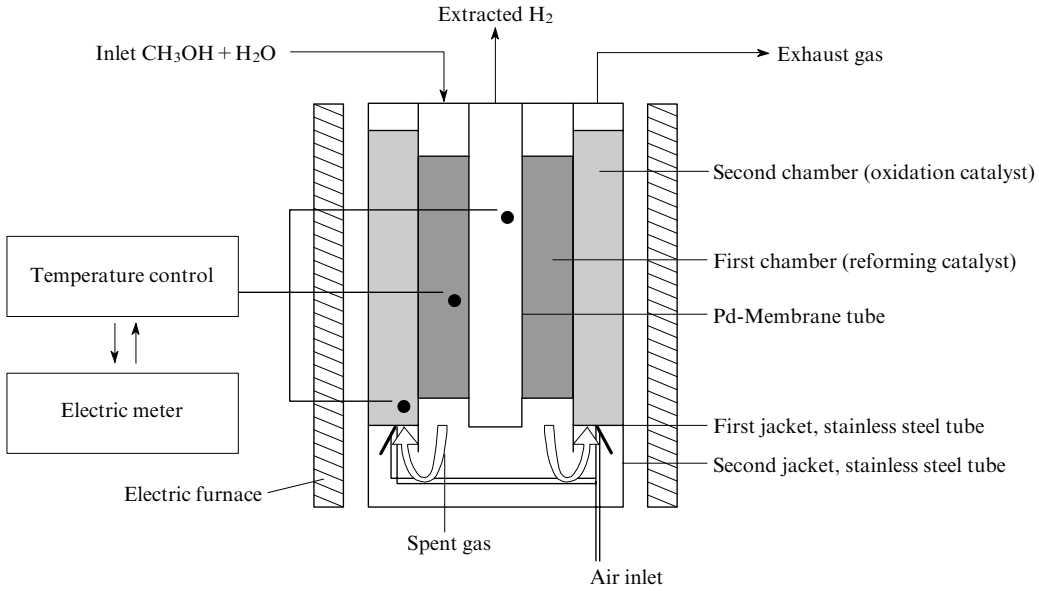


Figure 12. Scheme of double-jacketed membrane reactor.[72–74]

in the reactor and in the membrane modules were attained, methanol fuel was replaced by the off-gas containing (in vol.%) CH_3OH (2), H_2O (23), H_2 (31), CO_2 (37) and CO (7). The thermal efficiency of the fuel processor was ~75% and the degree of hydrogen extraction from reformate was 70%–75%. The thermal processor was tested on a Hyundai Santa Fe vehicle.

A double-jacketed membrane reactor (DJMR) with a palladium membrane and simultaneous occurrence of steam reforming of methanol and CO shift reaction was proposed.[72–74] The methanol steam reformer is heat-integrated with the oxidation of the gas not passed through the membrane (Fig. 12). Hydrogen was extracted from the reformate using the palladium tube. The reactor operated at 1.5 MPa and a temperature of 350 °C, the degree of methanol conversion was 97% and the yield of hydrogen was 73%. Combining steam reforming of methanol and oxidation reactions allowed the DJMR to operate under self-sufficient conditions with a hydrogen yield of 74%.[74]

Fixed-bed catalytic membrane reactors have been intensively studied to attain the highest performance with respect to hydrogen by optimising the volumes of the catalytic layer and the membrane, to choose the optimal grain size and to determine the minimum ratio of the membrane surface area to the reactor volume.[75] To improve the CMEMR characteristics, the optimal H_2O : MeOH ratio, temperature, pressure, duration of the reaction and the gas purge speed[76] or the optimal O_2 : MeOH ratio and temperature are determined.[77] In almost all studies the advantages of CMEMR over traditional tubular reactors for reforming of methanol were confirmed by an increase in the degree of MeOH conversion, which was limited by the equilibrium value, by high selectivity with respect to H_2 and by ultralow CO concentration, especially in the case of counterwise flows in the reforming and permeability zones.[78, 79]

Catalytic membrane reactors are used as reactors for PEM,[77] CO shift[80] and preferential CO oxidation.[81] However, information on the operation of such membrane reactors is scarce. The principle of their operation and designs are similar to that of CMEMR for steam reforming and autothermal reforming of methanol. The difference consists only in catalysts used for reforming of gas mixture and membrane types. For instance, a reactor for preferential CO oxidation operated with yttria-stabilised zirconia membranes[81] or with membranes containing platinum supported on silicon substrate.[82]

Catalytic membrane reactors have a high energy efficiency (⩾80%), small size, good dynamic characteristics, low temperature of reforming of hydrocarbon materials and make it possible to produce ultrapure hydrogen in one step and to achieve the degree of conversion, which exceeds the equilibrium value. Hydrogen thus produced contains no CO and is suitable for the use in low-temperature fuel cells. Currently, wide use of CMEMR is hampered by some reasons, such as a relatively short lifetime and insufficiently high mechanical strength of membranes and, which is the key reason, high cost of the key component, that is, palladium. However, advances in the development of ultrathin composite membranes on various substrates suggest good prospects for the use of membrane technology in the future hydrogen energetics.

d. Microchannel reactors

In the last decade a new direction in fuel processing using catalytic microreactors (MR) has been progressing rapidly. This is due to the need for efficient power supply to transport, micropower devices and portable electronics (laptops, cell phones, security cameras, players, *etc.*). A microreactor is a compact device containing microcatalytic plates with submillimetre channels (Fig. 13). Small size and the possi-

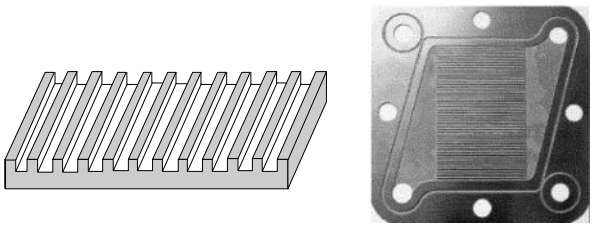


Figure 13. Microchannel reactor chip.[98]

bility of integration of various functions (reactions, mixing, heat exchange, separation) within the same device predetermine the advantages of MR over conventional reactors. In microreactors the ratio of the geometrical surface area to the total volume can be as high as 10 000 to 50 000 $m^2\ m^{-3}$ (*cf.* 100 – 1000 $m^2\ m^{-3}$ for conventional reactors), which provides very high rates of heat and mass transfer. The heat transfer coefficient in microchannels reaches 20 000 – 35 000 $W\ m^{-2}$, being an order of magnitude higher than in conventional systems. The mass transfer coefficient for the gas – liquid system in MR is in the range 5 – 15 s^{-1} (*cf.* 0.01 – 0.08 s^{-1} for a laboratory multiphase fixed-bed reactor). Microchannel reactors are especially efficient in the case of fast reactions with short contact times and high thermal effects, *e.g.* for reactions of complete and partial oxidation of hydrocarbons. Specific features of application of MR to gas-phase reactions have been analysed in a review.[83]

There are two methods of catalyst arrangement in microchannel reactors. In the first type of reactors (MR1) small catalyst granules fill the whole volume of submillimetre channels.[84] In the second type of reactors (MR2) the catalyst is immobilised on channel walls. MR1-type reactors usually have a much higher drag compared to MR2-reactors. Typical grain sizes for MR1 are 35 – 75 μm, which corresponds to the outer specific surface area $(40 - 86) \times 10^3\ m^2\ m^{-3}$. Isothermal conditions in this type of microreactors are achieved at channel diameters of at most 300 μm. MR2-reactors are more promising; they contain more than 10 000 channels (cross section 50 – 1000 μm, length 20 – 100 mm). These reactors are characterised by high specific performance (due to short contact times), gas mixture volume rates of about 100 $cm^3\ s^{-1}$ and laminar flow with parabolic cross-sectional velocity profile. Methods of fabrication of optimally shaped channels, catalyst immobilisation on channel walls and the fields of application of microreactors have been considered in monographs [85 – 87] and reviews.[88, 89]

Three types of MR for steam reforming of methanol have been developed and tested.[89] These are a cylindrical MR with external heating (CMR), a rectangular MR (RMR) and a heat exchange MR (HEMR). Figure 14 presents a stainless steel CMR (diameter 30 mm, length 60 mm) containing 130 disk-shaped microcatalytic plates and a copper vaporiser of water – methanol mixture at the inlet. The catalyst (40 vol.% Cu + 60 vol.% Zn) was pressed in microchannels. At an inlet flow rate of 100 ml h^{-1} and a reactor temperature of 260 °C, the degree of methanol conversion was 80%, the performance with respect to hydrogen being 130 litre h^{-1}. A brass rectangular MR (Fig. 15; dimensions $5 \times 90 \times 85$ mm) was assembled from modules as a block comprising 20 – 30 microcatalytic plates. Each block was tested using nickel foam microcatalytic plates with Cu – Ce – Al catalyst. At an inlet flow rate of 80 ml h^{-1} and a reactor temperature of 260 °C, the degree of methanol conversion was 80% (performance with respect to hydrogen was 106 litre h^{-1}). A stainless steel HEMR (diameter 40 mm, height 35 mm) is shown in Fig. 16. The MR was filled with microcatalytic plates in such a manner that the microcatalytic plates for steam conversion alternated with the microcatalytic plates for deep oxidation; the channels of the contacting microcatalytic plates were mutually perpendicular. At a reactor



Figure 14. Cylindrical microreactor for steam reforming of methanol containing embedded vaporiser of liquid water – methanol mixture and microcatalytic plates.[89]

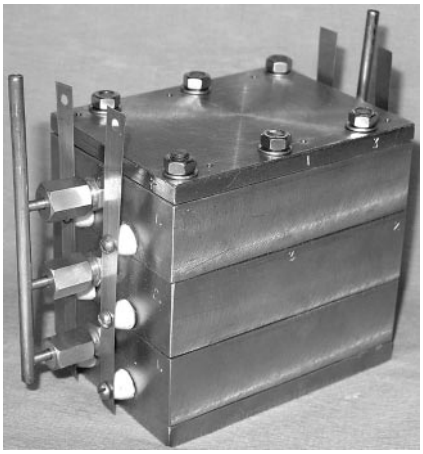


Figure 15. Modular rectangular microreactor for steam reforming of methanol containing replaceable microcatalytic plate modules and embedded electric heater.[89]



Figure 16. Heat-exchange microreactor for steam reforming of methanol.[89]

temperature of 270 °C, the performance with respect to hydrogen was 32 litre h^{-1}.

A microreactor for steam reforming of methanol with external electric heating was reported.[90] The reactor comprised three microcatalytic plates, three distributive plates and two copper plates for equilibration of the flow and temperature in channels. Each microcatalytic plate contains 20 parallel channels (dimensions $500 \times 200 \times 33\,000$ μm), the catalyst (Cu−Zn−Al) was immobilised on channel walls using pseudoboehmite. At 260 °C, the reactor (dimensions $70 \times 40 \times 30$ mm) showed a performance with respect to hydrogen of 12 litre h^{-1}. The same MR with heat supply from the reaction of deep oxidation of MeOH was reported in another study.[91] The reactor has three plates for steam reforming and three plates for oxidation of methanol. In each microcatalytic plate, 10 channels (dimensions $1000 \times 500 \times 45\,000$ μm) were fabricated photolithographically with subsequent chemical etching. Then, a porous layer of SiO_2 or γ-Al_2O_3 was immobilised on the surface and the active component (Cu/ZnO for steam reforming and Pt/ZrO_2 catalyst for the oxidation of methanol) was introduced into the porous layer. The performance of this MR with respect to hydrogen was 3.9 litre h^{-1}. Heat for the methanol steam reformer was transferred using heated oil passing through channels of the heat exchange plate.[92] The catalyst for steam reforming of methanol filled slit-like channels. Using this MR, a 300-mW microprocessor was fabricated and simulation using a 3D model (3D temperature and concentration profiles of reactants through channel cross-sections and along channel length) was performed.[93]

The amount of H_2 produced in a stainless steel MR (dimensions $75 \times 45 \times 110$ mm) with six microcatalytic plates containing 40 microchannels (dimensions $0.5 \times 0.35 \times 50$ mm) coated with Cu−Zn catalyst (Cu : Zn = 3 : 1, load 8 mass %) was sufficient for 28 W PEM fuel cells.[94] The degree of methanol conversion was 65%, the concentration of H_2 in the output gas was 45 vol.% at 275 °C and a contact time of 0.11 s; the CO concentration was ~1.45 vol.%. A higher MeOH conversion (80%) was obtained at a catalyst load of 16 mass %; the yield of and selectivity with respect to H_2 were 78% and 98%, respectively; the power attained was 84 W.

An 11-W microreactor using steam reforming of methanol with $Cu/ZnO/Al_2O_3$ catalyst [Cu : Zn = 50 : 50 (vol.%) (Ref. 95) and 14 mass % Cu + 6 mass % Zn (Ref. 96)] containing Ce additives (5 vol.%) was demonstrated.[95,96] The addition of cerium significantly enhances the catalyst activity and decreases the CO concentration.

A two-pass MR with heat integration of the steam reforming of methanol with complete oxidation of MeOH, *i.e.*, an autothermal MR, has been studied.[97] Its plates contained seventeen S-shaped microchannels, but only straight portions (width 320 μm, depth 100 μm and length 30 mm) of the channels were used in the reaction. The channel surface was coated with a copper-based industrial catalyst (G-66MR Südchemie) and a Co oxide catalyst was used for the catalytic oxidation of methanol. The assembled reactor system was placed in a housing (dimensions $21 \times 16 \times 14$ cm). A $MeOH + H_2O + Ar$ (37.7 : 45.3 : 17.0, by volume) mixture was fed to the methanol steam reforming unit and a $MeOH - O_2 - N_2$ (10.0 : 18.9 : 71.1, by volume) mixture was supplied to the complete oxidation unit. The microreactor operated in the direct flow regime of the steam reforming of methanol and complete oxidation of MeOH. The authors constructed a kinetic model and studied the dynamics of autothermal reforming of methanol of the microreactor.

A microchannel methanol oxidation reactor for transport with a highly active and relatively stable Pd−Zn/Cu−Zn−Al catalyst was studied.[98] The molar composition of $MeOH : H_2O : O_2$ mixture at the inlet was 1 : 1.2 : 0.3 and the volume flow rate with respect to gas was in the range 20 000 – 180 000 h^{-1}. Microchannels (dimensions $500 \times 170 \times 30\,000$ μm) were coated with the catalyst using the sol–gel technology. Anhydrous product gas contained 50.2 vol.% of H_2 (240 litre h^{-1}), 2 vol.% of CO, N_2 and CO_2 at a volume flow rate of 137 000 h^{-1} (corresponds to a contact time of 0.7 ms). The amount of hydrogen produced in the microreactor is sufficient for operation of a 0.1 to 1 kW PEM fuel cell. A five-plate MR with microchannels (dimensions $45 \times 1.0 \times 0.5$ mm) coated with zirconium sol for better adhesion between the substrate and industrial catalyst (CuO 50%, ZnO 33%, Al_2O_3 17%), produced 3 litre h^{-1} of hydrogen at 270 °C.[99] Heat was transferred to the microreactor through an electrically heated strip. The procedure for coating the microchannels with the catalyst was reported in original study.

The prospects for use of the microreactors considered above are mainly associated with their application in fuel processors for fuel cell powered electric vehicles and also as power plants for portable devices. These MR have not found wide application in fuel cell based automotive vehicles as yet. This is due to their short run. The US Department of Energy studied the distance of run for 59 vehicles, but none of them travelled a distance of 480 km. However, taking account of high energy efficiency and compactness of MR, they are expected to be used for fuel cell transport in the nearest future.

e. Portable microreactors for microfuel cells

Recently, 'power-plant-on-chip' and 'palm power' have been the latest fashion terms in microelectrical/micropower engineering. From the standpoint of energy sources the fuel cell technology reached its peak in the energy storage in a single piece based on the weight : volume ratio. Fuel cells have a higher power density than Li-ion cells (by a factor of $\geqslant 20$) at a comparable operating life.[100] Even if we assume a 5% efficiency of the transformation of the thermal energy of hydrocarbons to electric energy, the fuel cell will provide a higher power density compared to Li-ion cells. Replacement of conventional cells by portable microreactors for production of 'hydrogen on demand' for microfuel cells offers the most promising prospects and has started recently.[22,101–107]

A microscale fuel processor (volume 0.2 cm^3, see Fig. 17) has been developed.[100] It is made of '316' stainless steel and has five components, namely, two vaporisers/heaters, a reactor, a catalytic combustion unit and a heat exchanger. The reactor power is 200 mW and that of the

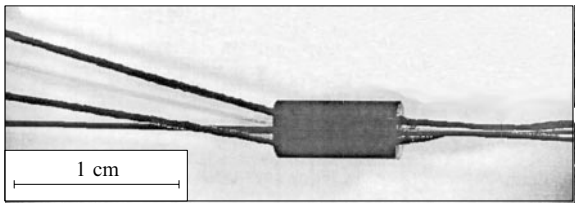


Figure 17. Integrated fuel processor.[100]

catalytic combustion unit is 3 W. A methanol/water mixture is fed to the reactor *via* a syringe pump at a flow rate of 0.02–0.1 $cm^3\ h^{-1}$. Pure methanol and air are fed to the catalytic combustion unit at a flow rate of 0.1–0.4 $cm^3\ h^{-1}$ and 8–20 $cm^3\ h^{-1}$, respectively. To achieve a 99% conversion of MeOH, the operating temperature in the catalytic combustion unit should be higher than 400 °C. The thermal efficiency of the reactor at 200 mW was 9%. At a fuel cell efficiency of 60% and degree of hydrogen utilisation of 80%–85%, the overall efficiency of the reactor–fuel cell system was ~50%, which thus provided a power of about 100 mW. A Battelle catalyst was used in the reactor; the activity of this catalyst is much higher compared to the industrial catalyst $CuO-ZnO-Al_2O_3$. A similar second-generation microscale fuel processor (thermal efficiency more than 20%, CO concentration lower than 100 ppm) was also developed by the same authors.[22]

A new fixed-bed radial MR based on steam conversion of MeOH was proposed for portable power plants (Fig. 18).[107] A traditional fixed-bed rectangular MR has a drawback due to a high pressure drop. Owing to the increase in the total number of moles in methanol-to-hydrogen conversion the rate of the gas mixture at the outlet of the fixed-bed catalyst layer increases while the pressure decreases, which leads to even greater increase in the flow rate at the outlet and, therefore, the efficiency of the catalyst decreases as the contact time shortens. Yet another problem of MR is associated with evaporation of liquid fuel. Namely, fast expansion of a boiling reactant leads to pulsations and oscillations of the pressure drop in the case of two-phase heat transfer in the MR.[108] These problems were solved using a new radial MR. The pressure drop was 0.0702 MPa for hydrogen production of 145 $cm^3\ min^{-1}$ (*cf.* 0.6545 MPa at 72 $cm^3\ min^{-1}$ for traditional MR). Thus, the pressure drop in the radial MR at doubled performance with respect to H_2 was nine times lower than in traditional MR. The radial MR operated using industrial catalyst $CuO/ZnO/Al_2O_3$ (grain size 50–70 μm) over a period of 10 days, produced a power of 20 W and had a tenfold power density compared to Li-ion cells.

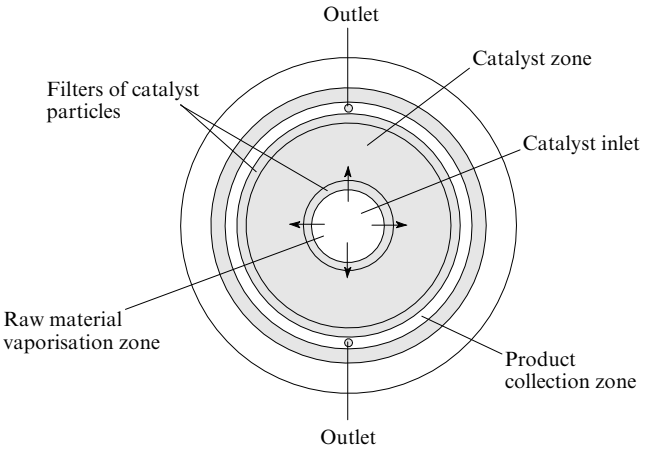


Figure 18. Scheme of radial catalytic reactor for autothermal conversion of methanol.[107]

A 15-W microreactor with vaporiser of liquid methanol and rectangular channels (dimensions 500 × 200 × 33 000 μm) was tested.[109] The authors of that study also developed a 59-W integrated microchannel fuel processor.[110] The methanol steam reformer operated using industrial catalyst $CuO/ZnO/Al_2O_3$ immobilised on channel walls. The combustion unit was loaded with a layer of Pt/Al_2O_3 granular catalyst. The amount of hydrogen produced by steam reforming of methanol in the microreactor on glass and silicon substrates (25 × 17 × 1.3 mm) with microchannels (dimensions 600 × 400 × 33 300 μm) coated with $Cu/ZnO/Al_2O_3$ catalyst was sufficient for operation of a 1-W microfuel cell.[111]

A portable 'bread-boarded' 15-W methanol fuel processor for the US Army (mass 1 kg including fuel cells, volume ⩽100 cm^3, mission life ~14 days) has been developed.[112] The fuel processor–fuel cell assembly showed an estmated power 14–80 W; at 13 W, the estimated efficiency was 22% at a fuel cell efficiency of 48%. The estimated power density was 720 W h kg^{-1}, being several times higher than that of Li-ion cells. The volume of the Battelle catalyst in the microchannel reactor was 0.5 cm^3 and the contact time was 100 ms. The term 'bread-boarded' refers to a 'process train' in which all components are connected, but not fully integrated. The fuel processor has a conventional design and comprises two vaporisers for $MeOH + H_2O$ and MeOH + air mixtures, a catalytic combustion unit and a methanol steam reformer. The fuel processor is switched on using an electric heater, which then switches off after 15 min. The fuel processor operated under thermally self-sufficient conditions. Owing to very short contact time (140 ms) the CO concentration was lower than the equilibrium value (0.8 vol.%). This eliminated the need for a CO shift reactor and significantly simplified the overall system. A glass methanol microreactor for micro-fuel cells was reported in another study.[113]

A monolithic integrated fuel processor for reforming of liquid methanol was proposed.[114] The operation of the integrated fuel processor (weight 1.8 kg, volume 0.5 litre; performance with respect to hydrogen 20 litre min^{-1}) involves all stages of the reforming process, that is, vaporisation of methanol/water mixture; the steam and autothermal reforming; preferential CO oxidation integrated with combustion of hydrogen in the reaction, which is the reverse of the CO shift reaction, on the CO shift catalyst and, finally, start of the integrated fuel processor on catalytic combustion of methanol. The authors used a powder metallurgy technology for pressing and sintering of the catalyst, for shaping of the functional units of the fuel processor and maintenance of heat transfer in various stages of the reforming process. Powder technology was used to avoid the major drawbacks of microreactors including poor gas distribution and the macroscopic mass and heat gradients. Nevertheless, the principles of design of microreactors were used in that study. The reforming unit was made of Cu–ZnO catalyst and copper powder (copper particle size 100–300 μm). Copper was used as matrix owing to its high heat conductivity and low melting point (1083 °C). Powdered copper or aluminium and inert matrix materials were used for fabrication of other functional units (channels, fins, diffusion layers). Various powders filled different zones and were pressed at room temperature at 10.0 MPa. The porisity and gas-transport characteristics were controlled by appropriately choosing powders and the degree of compression in corresponding zones. After pressing, particular regions of the plates were covered by a Pt catalyst necessary for exothermic oxidation. Porous steel or ceramic cylinders (diameter 7 mm, thickness 1 mm) for vaporisation of meth-

anol and water were placed on each plate prior to assembling the modular reactor. The next step was to sinter stacked plates. All functional units of the integrated fuel processor were mounted on individual plates (Fig. 19). Ten plates fabricated for the integrated fuel processor prototype in question were sintered to form a single piece. The plates were stacked in such a manner that the flows or the initial reactants or reaction products passed between them. The vaporiser was heated by the CO oxidation reaction; the temperature gradient normal to the plate was 10 deg, whereas the longitudinal temperature gradient could exceed 100 °C. The plates were permeable (porosity 60%, pore diameter ~2 μm), the pressure drop across the plate was at most 0.02 MPa under 100% load. Good isothermal conditions and short diffusion lengths in the porous plate ensured optimal heat and mass transport. The prototype integrated fuel processor showed a performance with respect to hydrogen of about 14.8 litre min^{-1} (methanol feed rate of 15 mol h^{-1}, water : methanol = 1 : 1, 280 °C, pressure at the outlet 0.15 MPa). Similarly to the known microchannel reactors this integrated fuel processor is compact and provides good heat and mass transfer, which leads to uniform temperature distribution and no problems with gas distribution.

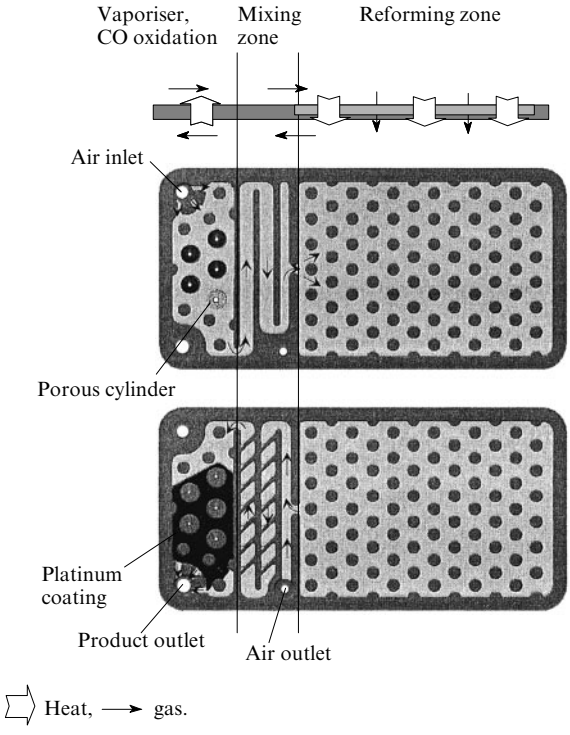


Figure 19. Functional units of a single plate of integrated fuel processor.[114]

The MR types considered above are characterised by high power density and operation life compared to Li-ion cells. The 'power spectrum' of portable microchannel reactors is rather broad and spans from a few mW to tens of Watts. In the last five years the development of portable microchannel reactors (PMCR) has been progressing significantly. However, these reactors offer not only the advantages, but also drawbacks of MR. Namely, (i) high rate of heat exchange in channels leads to high losses of heat; (ii) pressure drop in rectangular PMCR is rather high; therefore, the development of radial PMCR is topical; and (iii) efficiency of PMCR depends on the technology used for fabrication of microchannels and on the catalyst activity. The design of PMCR is in essence a new technology and improvement of the pilot samples should be followed by large-scale production of such systems.

e. String reactor

Recently, a compact string reactor for autothermal conversion of methanol has been proposed (Fig. 20).[115] A tubular glass reactor (internal diameter 9 mm, length 110 mm) was loaded with 217 catalytically active copper filaments (diameter 500 μm) coated with chromium-modified mixed-oxide catalyst Cu/Zn/Al. The reactor was tested at 0.1 MPa in the temperature range from 273 to 373 °C, the $MeOH : H_2O$ and $O_2 : MeOH$ ratios were 1 : 1 and 0.12 : 1, respectively. The results obtained are as follows: MeOH conversion 91.5%, the selectivity with respect to CO_2 98%, CO concentration ~2500 ppm, temperature drop along the reactor length ⩽3.5 deg; *i.e.*, almost isothermal conditions due to the high heat conductivity of copper (118 W m^{-1} K^{-1}). The steady temperature profile in the reactor was observed after 20 min. The string reactor has a high heat conductivity and the advantages of the microchannel geometry of monolithic reactors. It showed a short start time and a short transient period with fast change in temperature upon introduction of a controllable amount of oxygen into the reactor. The reactor can readily be integrated into conventional fuel processors.

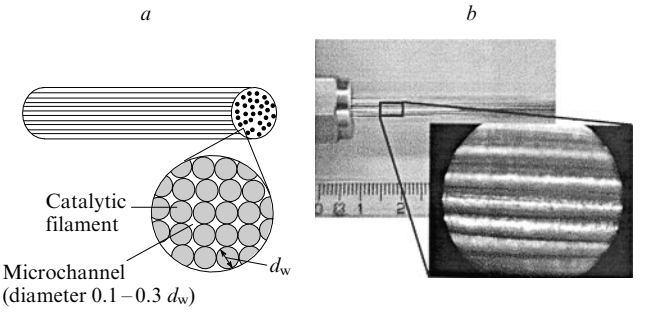


Figure 20. Schematic presentation (*a*) and photograph (*b*) of the compact string reactor.[115]

III. Catalysts for production of hydrogen from methanol

To reduce the size and weight of fuel processors and simultaneously increase their efficiency, one should design more active catalysts. Production of hydrogen-containing gas with low CO concentration depends on the efficiency of the catalyst in each segment of the fuel processor. In this Section we will consider the major advantages in the development of catalytic materials for generation of hydrogen by reforming of methanol and for the CO shift reaction and preferential CO oxidation. It should be noted that recently the number of publications devoted to catalysts for fuel processor apparatuses significantly increased (see, *e.g.*, Refs 116 and 117). The reason is the search for optimal catalyst compositions, development of novel methods for production of catalysts, determination of the arrangement

of catalysts in reactors and traditional investigations of their structural properties and resources. The size, mass, cost and technical limitations imposed on fuel processors are mainly determined by the characteristics of catalysts are used. Prospects for passage to hydrogen energy governed by the advances in the development of catalysts as well as improvement of characteristics of fuel cells.

1. Binary and ternary copper – zinc catalysts on Al_2O_3

Traditional copper-based catalysts for the synthesis of methanol, which are used at present for the reforming of methanol, have been known since 1921.[118] The available copper catalysts differ first of all in substrates and promoter materials. The best known substrates include alumina,[119] silica,[120] titania [121] and zirconia.[122] Zinc oxide [123] often acts as promoter; its action is probably due to the spillover effect. Despite the fact that these catalysts have long been known, intensive research has been carried out in the last decade. These investigations are aimed at enhancing the catalyst activity, selectivity with respect to CO_2, operational life and elucidating the mechanism of catalysis.[7–9, 124–139]

The first studies on the key characteristics and activity of $Cu-ZnO/Al_2O_3$ catalysts from the standpoint of application for automotive vehicles were carried out in the USA and Europe since 1995. General information on the subject is available from the proceedings of various conferences, as well as from theses and a review.[117] Numerous data on promoters for this class of catalysts are available; unfortunately, they have not been systematised. At present, no rigorous order of steps in the use of promoters can be determined. Complete information on the mechanism of their action and on the conditions for and methods of testing catalysts can be found in the original studies cited here.

The addition of Zr to the $Cu-ZnO-Al_2O_3$ system up to complete replacement of Al by Zr (Cu : Zn : Zr = 32.3 : 40.5 : 27.2) increases the dispersion of supported copper particles and improves the recoverability of the catalyst.[9, 128] Contrary to this, the addition of Ce (to 20 mass %) had no promoting effect, although the conversion of methanol and the yield of H_2 increased. For the Cu/Zn catalyst, the highest H_2 concentration close to the theoretical maximum was observed at a Cu : Zn ratio of 60 : 40 (mol %). In the case of zirconium-doped catalysts the copper content has a weaker effect: almost the same results were obtained for the zinc-free system (100% Cu) and for the compositions Cu : Zn = 80 : 20 and 60 : 40 (mol %).[124–126] Chromium additives promote the catalytic activity of the copper catalysts at high temperatures. Ternary catalysts Cu – Cr – Zn and Cu – Cr – Zr provide a lower CO concentration compared to the binary catalyts Cu – Cr-, Cu – Zn- and Cu – Zr. The catalyst $Cu-Zn-Al_2O_3$ is more active in steam reforming rather than autothermal reforming of methanol while the catalysts $Cu-Cr-Al_2O_3$ and $Cu-Zr-Al_2O_3$ allowed higher methanol conversion to be attained.[125] The stability of the catalyst Cu – Zn – Zr – Al was improved by adding yttrium (2 mol %).[127] The same catalyst behaves differently in steam reforming and in partial oxidation of methanol. For instance, an efficient catalyst of steam reforming of methanol is not always stable in the presence of O_2. A temperature-programmed reduction/oxidation study showed that binary catalysts Cu – ZnO are less stable than the catalysts containing ZrO_2 and Zr/Al_2O_3.[8, 128] The dispersion of copper in the catalyst plays a key role in the production of hydrogen. Catalysts prepared by homogeneous precipitation give highly dispersed copper.[130] If copper is highly dispersed, a metallic surface can be oxidised with ease in the presence of O_2, thus activating the inactive catalyst. The addition of oxygen in the course of steam reforming of methanol seems to be an efficient method of reducing the CO concentration in the product gas. It was found that initially O_2 is consumed to form CO_2 and H_2O in the reaction of complete oxidation of methanol and that an increase in the ratio $H_2O : CH_3OH$ suppresses the formation of CO. The addition of structural promoters Al_2O_3 and ZrO_2 increases the operational life of the catalyst of autothermal reforming of methanol.

Combining a copper foam substrate with industrial catalyst $Cu-ZnO-Al_2O_3$ led [129] to improved heat exchange and therefore to reduction of the temperature of steam reforming of methanol by 30 °C. A study of CO formation on industrial catalyst $Cu-ZnO-Al_2O_3$ confirmed that CO is mainly formed as the secondary product of the reaction, which is the reverse of the CO shift reaction.[128, 129] To reduce the CO concentration in the product gas, it is better to use very small catalyst grains with small intradiffusion limitations, but this leads to an increase in the pressure drop in the reactor.

The activity of the Cu catalyst strongly depends on the interaction with substrate. Catalysts with copper components not bonded to the substrate show the least activity in steam reforming of methanol. At optimal molar ratio (Cu : Zn = 1 : 1), the maximum conversion of methanol in the microreactor for steam reforming of methanol was 99.4 mol % at atmospheric pressure; the selectivity with respect to hydrogen was 99.9 mol % and the CO concentration was 0.007 mol % (catalyst contained 45 mol % of copper).[132] The results obtained in the same reactor under the same conditions using CeO_2-promoted (20 mass %) Cu/Al_2O_3 catalyst at 250 °C were as follows: methanol conversion 95.5%, selectivity with respect to H_2 99.9% and the CO concentration at the outlet 0.14 mol %.[133] The methanol conversion on the promoted catalyst after 200 h was 90.0%, whereas the Cu/Al_2O_3 catalyst deactivated after 100 h.

A study of copper catalysts prepared by impregnation or coprecipitation on various substrates revealed a higher rate of hydrogen production in the former case.[134] Catalysts prepared by doping the surface of completely leached skeletal copper with Cr, Zn, and Co significantly enhanced their activity in both CO shift reaction and steam reforming of methanol.[135]

The increase in the activity and stability of the promoted catalyst is due to higher dispersion of copper, smaller copper crystallite size and the synergistic effect of cerium. Similarly, the increase in the activity and stability of copper catalysts is due to doping with caesium (2 mass %).[136] After oxidation treatment at 400 °C the methanol conversion was 100.0%, whereas the undoped catalyst was highly deactivated.

Deactivation of the $Cu-ZnO-Al_2O_3$ catalyst [10 : 5 : 85 (mass %)] in steam reforming of methanol is due to coke deposition [137] and sintering.[140] The mechanism of coke formation was studied and a model was constructed, which relates the catalyst activity to the coke content. The classical studies [138, 139] are devoted to simulation of the steam reforming of methanol and CO shift reaction and to estimation of the kinetic parameters of the model and

elucidation of the reaction mechanisms. The model correctly predicts the rates of hydrogen, carbon dioxide and carbon monoxide production at pressures to 3.3 MPa.

Steam reforming of methanol on $Cu-ZnO-Al_2O_3$ catalyst was compared with methanol reforming on supported platinum metal (Pd, Pt, Co, Ni, Rh, Ir, Ru) catalysts.[141] The selectivity of steam reforming on these catalysts is lower than on $Cu-ZnO-Al_2O_3$; hydrogen and CO are mainly formed as a result of methanol decomposition.

Copper plate-shaped catalysts on aluminium substrate with intermediate iron coating were fabricated for a plate-fin reactor by chemical deposition.[142] The Cu–Fe–Zn catalysts showed high characteristics in steam reforming of MeOH.

The highest conversion of methanol in methanol steam reformers is achieved if the copper content in the catalyst is at least 50 mass % (25 mass % Cu for CO shift reaction).[143, 144] It was found that mixing of $Cu-SiO_2$ and $Zn-SiO_2$ can result in copper and zinc mixed oxides. To study the role of precursors, CuO, ZnO, TiO_2 and γ-Al_2O_3 nanoparticles (diameter 41, 77, 26 and 32 nm, respectively) were fabricated and mixed.[145] Activity tests of such a thin-layer nanostructured catalyst supported on microchannels (Fig. 21) showed that the better the mixing of CuO and ZnO the higher the MeOH conversion. The catalyst layers prepared from smaller particles exhibit higher activity. Stable reforming of MeOH was observed for 'wet' mixing of powders; ZnO additives suppressed sintering, while TiO_2 additives reduced the initial activity of the catalyst, but increased its stability.

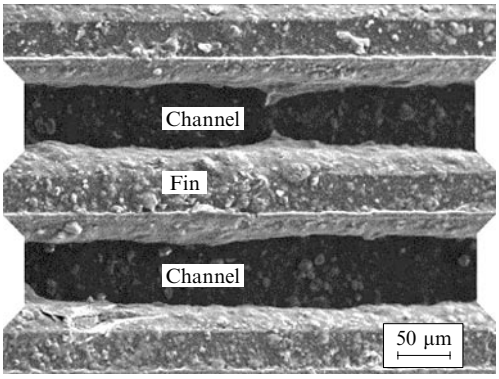


Figure 21. Microchannels coated with catalyst nanoparticles ('wet' mixing) prior to placing into the reactor.[145]

Autothermal (combined) reforming of methanol at 250–330 °C can be carried out with the same catalysts as those used in methanol steam reformer or with supported copper catalysts, which maintain a steady temperature profile in the reactor; this allows the active phase of the $Cu-ZnO-Al_2O_3$ catalyst to be retained.[61, 62, 124–127, 146–149] These catalysts are extremely sensitive to oxidative media, which cause problems in the operation of fuel processors. The modular fuel HS-processor (see Section II.3.a) operated using a noble-metal multicomponent catalyst (no chemical composition was reported), which produced hydrogen from methanol–water–air mixture.[61, 62]

A new nanosized Cu–Zn–Al catalyst with a spinel structure was prepared by hydrothermal method and tested.[10] At optimal molar ratios ($H_2O:CH_3OH = 6.5$ and $O_2:CH_3OH = 0.125$), the rate of hydrogen production was 575 mmol $kg_{cat}^{-1}\,s^{-1}$, methanol conversion 73 vol.% at 300 °C and no CO was detected. The selectivity with respect to hydrogen in autothermal reforming of methanol strongly depends on the methanol conversion, which is confirmed by the order of the oxidation and conversion reactions;[148] the rate of methanol oxidation and formation of reaction products is determined by the partial pressure of oxygen. There is an optimal pressure of O_2 at which the rate of formation H_2 is maximum. High partial pressure of O_2 deactivates the catalyst owing to the oxidation of the copper surface; this was confirmed by photoelectron spectroscopy. Deactivation of the $Cu-ZnO-Al_2O_3$ catalyst with time is due to agglomeration of active phase, that is, copper oxide.[149] Detailed studies on the kinetics of autothermal reforming of methanol under different oxidation conditions and analysis of the deactivation of industrial catalyst K3-110 (BASF; Cu — 40 mass %, ZnO — 40 mass %, Al_2O_3 — 20 mass %) showed that a slight increase in temperature leads to nonlinear O_2 flow rate followed by complete reduction of CuO to Cu, the steam reforming being predominant. The catalyst being in operation can be divided into two regions with a transient regime between them. Under different conditions the input catalyst layer remains oxidised; in this case the oxidation of methanol to water and CO_2 mainly occurs. Conventionally, under industrial conditions at high conversions of oxygen and methanol the region of the oxidised catalyst is short. In this region the oxidation of methanol occurs until complete consumption of oxygen. The heat of reaction rapidly increases the temperature of the catalyst, which undergoes reduction and now the reforming of methanol dominates. Deactivation of the catalyst under the oxidation conditions is due to a decrease in the surface area accessible to CuO. Sintering of CuO seems to be mainly due to the elevated temperature. The oxidised region of the catalyst layer decreases with time and almost all hydrogen is produced in the last segment of the reactor, where steam reforming of methanol dominates. This proves that the activity of supported copper catalysts is governed by the oxidation state of copper.

Partial oxidation of methanol is also performed using traditional binary $Cu-Zn/Al_2O_3$ catalysts modified with Cr, Ce, Sm and other promoters, which enhance their activity, selectivity with respect to CO_2 and the operational life.[11, 127, 150–152] Compared to $Cu-ZnO/\alpha$-Al_2O_3 and $Cu-ZnO/\gamma$-Al_2O_3 the Cu–ZnO–SDC catalyst (SDC is samaria-doped ceria) shows a higher activity in the reforming of MeOH and a higher selectivity with respect to hydrogen in autothermal reforming of methanol. Partial oxidation of methanol at stoichiometric reactant ratio in the presence of structured catalysts $Cu-ZnO/Al_2O_3$/cordierite is characterised by the yield with respect to hydrogen ~90%.[153] An increase in the oxygen content in the reaction mixture to the values exceeding stoichiometric ones leads to preferred formation of deep oxidation products. Zinc oxide present in the catalysts controls their redox properties (increases the reducibility of copper), which favours an increase in the yield of hydrogen and a decrease in the CO concentration.

Low-temperature CO shift reaction (180–240 °C) is carried out using Cu–ZnO catalysts modified with zirconium [7] or titanium,[154] which enhances their catalytic activity

and increases the operational life. However, all these catalysts are pyrophores and very sensitive to poisoning. In fuel processors, from 30% to 50% of the total mass and volume are occupied by CO shift reactors loaded with traditional Cu–ZnO catalysts. To improve the operation of these reactors and to make them more compact, air is fed to the tail segment.[155]

The copper–zinc catalysts considered should meet conventional requirements. Namely, they should be active towards a fuel chosen and thermally stable, withstand temperature shock, be poison- and coking-resistant and cause no high pressure drops in the system. Some of the catalysts mentioned above are of academic interest only. Copper catalysts are unstable at temperatures above 300 °C and prone to deactivation owing to the appearance of condensed water. Reduced Cu–Zn–Al catalysts are pyrophoric, which makes them less attractive to consumers of electronic devices. Research on Cu–Zn catalysts is continued because no compromise between their activity, cost, operational life and stability has found as yet.

2. Nanostructured copper–zirconium and zinc–chromium catalysts

A new $CuO-ZrO_2$ (8.5 mass %) catalyst synthesised by the sol–gel technique was studied to determine the activity, stability under operational conditions, formation of CO and the response to the introduction of oxygen to the organic raw material.[156] Tests were carried out with a fixed-bed reactor in the temperature range 250–300 °C at atmospheric presure; the results obtained were compared with the characteristics of industrial catalyst $Cu-ZnO-Al_2O_3$. The copper–zirconium catalyst appeared to be more active (per unit mass of copper) and stable (measurement duration to 250 h) than the $Cu-ZnO-Al_2O_3$ catalyst; the yield of CO was ~0.2 vol.% at 100% conversion of MeOH. The catalyst was activated by introducing oxygen into the organic raw material (50 cm^3 min^{-1} over a period of 5 min). Both catalysts compared deactivated with time. The deactivation of the catalyst in the process under study involves two stages, a nonlinear (interval 0–100 h) and a linear one (at process durations exceeding 100 h). A study[157] on the deactivation of industrial catalyst for the CO shift reaction used in methanol steam reformer carried out over a period of more than 2000 h made it possible to distinguish between the deactivation due to metal sintering and the deactivation due to poisoning with the hydrocarbon raw material. Exponential decrease in the catalyst activity in the early stage of the process is due to sintering of copper particles. The stability of the $CuO-ZrO_2$ catalyst and the lower rate of deactivation are probably due to macroporous zirconium substrate, which is more efficient in preventing copper from sintering than $ZnO-Al_2O_3$.

The addition of ceria to the copper–zirconium catalyst ($ZrO_2:CeO_2 = 1:1$) at a Cu content in the range 5 mass %–15 mass % even more increased the efficiency of the catalyst, the duration of stable operation and suppressed carbon monoxide formation (Fig. 22).[158] It was found that the optimal content of copper in the catalyst should be in the range 5 mass %–15 mass % and that a higher Cu content has no marked effect. A comparison of the $CuO-CeO_2$ and $CuO-ZrO_2$ catalysts for steam reforming of methanol showed that the highest activity corresponds to a Cu content of 80 mass % and an optimal ratio $H_2O:MeOH = 1.5$.[159] Once the process has started, the copper component of the catalyst had the chemical composition CuO and almost all catalysts were reduced to metallic Cu. The active phase Cu_2O appeared in the case of the $CuO-ZrO_2$ catalysts with 80 mass % and 90 mass % at $H_2O:MeOH > 1$. It was shown that the $CuO-ZrO_2$ catalyst has a longer operational life than $CuO-CeO_2$; however, the amount of ZrO_2 necessary for stabilisation of the Cu_2O form is still to be clarified.

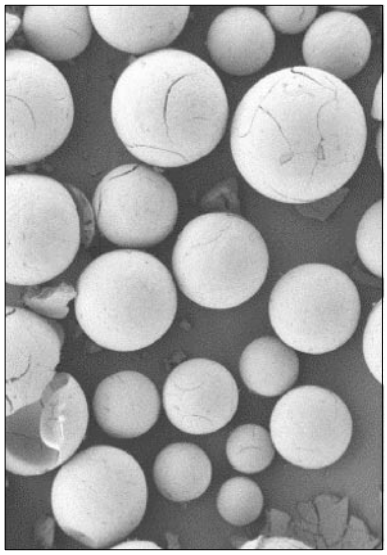


Figure 22. Micrograph of $Cu-ZrO_2-CeO_2$ catalyst after calcination.[158]

The stability of the $ZnO-Cr_2O_3/CeO_2-ZrO_2/Al_2O_3$ (Zn–Cr) catalyst in steam reforming of methanol was studied[160] using a microchannel reactor. The Zn–Cr catalyst supported on γ-Al_2O_3 was prepared by co-impregnation technique and coated on reactor channels. The content of (Ce–Zr) and (Zn–Cr) in the coatings was 25 mass % and 15 mass %, respectively (a total of 1.195 g). Tests showed that the introduction of ZrO_2 into the CeO_2 lattice significantly increases the oxygen capacity and the thermal resistance of the catalyst samples. It was also established that the catalyst containing ZrO_2/Al_2O_3 is highly stable and redox resistant. The introduction of water into the hydrocarbon raw material eliminated the deactivation of catalyst owing to coke formation throughout the tests (6 h). The Zn–Cr catalyst is highly stable, although a higher temperature is required to achieve the same degree of conversion as in the case of supported Cu and Pd catalysts. Three mechanisms of CO formation in methanol steam reformer studied in the tests included methanol decomposition and the direct and reverse CO shift reactions.

3. Gold catalysts on TiO_2-MO_x (M = Fe, Co, Zn)

Metallic catalysts containing non-noble metals are highly active at high temperatures, but at low temperatures their activity is low. Platinum-metal and gold catalysts have a higher activity in a wider temperature interval and therefore this class of catalysts also has been intensively studied.

Hydrogen production in partial oxidation of methanol (POM) on Au/TiO_2-MO_x (M = Fe, CO and Zn) catalysts was studied in the temperature range 150–275 °C.[161] The POM process on copper[150–152] and palladium[162,163] catalysts has been studied earlier. Gold catalysts prepared by deposition-precipitation technique appeared to be active in POM. The main problem in H_2 production on supported

gold catalysts is their deactivation due to the growth of particles and reduction of gold ions to metallic gold. It is known that the addition of metal oxides changes the properties of platinum-metal catalysts. Additives can increase the metal dispersity, thus acting as chemical and structural promoters or as co-catalysts. For instance, the oxidation of CO on noble-metal catalysts can be improved by adding MnO_x, CoO_x, LaO_x and CeO_x. Metal oxide additives (Cr, Mn, Fe, Co, Ni, Cu or Zn oxide) also change the catalytic activity of the $Au-Al_2O_3$ catalysts in the oxidation of CO and CH_4. Activity measurements of the Au/TiO_2-MO_x catalyst revealed the following order: $Fe_2O_3 > Co_3O_4 > ZnO$. Metal additives play a dual role, namely, they stabilise gold particles, thus preventing them from sintering, and provide with active oxygen for the reaction, simultaneously suppressing the reduction of gold ions. The size of nanoparticles with various additives was the same and provided a higher thermal stability of the catalysts.

4. Binary palladium–zinc catalysts

Similarly to other platinum metals (Pt, Rh), palladium exhibits high activity in the decomposition of methanol to CO and H_2. Selective formation of hydrogen in the POM process with air as oxidising agent was studied using a number of Pd/ZnO catalysts[163] prepared folowing a conventional saturation technique using microemulsion synthesis. Activity tests of the catalysts were carried out in the temperature range 230–300 °C. It was shown that the selectivity with respect to CO is related to the Pd particle size, namely, the larger the Pd particles the more intense the formation of CO. A study on the POM mechanism revealed initial combustion of the whole amount of oxygen and partial combustion of methanol. Direct POM process affords water and CO and is followed by the CO shift reaction resulting in CO_2 and H_2 and finally, when the whole amounts of oxygen and water are consumed, methanol decomposes to CO and $2\,H_2$.

Recently, it was found that Pd supported on ZnO exhibits high activity and selectivity with respect to CO_2 in steam reforming of methanol; this was previously unknown for noble-metal catalysts.[164] Under conditions of steam reforming of methanol the Pd/ZnO catalyst mainly produces CO_2 and H_2 and a minimum amount of CO. The rate and selectivity of the process appeared to be dependent on the type of substrate.[165] For instance, a 10% Pd/ZnO catalyst shows a low rate of steam reforming of methanol but a nearly 100% selectivity with respect to CO_2. Contrary to this a 10% Pd/CeO_2 catalyst provides a high rate of steam reforming of methanol, but a lower selectivity with respect to CO_2. Industrial Cu-catalysts, are pyrophores and unstable at high temperatures (> 270 °C), whereas Pd-catalysts are more stable and can operate in a wider temperature interval.

A highly active and selective Pd/ZnO catalyst was developed[166] for steam reforming of methanol. A change in the Pd content in the catalyst from 4.8 mass % to 16.7 mass % caused the profiles of MeOH conversion to shift towards lower temperatures and complete conversion was achieved at temperatures below 300 °C. The catalyst containing 16.7 mass % of Pd showed the lowest selectivity with respect to CO. The composition of nitrogen-free anhydrous gas produced using this catalyst was as follows (in vol.%): CO (1), CO_2 (26) and H_2 (73). To explain differences in the selectivities with respect to CO and CO_2, steam reforming of methanol on Pd/ZnO and Pd/CeO_2 catalysts was studied using various substrate types and amounts of Pd.[167] The conclusions drawn by the authors were in excellent agreement with the results of study.[165] High selectivity of the Pd/ZnO catalyst with respect to CO_2 was explained by a higher density of acid centers, which favour the formation of CO_2 as compared to Pd/CeO_2 having a higher density of base centers, which are more preferable for CO production.

The study of Pd/ZnO catalysts in autothermal reforming of methanol was carried out[168] at variable content of Pd (from 1 mass % to 45 mass %). Catalysts were prepared using the co-impregnation and co-precipitation techniques. The catalytic activity was strongly dependent on the Pd content, the highest activity and selectivity of the catalysts were attained in the range 5 mass %–37.5 mass % Pd. Excess amounts of Pd reduced the catalyst activity and increased the CO concentration. A comparison of a 20% Pd/ZnO catalyst with the industrial catalyst Cu/ZnO showed (after 4 h) that it is more stable, gives a higher yield of hydrogen; however, the CO concentration was higher (8000 ppm *vs.* 3300 ppm in the case of Cu/ZnO).

A Pd/ZnO catalyst prepared by the co-precipitation technique was modified[169] by introducing the third metallic component (M) (M = Mg, Al, Zr, Ce, La, Ru or a first-row transition metal). Tests were carried out at a pressure of 0.1 MPa. It was found that doping of the catalyst with a small amount of Cr, Fe or Cu ($M:Zn < 0.04$ or $M:Pd < 0.7$) suppresses the formation of CO and causes enhancement of hydrogen production. On the contrary, the CO concentration significantly increases upon adding Co, Ni and Mg. The modification with Al, Zr, La, Ce, Ru or Mn also led to an increase in the CO concentration, although to different extent. The addition of the third metal element reduced the size of the ZnO support crystals; as a result, smaller Pd–Zn crystallites were obtained at higher reduction temperatures. The interaction of the additives with ZnO or Pd results, on the one hand, in mixed binary oxides ($ZnAl_2O_4$, $ZnCr_2O_4$ and $ZnFe_2O_4$), and, on the other hand, in elemental Pd in addition to the Pd–Zn alloy, which increases the concentration of CO.

A study on autothermal reforming of methanol on Pd–Zn–Al catalyst, which contained 1%–2% Pd and was prepared by impregnating a spinel-oxide mixture ($ZnAl_2O_4/ZnO$) obtained by thermal decomposition of synthetic Zn–Al-hydrotalcite was reported.[170] It was found that the metal phase contained 93%–95% of Pd/Zn (1 : 1) alloy. The catalyst showed a high activity (MeOH conversion 100% at 450 °C and a selectivity of 11.5% with respect to CO and 88.5% with respect to CO_2), which is due to high dispersion of the Pd/Zn alloy. The presence of a small amount of non-alloyed palladium phase in the catalyst causes undesired formation of CO.

Hydrogen production by decomposition of methanol on Pt/Al_2O_3 catalyst and cerium-promoted $Pt-CeO_2/Al_2O_3$ catalyst was studied.[171] The cerium-promoted Pt- and Pd-catalysts exhibit an identical activity, namely, a 100% conversion is achieved at ~315 °C. Among all catalysts, the system Pt (9%)–CeO_2 (10%)/Al_2O_3 showed the highest activity exceeding that of the industrial copper catalyst. The selectivity with respect to hydrogen was higher than 99%.

Thus, the Pd–Zn catalysts are comparable in activity with the Cu–Zn catalysts, being more stable over a wider interval of operating temperatures and therefore real candidates for the use in reactors for fuel processors. Wide use of

these catalysts requires reduction of CO concentration down to at least the CO content achieved using Cu–Zn catalysts.

5. 'Catalytic paper' or Cu–Zn catalysts on ceramic fibre

Using copper–zinc catalytic powders, catalysts for reforming of methanol were successfully prepared in the form of paper-like composites (Fig. 23) called 'catalytic paper'† with ceramic fibres as matrix supports.[172–174]

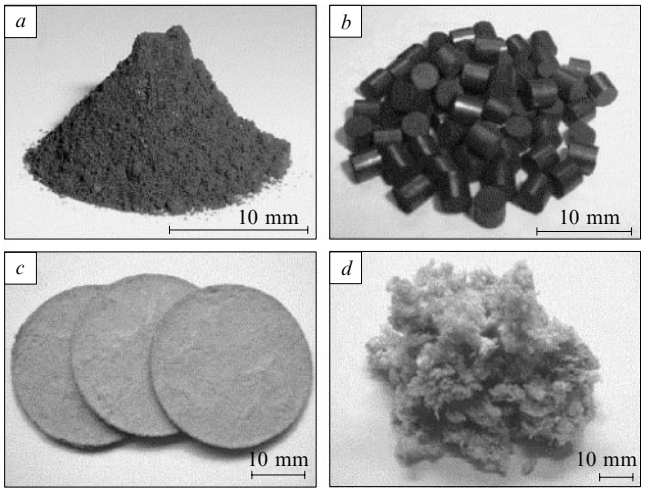


Figure 23. Visual appearance of variously shaped catalysts.[172] Powder (*a*), grain (*b*), paper-like Cu/ZnO composite ('catalytic paper') (*c*) and a catalyst–fibre mixture (*d*) of the same composition as the 'catalytic paper'.

Catalytic powders were prepared by spraying industrial Cu/ZnO catalyst grains and griddling them using a 100-mesh sieve. The paper composite consisted of catalyst powder (1.5 g), ceramic fibre (5 g), aluminium sol (1 g) and pulp (0.1–5.0 g). The composite was heat treated at 350 °C for 24 h to extract organic components. The porous structure was controlled by adding pulp. Ten round samples of 'catalytic paper' (1 mm thick, surface area 800 mm^2) were prepared. A stack of samples (volume 8×10^3 mm^3) was compared with the granular industrial catalyst of the same volume under conditions of steam reforming of MeOH. 'Catalytic paper' showed a lower CO concentration and a higher activity in production of hydrogen compared to the industrial catalyst. The low CO concentration was due to a large volume of macropores (70%), whereas a comparison of nanopore size (10–20 nm) in the catalyst samples under study gave almost indistinguishable results. Autothermal conversion of methanol on catalytic powder, grains and on 'catalytic paper' at 250 °C was compared.[171] Methanol conversion was much higher on 'catalytic paper' than on the granular industrial catalyst; the efficiency of 'paper' was equivalent to that of the initial catalytic powder. Hydrogen production was twice as high as that obtained with the granular catalyst. The CO concentration in the product gas usually increases as the MeOH conversion increases; however, it decreased when the 'catalytic paper' was used. Probably, the unique porous structure of 'catalytic paper' caused 'intrinsic improvements' in the flow of the gas being reformed. In addition, autothermal reforming of methanol occurs at lower (by 50 °C) temperatures than steam reforming of methanol, which reduces the contribution of the CO-producing reaction (reverse of the CO shift reaction).

Ceramic and silicon–carbon fibres were impregnated with copper–zinc powders and then 'catalytic paper' was prepared.[174] Owing to high heat conductivity of the SiC fibre this catalyst showed a higher MeOH conversion and a lower CO concentration as compared to the industrial Cu–Zn catalyst. The SiC-fibre present in the catalyst improved the heat distribution and, probably, suppressed the reverse reaction with respect to the CO shift reaction.

Catalysts prepared by paper technology allow one to control the porous structure by adding pulp and thus to achieve a higher efficiency of the hydrogen production process compared to conventional copper–zinc catalysts.

6. Layered double hydroxide-derived catalysts

Catalytic production of hydrogen in four reactions (decomposition, partial oxidation, steam and autothermal conversion of methanol) was studied using a number of layered double hydroxide-derived catalysts (LDH) (Mg/Al, Cu/Al, Co/Al and Ni/Al).[5,173,174] The LDH catalysts Co/Al and Ni/Al were active in all four reactions. The major products were H_2, CO and/or CO_2 with a small amount of dimethyl ether (DME) and CH_4. Among the reactions studied, autothermal reforming of methanol was the most efficient with respect to the methanol conversion and to the selectivity with respect to H_2. At 300 °C, a 100% conversion of MeOH can be attained with the highest selectivity with respect to H_2 and CO_2 (only traces of CO) on the Co/Al-LDH catalyst.[6] Partial replacement of Al by Sn in Ni/Al- and Co/Al-LDH catalysts suppressed the reforming of methanol, but simultaneously suppressed the formation of DME and CH_4 and increased the selectivity with respect to H_2. Tin present in the Ni/Al- and Co/Al-LDH catalysts improved their recoverability. The most active catalyst in steam reforming of methanol was Cu/Al-LDH, which was activated at 230 °C. The catalysts Ni/Al and Co/Al-LDH also were active in steam reforming of methanol, but activated at 315–320 °C.[175] For the Ni/Al-LDH catalyst the main reaction route was the decomposition of methanol. No activity of the Mg/Al-LDH catalyst was observed in steam reforming of methanol. The recoverability of divalent cations present in LDH was the critical parameter in determining the activity of the catalysts. In the Cu/Al-LDH catalyst, Cu^{2+} cations were reduced with ease; therefore, it was the most active in steam reforming of methanol. The introduction of noble metal ions (Au, Rh or Ir) into the Ni/Al-LDH catalyst with partial replacement of Al led to significant acceleration of the methanation reaction.[176] Methane is undesired side product and its production dramatically decreases the yield of hydrogen. Probably, Ni/Al-LDH catalysts modified with the noble metals are inappropriate for hydrogen production from methanol.

7. High-temperature Ir catalysts and bimetallic Ir–Pt catalysts

Iridium and Ir–Pt catalysts on various substrates for high-temperature steam reforming of methanol (~400 °C) were investigated.[177] Pd/ZnO catalysts considered earlier,

† Earlier, these authors reported the preparation of photocatalytic paper containing TiO_2 and zeolite powders. This catalyst is used in practice for indoor photocatalytic decomposition of volatile organic components and NO_x and for extraction of chemical substances from water. — S Fukahori, H Ichiura, T Kitaoka, H Tanaka *Environ. Sci. Technol.* **33** 1048 (2003).

although showed a higher selectivity with respect to CO_2 compared to traditional Cu/ZnO systems, can be used at temperatures below 300 °C. New catalysts Ir/Al_2O_3, Ir/ZrO_2, Ir/CeO_2 and Ir/CeO_2-ZrO_2 show a higher activity and stability at temperatures up to 400 °C and can be integrated with the Pd-membrane reactor. Four types of substrates were tested to determine their effect on the characteristics of the catalyst. It was found that Ir coated on CeO_2 is the most active in steam reforming of methanol. The characteristics of the Ir/CeO_2 catalyst, especially its stability, can be significantly improved using a mixed oxide CeO_2-ZrO_2 instead of CeO_2 (optimum composition $CeO_2:ZrO_2 = 1:1$) as substrate. The addition of Pt to the Ir/CeO_2-ZrO_2 catalyst leads to synergistic effect with Ir, which allows one to efficiently reduce the yield of CO and to increase the H_2 concentration in the reformate. The optimal bimetallic Ir–Pt catalyst (0.3 mass % Ir–0.3 mass % Pt supported on $CeO_{0.5}Zr_{0.5}O_2$) showed the highest stability and activity over a period of 200 h, which is better than the corresponding parameters of traditional Cu/ZnO catalysts.

8. Catalysts for preferential CO oxidation

Copper catalysts supported on mixed oxides are good extractants of CO from the product gas in steam reforming of methanol in the CO shift reaction. Although the $Cu-ZnO/Al_2O_3$ catalyst exhibits an excellent activity in the CO shift reaction, a PEM fuel cell requires that the CO concentration be reduced to $\leqslant$10 ppm. Extraction of CO from reformate to trace amounts by the CO shift reaction presents some difficulties owing to high concentration of hydrogen in the product gas. However, the addition of small amounts of O_2 ($\sim$2 vol.%) to the reformate efficiently reduces the CO concentration (to 100 ppm) in the preferential CO oxidation on the 30 mass % $Cu-ZnO/Al_2O_3$ catalyst at 150 °C.[178] The lower the temperature and the higher the oxygen concentration the higher the degree of CO extraction. Preferential CO oxidation in excess hydrogen on the $CuO/Ce_xSn_{1-x}O_2$ catalyst was studied.[179] The most active was the catalyst of composition CuO (7 mass %)/$Ce_{0.9}Sn_{0.1}O_2$; its activity exceeded that of the catalyst with the same CuO content on pure CeO_2. In addition, the temperature of 100% MeOH conversion on the first catalyst (80–85 °C) was 15 °C lower than on the second catalyst (95–100 °C). The catalyst CuO (7 mass %)/$Ce_{0.9}Sn_{0.1}O_2$ was almost inactive in the oxidation of hydrogen at temperatures below 110 °C. The activity of this catalyst is comparable with that of the Pt (5 mass %)/Al_2O_3 catalyst, but the selectivity is much higher.

Regularities of preferential CO oxidation in the surface ignition regime of a modified platinum catalyst and a Ru/Al_2O_3 catalyst were investigated.[180,181] In the surface ignition regime the catalyst 0.1% Ru/Al_2O_3 makes it possible to reduce the residual CO concentration from 0.8 vol.% to 10–15 ppm at $O_2:CO = 1$ even in the presence of H_2O and CO_2 (to 20 vol.%) at volume rates of 100 litre $g_{cat}^{-1}\,h^{-1}$. Four monolithic catalysts (cordierite coated with γ-Al_2O_3 with applied Pt, Pd, Rh and Ru) were studied for preferential CO oxidation under the operating conditions of a PEM fuel cell.[182] The reaction mixture containing (vol.%) CO (1), O_2 (1), CO_2 (20), H_2 (50) (anhydrous gas) and N_2 simulated a real gas conversion of methanol. It was established that 0.5 mass % Pt/Al_2O_3 catalyst is the most active and selective with respect to CO_2. In the one-step reactor the addition of 1 vol.% of O_2 ($O_2:CO = 1:1$) reduced the CO concentration from 10 000 to less than 70 ppm. The catalyst was very stable during 1000-h tests, and only after 900 h the CO concentration increased to 100 ppm. The catalyst was scaled and successfully used in a hydrogen-based power supply for 5-kW PEM fuel cell. Kinetic models for the CO shift reaction on industrial catalyst Cu/ZnO/Al_2O_3 and for preferential CO oxidation on $Pt-Fe/Al_2O_3$ catalyst were constructed.[183,184] The results obtained[185–187] confirm that gold catalysts are potential candidates for industrial applications, especially for preferential CO oxidation.[188,189]

9. Membranes as catalysts for reforming of methanol

Steam reforming of methanol was carried out using an industrial CuO/ZnO catalyst and using two modified catalysts, 1% Pd–CuO/ZnO and 1% La_2O_3–CuO/ZnO, at 270, 310 and 350 °C and pressures of 0.1, 0.4 and 0.9 MPa.[190,191] An unexpected acceleration of the direct steam reforming of methanol by 50%–100% compared to the same reaction without Pd-membrane was observed. This phenomenon is due to spillover of hydrogen, *i.e.*, direct transfer of hydrogen newly formed on the copper catalyst to the membrane surface. The CuO/ZnO catalyst on the membrane enhances the permeability of H_2 across the membrane. This shows that spillover of hydrogen plays the role of a 'kinetic bridge' between the catalytic site and the membrane surface. Thus, a higher degree of MeOH conversion in the membrane reactor is due to fast release of hydrogen from the catalytic site rather than a decrease in the rate of the reverse reaction, as was assumed earlier.

10. Comparison of catalytic systems for reforming of methanol

A comparative study of three catalytic systems (granular layer; foam block coated with catalyst; heat exchanger with wall coated with catalyst) in steam reforming of methanol was carried out.[102] General conditions are as follows: fixed-bed layer (grain size 3 mm, total weight 74 g) for conventional industrial copper catalyst for reforming of methanol; aluminium cylinder (length 10 cm, diameter 5 cm, total mass of catalyst 17 g) for the foam block; and an aluminium heat exchanger (volume 0.23 litre, catalytic wall, total mass of catalyst 18 g). At high methanol conversion (>95%), the temperatures of the process were different, being equal to 280 °C for the fixed-bed layer, 250 °C for the foam block and 230 °C for the heat exchanger. After 150 h the systems with catalytic coating deactivated to a greater extent (10%–15%) than the fixed-bed system (1.5%) due to the low content of the active component in the aluminium structure. However, raising the temperature by 10 °C after 150 h made it possible to maintain the methanol conversion at a high level (>90%) over a period of 450 h. The heat exchanger showed the maximum performance with respect to hydrogen (650 litre h^{-1}) at a raw material feed rate of 3600 h^{-1}, pressure of 0.15 MPa and a methanol conversion of 70%. At 320 °C (MeOH conversion >90%), the outlet CO concentration increased to 8000 ppm. To provide a 20-kW power for a mass transit bus, a 6-litre heat-exchange reactor is needed. The advantages of the methanol reactors with catalyst-coated devices over the fixed-bed reactors are as follows: no heat transfer problem, no 'hot' and 'cold' points at the inlet, lower pressure drop in the reactor and better dynamic response on startup and in transient regimes.[192]

IV. Conclusion

Materials considered in this review are convincing illustration of rapid progress of hydrogen production from methanol for stationary, mobile and portable fuel-cell power plants. About 2% of energy produced worldwide are spent for hydrogen production ($\sim 50\,000\,000$ t = $550\,000\,000$ m^3).[193, 194] Production of 1 Nm^3 of H_2 requires ~ 0.65 kg of methanol. Most experts believe that methanol is the most promising fuel for electric transport vehicles except hydrogen. Since 2004, researchers and engineers in the USA no longer do research and development in the field of fuel processors with hydrogen production from petrol.

The number of environmentally hazardous cars and trucks reaches a value of 705 000 000 worldwide and there has been a trend towards a threefold increase in this number to the year 2050, with the major contribution from China.[193] Taking into account the fact that 97% of fuel for automotive vehicles is produced from oil, its consumption should be reduced to decrease the emission of carbon compounds. In the nearest decade the greatest interest will be focussed on electric vehicles and hydrogen-driven vehicles with 'green' power plants rather than new vehicles with minimum consumption of petroleum products.[195] When using hydrogen-based fuel cells, the overall emission of greenhouse gases per 1-km distance is 110 g (*cf.* 150 g for a hybrid and 195 g for automotive vehicles). There are two methods of hydrogen supply to vehicles, namely, filling tanks and on-board production. The first method was demonstrated by Honda and Toyota (both from Japan) in the year 2005. A prototype vehicle travelled a distance of 450 km with a tank filled with compressed hydrogen (pressure 70.0 MPa). A new eco-mobile made by Toyota travelled a distance of 560 km from Osaka to Tokyo bearing a doubled-volume hydrogen tank at the same pressure.[196] This means that Japan is ready to turn to 'green' fuel, although large-scale production of such vehicles is at present impossible owing to their high cost.

However, there are a few hydrogen fuel stations (~ 100 worldwide *vs.* 170 000 filling stations); therefore, on-board production of hydrogen seems to be more appropriate. In spite of substantiated calculations,[197] which show that the development of hydrogen infrastructure is cheaper than the development of on-board fuel processors, at present the development of compact and reliable on-board fuel processor with long operating life seems to be more preferable. Intensive research on catalysts and reactors for fuel processors has been carried out. As the number of fuel cell driven vehicles will be as large as 25% of the total number of automotive vehicles (the estimate[196] for the USA is 0.83%, *i.e.*, $\geqslant 1\,500\,000$ vehicles), filling hydrogen tanks will be cheaper than on-board hydrogen production.[193] Unfortunately, cheap multifuel (from natural gas to gas oil) reactors for on-board fuel processors have not been developed so far.[198] To reduce the cost of fuel cells and the system of methanol reforming in stationary, mobile and portable power plants, international co-operation in the framework of certain research programmes is necessary. These should be interdisciplinary programmes with participation of petroleum-refining industry, automotive industry, production of catalysts, research institutions and universities, as well as governments and legislatives.

The author expresses his gratitude to Academician V N Parmon and DSc L L Makarshin for useful discussions and valuable recommendations.

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