ISSN 1070-3632, Russian Journal of General Chemistry, 2007, Vol. 77, No. 4, pp. 676–684. © Pleiades Publishing, Ltd., 2007.
Original Russian Text © L.L. Makarshin, V.N. Parmon, 2007, published in Russkii Khimicheskii Zhurnal, 2007, Vol. 50, No. 6, pp. 19–25.

Microchannel Catalytic Systems for Hydrogen Energetics

L. L. Makarshin and V. N. Parmon

Boreskov Institute of Catalysis,
pr. Akad. Lavrent'eva 5, Novosibirsk, 630090 Russia
tel: (383)330-78-31
fax: (383)330-80-56
e-mail: makarshin@catalysis.nsk.su

Received September 26, 2006

Abstract — The concept of hydrogen energetics envisages economically reasonable hydrogen production from various organic compounds in stationary and mobile devices of low and medium performance, called "fuel processors." Fuel processors with a high specific performance in hydrogen can be developed with the aid of microchannel catalytic systems. The paper considers the present situation with microchannel catalytic reactors for fuel processors.
DOI: 10.1134/S1070363207040305

INTRODUCTION

The onrushing decrease of oil resources requires new chemical energy carriers and alternative and nontraditional energy sources to be developed already in the XXI century [1]. Main focus is on hydrogen which is contained in all organic substances and water. The unique properties of hydrogen make it a universal and an ecologically clean energy carrier appropriate for all types of heat engines and power-generating devices. Active search for ways to transfer power-consuming industries and transport to hydrogen fuel and electrochemical generators on the basis of fuel cells (FCs). Therewith, of particular importance are fuel processors, specifically compact generators of hydrogen from organic compounds: hydrocarbons, alcohols, and ethers.

Beginning in 2001, many industrially developed countries have announced big state programs in hydrogen energy. Presently almost all major motor and energy companies, as well as hundreds of medium and small innovation institutions are involved in research in this field. The large-scale research programs are planned for a period of up to 2020 and aimed at reducing dependence of developed countries on imported energy resources [2]. In Russia developments in the field of microreactor technics have only been initiated.

The conversion of a starting chemical compound into a hydrogen-containing gas is generally performed by means of catalytic processes [3]. Therewith, is hydrogen is intended for use in low-temperature FCs, additional rigid requirements for its purity, especially to its CO content, arise. Thus, for instance, for low-temperature FC applications, the CO content of hydrogen should be less than 10 ppm. The catalytic purification of hydrogen generated by catalytic conversion of methanol for FC vehicles is reported in [4, 5]. Various systems for hydrogen production from hydrocarbons and alcohols for autonomous energetics are being developed [6–9]. Of considerable promise is on-site hydrogen production with fuel processors, which much reduces energy consumption for its storage and delivery, as well as favors safer operation of hydrogen-fueled devices. Particular attention is presently given to fuel processors based on microchannel catalytic systems, since they are more efficient than traditional catalysts.

The use of microelectronics in manufacturing chemical systems has been first reported in 1989 [10]. The Research Center in Carlsruhe and Institute of Microtechnology in Mainz (Germany) have been the first to manufacture multichannel reactors, micromixers, and microheat exchangers by means of lithography, electroplating, electrosparking, and machining [11]. Possible fields of application of microchemical devices and advantages they offer over conventional systems have been discussed in detail in the monograph [12].

The aim of the present paper is to outline Russian activities in the field of microreactor technics for hydrogen energetics.

HYDROGEN PRODUCTION BY CATALYTIC CONVERSION OF ORGANIC COMPOUNDS

Catalytic conversion of accessible organic fuels, specifically hydrocarbons, alcohols, and ethers, is the simplest and lowest cost technology for the production of hydrogen for mobile devices (transport, mobile power devices, portable current supply systems, etc.). This is explained by the fair operability and lower power inputs of catalytic hydrogen production processes compared with most physical methods: plasmo-, thermo-, electro-, and photochemical. Importantly, hydrocarbons, alcohols, and ethers used for hydrogen production are fairly cheap, highly power-intensive, readily transportable, and can be used for fueling power devices. Lower alcohols, such as methanol, dimethyl ether, and liquid hydrocarbons are considered to be the most suitable hydrogen carries for mobile and portable FCs, whereas methane and natural gas are the most suitable for high-capacity stationary power devices.

Microreactors on methanol has been most frequently used for hydrogen production. This is explained by the fact that, unlike other organic fuels, methanol has a fairly low temperature (250–300°C) of the catalytic conversion into hydrogen and CO_2, which favors a much simpler microreactor design.

The main methods of the catalytic production of hydrogen from organic compounds are steam reforming (SR), autothermal steam–oxygen reforming (ATR), and partial oxidation (PO) [7]. These processes all can be performed with any available hydrocarbons, alcohols, and ethers. As a result, the so-called synthesis gas (mixture of hydrogen with hydrocarbon oxides) is obtained. Let us consider the example of hydrogen production from methanol.

The steam reforming of methanol is an endothermic reaction and requires heat delivery to the reaction zone:

$$CH_3OH + H_2O \longrightarrow CO_2 + 3H_2, \quad (1)$$
$$\Delta_r H^0_{298} = 49.4 \text{ kJ mol}^{-1}.$$

Copper catalysts allow the steam reforming to be performed at 200–300°C [13–15]. Therewith, for 100% methanol conversion not infrequently a very short contact (no longer than 0.1–1 s) with catalyst suffices.

Autothermal reforming invoves two concurrent reactions: endothermic steam reforming and exothermic complete oxidation. The resulting enthalpy of the process is close to zero, and no heat supply from the outside is required:

$$4CH_3OH + 3H_2O + 0.5O_2 \longrightarrow 4CO_2 + 11H_2, \quad (2)$$
$$\Delta_r H^0_{298} \approx 0 \text{ kJ mol}^{-1}.$$

The partial oxidation of methanol with oxygen occurs exothermally, and the heat resealed during the reaction should be withdrawn:

$$CH_3OH + 0.5O_2 \longrightarrow CO_2 + 2H_2, \quad (3)$$
$$\Delta_r H^0_{298} = -192 \text{ kJ mol}^{-1}.$$

The most common catalysts for ATR and PO are Group VIII Metals and lanthanides [16–20]. Therewith, independent of the nature of the catalyst, these processes occur at 600–700°C, and the contact time is 0.01–0.001 s.

Equations (1)–(3) can be written in the general form:

$$C_nH_mO_p + xO_2 + (2n - 2x - p)H_2O(l) = nCO_2 + (2n - 2x - p + m/2)H_2, \quad (4)$$

where $\Delta_r H = (2n - 2x - p)\Delta_f H_{H_2O(l)} + \Delta_f H_{\text{fuela}} - n\Delta_f H_{CO_2}$.

The character of the process and its management features depend on the molar fraction x of oxygen in the starting mixture. At $x = 0$, equation (4) corresponds to the endothermic steam reforming of the carbon fuel, while at $x = n + m/4 - p/2$, the strongly exothermic complete oxidation of the organic compound occurs. Intermediate x values relate to partial oxidation which usually involves heat release.

For example, if the starting fuel is methane, then: at $x = 0$ (SR), $\Delta_r H^0_{298} = +250.1$ kJ mol^{-1}, whereas at $x = 0.44$ (ATR), $\Delta_r H^0 \approx 0$, and at $x = 2$ (complete oxidation), $\Delta_r H^0_{298} = -890$ kJ mol^{-1}.

In the absence of catalysts, to produce hydrogen from hydrocarbons and alcohols requires temperatures of above 1000°C. This increases energy consumption in the endothermic process, thereby enhancing requirements for heat resistance of reactor material.

Even though steam reforming is an endothermic process, and, therefore, the design of the corresponding reactor is more complicated than in the exothermic ATR and PO oxidation processes, preference is usually given to SR. Hydrogen produced by SR is not diluted with air nitrogen and has a higher concentration at the reactor outlet; with a liquid hydrocarbon fuel, the pressure of the reaction mixture in the reactor can be raised by means of a fairly simple liquid pump rather than energetically uneconomical gas compressors used in ATR and PO. Moreover, for the

external heat source in steam reforming one can use to the hot anodic gas released from the high-temperature FR. Such energy-compensating schemes enhance the total performance of a power device comprising a fuel processor and a fuel cell. Energy-compensating schemes for PO and ATR processes are still lacking.

CATALYTIC MICROCHANNEL SYSTEMS

A catalytic microchannel system (CMS) is a compact reactor with submillimeter channel plates in the inside. Microchannel plates (MCPs) are carriers of a catalytically active component and usually manufactured for materials with a high heat conductivity. The CMS design allows a series of important problems of traditional chemical reactors to be solved. These problem include, in particular, a low radial heat conductivity of fixed catalyst layer, which hinders heat exchange in the reaction zone, as well as insufficiently effective use of catalyst. Experimental evidence shows that the use of catalytic microchannel systems makes hydrogen production much more efficient than in traditional chemical reactors [21, 22].

The principal advantages of CMSs are as follows.

(1) The ratio of the surface area of an MCP to its total volume can attain 10000–50000 $m^2\ m^{-3}$, which is many times the respective ratio for traditional chemical reactors (100–1000 $m^2\ m^{-3}$).

(2) Lack of reagent concentration gradients along the MCP channel cross-section.

(3) At equal cross-sections of MCP channels, the reagent–catalyst contact times are short and have a narrow distribution.

(4) The high rate of heat and mass transfer ensures a uniform temperature distribution over the reactor.

The above-listed advantages of CMSs result in a much enhanced catalyst specific performance and, in certain cases, enhanced the selectivity of processes in the microreactor. These advantages are best manifested in fast reactions with short contact times and large heat effects, such as complete or partial oxidation of hydrocarbons [23–25]. The use of CMSs for gas-phase reactions has recently been reviewed [9].

There are presently two modes of catalyst arrangement in microchannel reactors (MRs). In first-type reactors MR1, submillimeter microchannels are filled up with small granules of catalyst; therewith, the reagents flow moves between granules [26, 27]. In second-type reactors MR2, catalyst is fixed on channel walls; therewith, the reagent flow moves along the channel void. The hydrodynamic resistance of first-type reactors MR1 is usually much higher than that of MR2. In this connection the reagent–catalyst contact time in MR2 can be much shorter.

Reactors of the MR1 type are similar to traditional reactors with a fixed catalyst layer, and approaches to calculating various parameters of catalytic processes in them are fairly well developed. This allows reliable model calculations of temperature and reagent concentration distributions over MR1 cross-sections, kinetic studies, catalyst activity testing, and reactor optimization. Reactors of the MR1 type are easy to manufacture in view of the lack of problem with fixing catalyst. Isothermal conditions in these reactors are attained if the channel diameter is no larger than 300 μm. However, a considerable hydrodynamic resistance therewith develops. The typical catalyst granule size is 35–75 μm, which corresponds to an outer granule surface area of $(40–86) \times 10^3\ m^2\ m^{-3}$.

More promising constructions are MR2 reactors with more than 10000 channels 50–1000 μm in cross-section and 20–100 mm in length. Such reactors offer essential advantages over MR1 in the case of fast reactions with large heat effects. Second-type reactors recators MP2 have a low hydrodynamic resistance [28] and, in view of short contact times, high specific performance. In real MR2 reactors the flow rates of gaseous mixture ~100 $cm^3\ s^{-1}$, and, therewith, a laminar flow with a parabolic velocity profile over the cross-section of the microchannel is realized. The reagent concentration profile over the channel cross-section depends on the axial-to-radial particle velocity ratio. Thus, for a circular pipe, the effective axial diffusion factor D_{ax} is given by the equation

$$D_{ax} = D + d^2u^2/(192D), \quad (5)$$

where D is the molecular diffusion coefficient; u, mean linear velocity of the pipe flow; and d, pipe diameter [29].

As seen, as the pipe diameter decreases, the second summand in Eq. (5) can become smaller than the first. As a result, D_{ax} gets closer to D, and the radial and axial flow velocities equalize. This results in equalization of the reagent concentrations over the pipe cross-section, i.e. to a more effective mass transfer between the central part of the channel and the catalyst layer on its walls. According to theoretical and experimental data [30, 31], such situation is realized in channels whose characteristic cross-section is smaller than 0.5 mm.

For high-performance of MRs the geometry of microchannels should be optimized with account for the activity of the catalyst used. Rouge et al. [32]

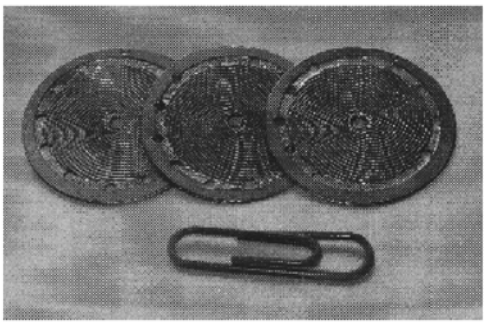

Fig. 1. Disc microchannel plates.

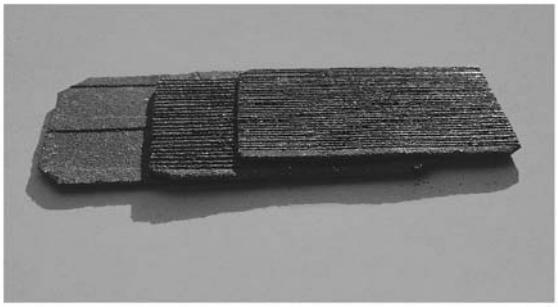

Fig. 2. Microchannel catalytic plate with rectangular channels fabricated by molding foamed-nickel plates prefilled with powdered catalyst.

made use of a three-dimensional model to calculate gas flow distribution and found an optimal microchannel geometry in a reactor of an MR2 type. Furthermore, as the amount of an active component fixed on the channel walls is increased, the MR volume performance increases. The optimal channel diameter and fixed catalyst layer thickness are 500 μm and 95 μm or 200 μm and 35 μm, respectively. Various techniques for fabricating and fixing a uniform thin porous layer on microchannel walls were developed. They include anodic oxidation of aluminum [33]; high-temperature treatment of a ferrochromium alloy (fechral) with subsequent chemical deposition of a high-porosity γ-Al_2O_3 layer [34, 35]; cementing a ready catalyst power on a metal support [36, 37]; fabricating a porous layer of channel walls by the zol–gel procedure [38, 39]; hydrothermal deposition of a ZSM-5 zeolite on a stainless-steel surface [40]; chemical vapor deposition of aluminum salts with subsequent fabrication of a high-porosity γ-Al_2O_3 layer [41]; plasmochemical deposition of metal nanoparticles [42, 43]; deposition of nanocarbon structures [44], etc.

Channels are fabricated by various techniques, many of which being adopted from microelectronics. They include photo- and laser lithography with subsequent chemical and electrochemical plate etching, precision milling or electrospark cutting, molding, and crimping. The development of a microreactor with microchannels fabricated from multilayer structures of diffusion-welded metal plates and spacers [45].

Figure 1 shows a photograph of a typical MCP 29 mm in diameter, made of stainless steel at the Institute of Catalyst, Siberian Branch, Russain Academy of Sciences, by means of laser lithography followed by electrochemical etching [46]. Twenty channels of the MCP have a shape of Archimed spirals with a cross-section of 0.2–0.2 mm. Catalyst deposition and fixation in microchannels of this MCP were performed by two techniques. In the first case, a mixture of a ready catalyst with a particle size of 1–5 μm and a pseudo-bemit binder was pressed in the channels. In the second, a layer of a high-dispersity γ-Al_2O_3 was chemically deposited on an aluminum buffer layer obtained by detonation spaying of α-Al_2O_3, after which an active component was applied by impregnation [19]. Good results are obtained with MCPs fabricated from metal foams. Figure 2 shows a foamed-nickel MCP with rectilinear channels. A ready catalyst powder was infused into the starting plate by means of ultrasound [47]. Further on, using a special press form, this catalyst-filled plate was molded into an MCP 0.3–0.8 mm thick under a pressure of 25 MPa. The molded MCP had channels with cross-sections of 0.2×12, 0.5×0.5, or 0.1×0.1 mm (Fig. 2).

MICROCHANNEL REACTORS FOR HYDROGEN PRODUCTION FROM METHANOL AND METHANE

A pool of experience is presently accumulated in developing various types of microreactors for chemical processes. These developments made it possible to decrease considerably the size of chemical reactors and to extend their application field, for example, to catalytic processes involving toxic and explosive substances, strongly exothermic and endothermic reactions, etc. [48]. A series of monographs devoted to application of microreactors and microthechnologies in chemical processes [12, 49, 50].

Gu-Gon Park et al. [51] described an MR with external heating for steam conversion of methanol. The reactor comprises three MCPs, three distribution plates, and two copper plates for equating the flow and temperature in the channels. Each MCP contains 20 parallel channels 0.5 mm in width, 0.2 mm in depth, and 33 mm in length. Commercial Cu–Zn–Al catalyst was used, which was fixed on the channel walls by pseudobemit. The dimensions of a device

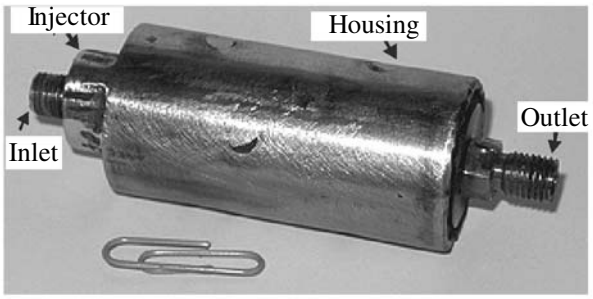

Fig. 3. Cylindrical microreactor for methanol steam reforming with built-in injector for liquid water–methanol mixture.

comprising the MR and an injector for water–methanol mixture were $70 \times 40 \times 30$ mm. At an operating temperature of 260°C, the hydrogen performance was 12 l h^{-1}. The composition of the outgoing dry gas was as follows, %: H_2 73.4, CO_2 25.0, and CO 1.6.

An MR for steam conversion of methanol with an exothermic profound oxidation of methanol as a heat source was described by Jung Yeon Won et al. [52]. The MR comprises three MCP for steam reforming of methanol and three plates for methanol oxidation (80×35.5 mm). Each plate contains 10 channels 1.0 mm in width, 0.5 mm in depth, and 45 mm in length, fabricated by photolithography followed by chemical etching. A porous SiO_2 or γ-Al_2O_3Ha layer was fixed on the channel surface, containing a Cu/ZnO catalyst (by 96 mg per one MCP) for methanol reforming and a Pt/ZrO_2 catalyst (by 66 mg per one MCP) for methanol oxidation. The MR effective performance was 3.9 l H_2/h.

Cao et al. [53] described an MR with effective heat exchange for steam methanol reforming. This reactor contains slit-like microchannels 0.508 in width, filled with granulated catalyst. The MR was heated with an oil flowing over channels of a heat-exchange plate positioned between the MCP and catalyst. This MR design made it possible to simply model processes occurring in this device, including a three-dimensional temperature and reagent concentration profiles over the length and cross-section of a microchannel [54]. On the basis of the resulting data, a prototype small fuel processor combined with a FC with 300-mW power was fabricated.

The key role in providing target operation parameters of a MR belongs to catalyst activity. For example, Zhang et al. [55] compared the catalytic activities of Cu–Al–Zr and Cu–Al in the steam reforming of methanol in a MR as a function of the water/methanol ratio in the starting reaction mixture, reaction temperature, and volume methanol delivery rate. The Cu–Al–Zr catalyst containing 15 wt% of ZrO_2 proved to be more active than Cu–Al at 250°C. Therewith, the methanol conversion was 95.0%, H_2 selectivity 99.9 vol%, and reactor outlet CO concentration 0.17% vol%. After 200-h operation the methanol conversion was about 90 vol%. According to X-ray diffraction data, addition of ZrO_2 to Cu/Al_2O_3 enhances dispersity of copper on the catalyst surface and prevents conglomeration of particles. It is these factors that are responsible for the enhanced efficiency of the catalyst.

In Russia research and development of microchannel catalytic reactors have been initiated some years ago and still concentrate at the Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences. Below we describe several Russian microreactors. A series of flow circulatory research devices were developed and used to success in kinetic studies on heterogeneous processes and determination of catalyst activity [56, 57]. Three types of MRs for methanol steam reforming with external heating were developed: cylindrical (CMR), rectangular (RMR), and heat-exchange (HEMR) [46, 47, 58].

Figure 3 shows a photograph of a stainless-steel CMR (diameter 30 mm, length 60 mm) comprising 130 disk MCPs. At the inlet, the reactor has a copper injector for a water–methanol mixture. A gaseous water–methanol mixture (molar ratio 1 : 1) after the injector passes to the central part of disk microchannel plates. From the central part, the reaction mixture passes, through spiral channels, to disk periphery where these flows unite into a common flow outgoing from the microreactor. The catalyst is a copper–zinc composite with a 40 : 60 Cu : Zn molar ratio, synthesized by the procedure in [59]. A mixture of powdered catalyst and pseudobemit was pressed into the microchannel bottom. As a result, the disk MCP contains channels with a cross-section of 0.2×0.15 mm. At the inlet flow rate of 100 ml h^{-1} and reactor temperature of 260°C, the methanol conversion in the MR was 80%, hydrogen performance 130 l h^{-1}. The specific performance of the MR per catalyst weigh and total MCP volume was 67 l g^{-1} h^{-1} and 5.4 l cm^{-3} h^{-1}, respectively.

Figure 4 shows a brass RMR, dimensions $65 \times 90 \times 85$ mm. The reactor comprises three isolated dismountable sections heated with built-in electric heaters. The MCPs in the microreactor have parallel submillimeter channels (Fig. 2). The MR design allows the number of sections to be varied to ensure desired reactor performance. The MR is tightened by means of graphite seals. For convenient reactor re-

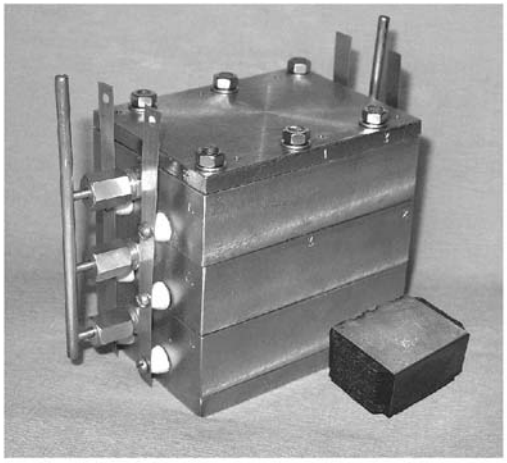

Fig. 4. Rectangular sectional microreactor for methanol steam reforming with interchangeable MCP blocks and built-in electric heater.

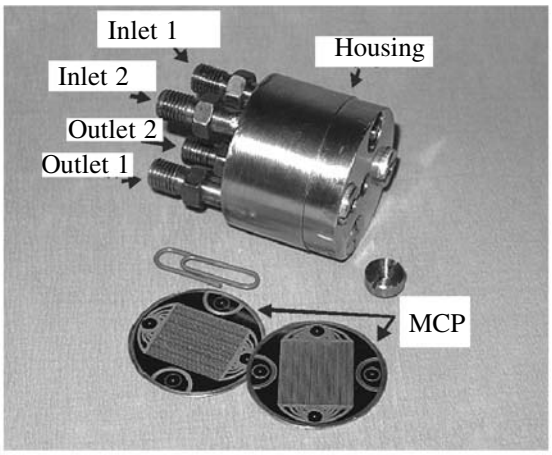

Fig. 5. Heat-exchange microreactor for methanol steam reforming.

loading, 20–30 MCPs are assembled into a block ($40 \times 30 \times 18$ mm) which is then embedded into the microreactor section. As a result, the microchannel block is fairly easy to change. Testing of one microreactor section was performed using a foamed nickel MCP with a CuCe–Al catalyst synthesized by the procedure in [60]. At the inlet liquid methanol–water flow of 80 ml h^{-1} and reactor temperature 260°C, the methanol conversion was 80%, hydrogen performance of one RMR section 106 l h^{-1}, and specific microreactor performance per total MCP volume 4.9 l cm^{-3} h^{-1}.

An HEMR microreactor 40 mm in diameter and 35 mm in height, fabricated from stailess steel is shown in Fig. 5. In this reactor, the endothermic methanol steam reforming reaction is combined with the exothermic reaction of methanol profound oxidation with air, which occurs in an isolated volume. The MCPs were made of stainless steel and had 40 parallel channels 0.1×0.1 mm in cross-section and 20 mm in length. The MCP and MR were tightened with graphite seals. The microreator was packed so that MCPs for methanol steam reforming alternated with MCPs for methanol profound oxidation. Therewith, contacting MCPs were arranged so that their channels were perpendicular to each other. The steam reforming catalyst was Cu/ZnO, and the profound oxidation catalyst, Pt/ZrO_2. During tests, an MR was thermoisolated and heated to the initial methanol catalytic oxidation temperature of 250°C, after which the heater was turned off, and the MR was let to operate autonomously. At the reactor temperature of 270°C, the recorded hydrogen HEMR performance proved to be 32 l h^{-1}.

Under support of the "Novel Energy Projects" Innovation Company, the Institute of Catalysis SB RAS developed a laboratory microchannel reactor for partial methane oxidation [61]. Figure 6 shows a photograph of the reactor ($36 \times 24 \times 26$ mm). The useful volume occupied by MCPs is 4.0 cm^3. The inlet gas mixture enters through a socket to the upper part of the reactor, where it is heated and uniformly distributed over the cross-section of the void with MCPs. The latter ($20 \times 20 \times 0.8$ mm) were fabricated by crimping of fechral 50 μm thick. The plate surface was coated, by means of detonation spaying, with a thin continuous α-Al_2O_3 film which serves as a buffer layer for subsequent fixing high-porosity γ-Al_2O_3. Further on a catalytically active component ($La_{0.2}Zr_{0.4}Ce_{0.4}$/LaNiPt, 80 mg per one plate) was applied by impregnation/hardening. The microreactor was loaded with ten crimped plates ($20 \times 20 \times 0.8$ mm)

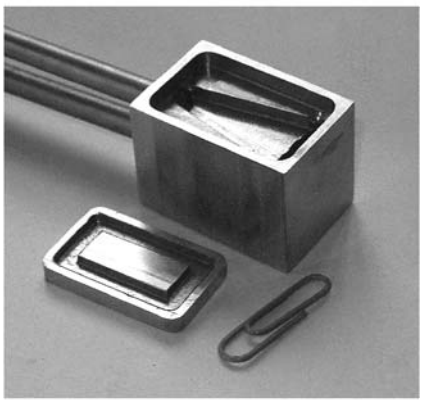

Fig. 6. Microreactor for catalytic partial oxidation of methane.

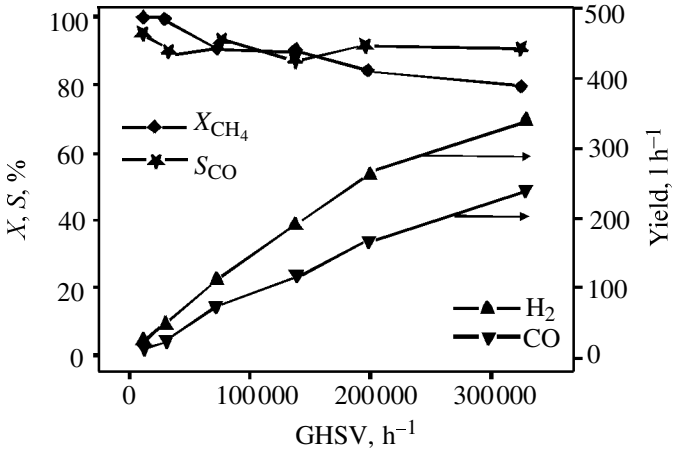

Fig. 7. Methane conversion (X), CO selectivity (S), and yields of hydrogen and CO vs. reciprocal contact time.

which alternated with plane plates of the same size. A gas–air mixture containing 29.4% of pure methane was fed to a microreactor inlet at a rate of 316 ml s^{-1}. The microreactor was tested at 804°C, measuring methane conversion, selectivity, CO selectivity, and hydrogen performance as functions of the GHSV parameter (reciprocal contact time). The resulting data are shown in Fig. 7. As seen, at fairly short contact times of about 11 μs the hydrogen performance of an MR with ten crimped and plane plates is 350 l h^{-1} at 80% methane conversion. This corresponds to the specific performance per MCP volume of 87.5 l cm^{-3} h^{-1}. Therewith, the CO selectivity was 90%, and the gas mixture (dry) at the reactor outlet had the following composition: 31.6 H_2, 4.6 CH_4, 44.5 N_2, 17.1 CO, and 1.9 CO_2 vol%. This corresponds to an equilibrium concentration ratio of products of methane oxidation with air for an adiabatic reactor at 804°C.

CONCLUSIONS

Creation of microchannel catalytic reactors is a new and rapidly progressing filed of hydrogen energetics, which makes active use of advances in microelectronics. There is no doubt that developments in this field will bring chemical industry to a new qualitative level. Unique properties of microchannel reactors, such as small size of channels, short times of contact of reaction mixtures and catalysts, and high rates of mass transfer, allow compact devices to be developed both for highly exothermic and highly endothermic catalytic processes, including those involving toxic and explosive compounds. Combining microreactors with fuel cells makes possible creation of power-generating devices bypassing in their specific performance a lot of known sources of electric current.

Among foreign institutions most active in development and prototyping microchannel reactors we can mention the Research Center in Carlsruhe and Institute of Microtechnology in Mainz (Germany), as well as Pacific Northwest National Laboratory (USA). In Russia developments in this field are still restricted by laboratory prototyping microchannel reactors. The greatest progress in this field has been made by Boreskov Institute of Catalysis SB RAS.

ACKNOWLEDGMENT

The work was supported by the Russian Ministry of Science and Technologies (2005–2006), National Innovation Company (*New Energy Projects* Program), and Russian Ministry of Education (grant no. NSh-6526.2006.3).

REFERENCES

1. *Chemistry for the Energy Future,* Parmon, V.N., Bridgewater, A., and Tributsch, H., Eds., London: Blackwell, 1999.
2. Malyshenko, S.P., *Energiya: Ekon., tekhn., ekol.,* 2003, no. 7, p. 33.
3. Krylov, O.V., *Kataliz v prom-sti,* 2004, no. 3, p. 57.
4. Tret'yakov, V.F., Burdeinaya, T.N., Berezina, L.A., and Lyubushkin, R.A., *Bezopasn. Zhiznedeyat.,* 2004, no. 11, p. 27.
5. Mischenko, A.I., *Primenenie hydrogena dlya avtomobil'nyh dvigatelei* (Application of Hydrogen for Car Engines). Kiev: Naukova Dumka, 1984.
6. Dicks, A.L., *J. Power Sources,* 1996, vol. 61, p. 113.
7. Pena, M.A., Gomez, J.P., and Fierro, J.L.G., *Appl. Catal. A: General,* 1996, vol. 144, p. 7.
8. Ogden, J.M., Steinbugler, M.M., and Kreutz, T.G., *J. Power Sources,* 1999, vol. 79, p. 143.
9. Kiwi-Minsker, L. and Renken, A., *Catal. Today,* 2005, vol. 110, p. 2.
10. Schubert, K., Bier, W., Linder, G., and Seidel, D., *Chem. Ing. Tech.,* 1989, vol. 61, p. 172.
11. Ondrey, G., *Chem. Eng.,* 1995, vol. 102, p. 52.
12. Ehrfeld, W., Hessel, V., and Lowe, H., *Microreactors: New Technology for Modern Chemistry,* Weinheim: Wiley–VCH, 2000.
13. Agrell, J., Boutonnet, M., and Fierro, J.L.G., *Appl. Catal. A: General,* 2003, vol. 253, p. 213.
14. Fukahori, S., Kitaoka, T., Tomoda, A., Suzuki, R., and Wariishi, H., *Ibid.,* 2006, vol. 300, p. 155.

15. Zhang, X.R., Shi, P., Zhao, J., Zhao, M., and Liu, C., *Fuel Process. Tech.,* 2003, vol. 83, p. 183.
16. Freni, S., Calogero, G., and Cavallaro, S., *J. Power Sources,* 2000, vol. 87, p. 28.
17. Matsumura, Y. and Nakamori, T., *Appl. Catal. A: General,* 2004, vol. 258, p. 107.
18. RU Patent no. 2244589.
19. RU Patent no. 2248932.
20. Liu, S., Xiong, G., Sheng, Sh., and Yang, W., *Appl. Catal. A: General,* 2000, vol. 198, p. 261.
21. Coronas, J. and Santamaria, J., *Chem. Eng. Sci.,* 2004, vol. 59, p. 4879.
22. Makarshin, L.L., Andreev, D.V., and Parmon, V.N., *IHEC 2005 Int. Hydrogen Energy Congress,* Istanbul, Turkey, July 13–15, 2005.
23. Baea, J.-M., Ahmedb, S., Kumarb, R., and Doss, E., *J. Power Sources,* 2005, vol. 139, p. 91.
24. Younes-Metzler, O., Svagin, J., Jensen, S. et al., *Appl. Catal. A: General,* 2005, vol. 284, p. 5.
25. Stutz, M.J. and Poulikakos, D., *Chem. Eng. Sci.,* 2005, vol. 60, p. 6983.
26. Jensen, K.F., *Chem. Eng. Sci,* 2001, vol. 56, p. 293.
27. Ajmera, S.K., Delattre, C., Schmidt, M.A., and Jensen, K.F., *J. Catal.,* 2002, vol. 209, p. 401.
28. *VDI-Warmeatlas. Bd. 9. Verein Deutscher Ingenieure,* Berlin, Heidelberg, New York, 2002.
29. Baerns, M., Hofmann, H., and Renken, A., *Lehrbuch der technischen Chemie,* Baerns, M., Fetting, F., Hofmann, H., Keim, W., and Onken, U., Eds., Stuttgart: Thieme, 1999.
30. Rouge, A., Spoetzl, B., Gebauer, K., Schenk, R., and Renken, A., *Chem. Eng. Sci.,* 2001, vol. 56, p. 1419.
31. Commenge, J.M., Rouge, A., Renken, A., Corriou, J.P., and Matlosz, M., *Recents Progresen Genie des Procedes,* 2001, vol. 15, p. 329.
32. Delsman, E.R., de Croon, M.H.J.M., Pierik, A., Kramer, G.J., Cobden, P.D., Hofmann, C., Cominos, V., and Schouten, J.C., *Chem. Eng. Sci.,* 2004, vol. 59, p. 4795.
33. Ganley, J.C., Riechmann, K.L., Seebauer, E.G., and Masel, R.I., *J. Catal.,* 2004, vol. 227, p. 26.
34. Reuse, P., *Ecole polytechnique federale de Lausanne,* 2003, thesis no. 2830.
35. Aartun, I., Gjervan, T., Venvik, H., Gorke, O., Pfeifer, P., Fathi, M., Holmen, A., and Schubert, K., *Chem. Eng. J.,* 2004, vol. 101, p. 93.
36. Reuse, P., Renken, A., Haas-Santo, K., Gorke, O., and Schubert, K., *Ibid.,* 2004, vol. 101, p. 133.
37. Bravo, J., Karim, A., Conant, T., Lopez, G.P., and Datye, A., *Ibid.,* 2004, vol. 101, p. 113.
38. Brinker, C.J. and Scherer, G.W., *Sol–Gel Science,* New York: Academic, 1990.
39. Lim, M.S., Kim, M.R., Noh, J., and Woo, S.I., *J. Power Sources,* 2005, vol. 140, p. 66.
40. Rebrov, E.V., Seijger, G.B.F., Calis, H.P.A., de Croon, M.H.J.M., van den Bleek, C.M., and Schouten, J.C., *Appl. Catal. A: General,* 2001, vol. 206, p. 125.
41. Janicke, M.T., Kestenbaum, H., Hagendorf, U., Schuth, F., Fichtner, M., and Schubert, K., *J. Catal.,* 2000, vol. 191, p. 282.
42. Stark, W.J., Wegner, K., Pratsinis, S.E., and Baiker, A., *Ibid.,* 2001, vol. 197, p. 182.
43. Thybo, S., Jensen, S., Johansen, J., Johannessen, T., Hansen, O., and Quaade, U.J., *Ibid.,* 2004, vol. 223, p. 271.
44. Schimpf, S., Bron, M., and Claus, P., *Chem. Eng. J.,* 2004, vol. 101, p. 11.
45. Matson, D.W., Martin, P.M., Tonkovich, A.Y., and Roberts, G.L., *SPIE Proc.,* 1998, vol. 3514, p. 386.
46. Makarshin, L.L., Andreev, D.V., Nikolaeva, O.I., Parmon, V.N., *Materialy 9 Mezhd. seminara "Rossiiskie tekhnologii dlya industrii"* (Proc. 9th Int. Seminar "Russian Technologies for Industry"), St. Peterburg, May 30–June 1, 2005, p. 13.
47. Makarshin, L.L., Andreev, D.A. et al., *Mezhd. forum "Vodorodnye tekhnologii dlya proizvodstva energii"* (Proc. Int. Forum "Hydrogen Technologies for Energy Production"), Moscow, February 6–10, 2006, p. 65.
48. Belyaeva, N.P., *Kataliz v prom-sti,* 2004, no. 2, p. 16.
49. Menz, W., Mohr, J., and Paul, O., *Microsystem Technology,* Weinheim: Wiley–VCH, 2001.
50. Hessel, V., Hardt, S., and Lowe, H., *Chemical Micro Process Engineering: Fundamentals, Modelling and Reactions,* Weinheim: Wiley–VCH, 2004.
51. Gu-Gon Park, Dong Joo Seo, Seok-Hee Park et al., *Chem. Eng. J.,* 2004, vol. 101, p. 87.
52. Jung Yeon Won, Hee Kwon Jun, Min Ku Jeon, Seong Ihl Woo, *Catal. Today,* 2006, vol. 111, p. 158.
53. Cao, S.S., Wang, Y., Holladay, J.D., Jones, E.O., and Paio, D.R., *AIChE J.,* 2005, vol. 51, p. 982.
54. Cao, C., Xia, G., Holladay, J., Jones, E., and Wang, Y., *Appl. Catal. A: General,* 2004, vol. 262, p. 19.
55. Zhang, X.R., Shi, P., Zhao, J., Zhao, M., and Liu, C., *Fuel Process. Tech.,* 2003, vol. 83, p. 183.
56. RU Patent no. 2078611.
57. Bobrov, N.N., *Promyshlennyi kataliz v lektsiyakh* (Industrial Catalysis in Lections), Noskova, A.S., Moscow: Kalvis, 2006, p. 41.
58. Makarshin, L.L., Andreev, D.A., Gribovskii, A.G., et al., *Mezhd. nauchno-prakt. konf. "Innovatsionnaya*

energetika" (Proc. Int. Scientific and Practical Conf.), Novosibirsk, November 15–16, 2005.

59. Agrell, J., Boutonnet, M., and Fierro, J.L.G., *Appl. Catal. A: General,* 2003, vol. 253, p. 213.
60. Xinrong Zhang and Pengfei Shi, *J. Mol. Catal. A: Chemical,* 2003, vol. 194, p. 99.
61. Makarshin, L.L., Andreev, D.V., Pavlova, S.N. et al., *XVII Int. Conf. on Chemical Reactors "CHEMREACTOR-17,"* Athens, Greece, May 15–19, 2006, p. 451.

Lev L'vovich Makarshin, Dr. Sc. (Chem.), Leading Researcher, Laboratory of Catalytic Methods of Conversion of Solar Energy, Boreskov Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences (SB RAS). Scientific areas of focus: physical chemistry, catalysis.

Valentin Nikolaevich Parmon, Dr. Sc. (Chem.), Member of RAS, Director, Boreskov Boreskov Institute of Catalysis, Siberian Branch, RAS. Scientific areas of focus: physical chemistry, catalysis.