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FIFTY YEARS
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Efficiency of Zn/TiO_2 Catalyst Operation in a Microchannel Reactor in Methanol Steam Reforming

A. G. Gribovskii[a], L. L. Makarshin[a], D. V. Andreev[a], S. V. Korotaev[a], P. M. Dutov[b], R. M. Khantakov[b], S. I. Reshetnikov[a], and V. N. Parmon[a]

[a] *Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences, Novosibirsk, 630090 Russia*
[b] *Novosibirsk State University, Novosibirsk, 630090 Russia*
e-mail: gribovsk@catalysis.ru

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Abstract—The activity of a Zn/TiO_2 catalyst deposited on metal microchannel plates in methanol steam reforming was studied. The catalyst exhibited maximum activity upon deposition on microchannel plates made of copper foam. In this case, the specific hydrogen production of a microreactor at 450°C was 78.6 l $(g\ Cat)^{-1}\ h^{-1}$. The catalysts deposited on a microchannel plate of nickel foam and on corrugated brass foil exhibited lower activity because of the lower efficiency of heat transfer to the reaction zone. A correlation between the thermal conductivity of the microchannel plate material and the activity of the catalyst was observed in the following order: copper, brass, and nickel. The kinetic parameters of the process of methanol steam reforming in a microreactor were calculated with the use of a plug-flow reactor model. In this case, the calculated formal activation energy of 132 kJ/mol was independent of the microchannel plate material. A comparison of the equilibrium concentrations of reaction products at the reactor outlet, which were calculated from thermodynamic data, with the experimental data demonstrated that methanol steam reforming at a temperature higher than 400°C occurred in the nonequilibrium region. The concentration of carbon monoxide at the microreactor outlet was lower than 1 mol %, which is lower than the equilibrium concentration by one order of magnitude. This effect was attributed to the suppression of the reversed water gas shift reaction on the catalyst.

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INTRODUCTION

The endothermic reaction of methanol steam reforming on copper-containing catalysts proceeds at 160–270°C. Traditional catalysts are the binary copper-containing compositions Cu/ZnO [1–3], Cu/ZrO_2 [4], and Cu/SiO_2 [5]. However, depending on synthesis conditions, these catalysts can undergo relatively rapid deactivation. Thus, an important goal in the development of compact fuel processors based on methanol steam reforming is to find catalysts that are more stable. An approach to solve this problem consists in the stabilization of the active catalyst phase by doping binary compositions with Ce, Zr, Mn, and Al cations. For example, the use of CeO_2 as a promoter decreased the sintering of copper microparticles and simultaneously increased their degree of dispersion to result in an increase in the activity of the catalyst [6]. The $Cu/ZnO/ZrO_2/Al_2O_3$ catalyst exhibited high activity and stability in the process of methanol steam reforming [7, 8]. Among the catalysts containing no copper, the compositions Pd/ZnO [9] and Zn/TiO_2 [10] exhibited high activity. These catalysts operated efficiently at higher temperatures, as compared with copper-containing catalysts. Thus, the Zn/TiO_2 catalyst at 400–450°C exhibited higher activity and longer operation times [11, 12].

Karim et al. [13] studied the kinetics of methanol steam reforming in a fixed-bed reactor with the $CuO/ZnO/Al_2O_3$ catalyst. They found that high radial temperature gradients, which appeared in the course of the reaction, decreased the efficiency of catalyst operation. The highest efficiency was reached in a reactor 1.0 mm in diameter; this fact suggests that the methanol steam reforming process was limited by heat transfer from the external heater to the catalyst.

Idem and Bakhshi [14] performed kinetic studies of methanol steam reforming on the Cu/Al_2O_3 catalyst promoted with Mn over the temperature range of 170–250°C. An analysis of experimental results in terms of the Langmuir–Hinshelwood model demonstrated that methanol steam reforming proceeded by different mechanisms in low-temperature and high-temperature regions. In the temperature ranges of 170–190 and 190–250°C, the process proceeded through the dissociation of methanol with O–H bond cleavage and the hydrolysis of methyl formate, respectively. In this case, the apparent activation energy of methanol steam reforming in the

Table 1. Characteristics of the microchannel plates

Characteristic	Microchannel plate material		
	copper foam (MCP1)	nickel foam (MCP2)	corrugated brass foil (MCP3)
Thermal conductivity of the microchannel plate material (at $T = 600$ K, W m^{-1} K^{-1})	379	66	140
Deposited catalyst weight (g)	1.51	1.51	0.77
Number of microchannel plates in the microreactor	16	16	7
Microchannel plate thickness, mm	0.40	0.40	0.85

low-temperature region was lower than that in the high-temperature region by a factor of 1.5.

Agarwal et al. [15], who experimentally studied the methanol steam reforming process, found that copper-containing catalysts are unstable in operation and undergo relatively rapid deactivation. Because of this, we used the Zn/TiO_2 catalyst to study methanol steam reforming in a microreactor. Gribovskii et al. [11] found that this catalyst can stably and efficiently operate for a long time up to relatively high temperatures (~450°C). Thus, the activity of the Zn/TiO_2 catalyst deposited on a microchannel plate made of copper foam after continuous operation for 160 h decreased by only 8%.

This work was devoted to the effect of the material of microchannel plates (MCp) and the procedure used for the deposition of the Zn/TiO_2 catalyst on these plates on the efficiency of catalyst operation in methanol steam reforming in a microchannel reactor.

EXPERIMENTAL

A stainless steel microreactor with a rhombic cross section, dimensions of $30 \times 30 \times 10$ mm, and a volume of 3.6 cm^3 filled with microchannel plates was used in the experiments [11, 12]. Microchannel plates of size 20×30 mm were placed in the microreactor. An input flow of reactants arrived at the trapezoid free space of the microreactor; then, it was uniformly distributed over all of the channels. Microchannel plates MCP1 and MCP2 were made of copper foam and nickel foam, respectively, by cold pressing at 250 atm [16]. In this case, rectangular channels with a cross section of 0.15×5.0 mm and 20 mm in length were formed on each of the microchannel plates. Microchannel plate MCP3 was made of corrugated brass foil. Channels with a triangular cross section, 0.5 mm in height and 1.0 mm in width, were prepared by alternating corrugated and flat plates in the course of packing in the microreactor. The procedure used in catalyst deposition on these microchannel plates was described elsewhere [11, 12]. The Zn/TiO_2 catalyst powder was synthesized in accordance with a procedure described by Pinzari et al. [10]. Table 1 summarizes the geometric dimensions, the total weight of the deposited catalyst, and the numbers of microchannel plates loaded into the microreactor.

The microreactors were tested using a catalytic system [16] designed at the Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences. Aqueous methanol was supplied to an evaporator with a peristaltic pump; the evaporator temperature was maintained at 200°C. Then, the methanol–water vapor mixture was fed into the microreactor through a thermally insulated line. The microreactor was heated using an external electric heater controlled by a Miniterm-300 microprocessor regulator. The microreactor temperature was measured with a Chromel–Alumel thermocouple welded to the body at the microreactor outlet. Preliminary experiments in a similarly shaped model reactor with microchannel plates of nickel foam demonstrated that a maximum temperature gradient of 5–7 K was reached in methanol steam reforming with a methanol conversion of 90%. The reaction products from the reactor outlet arrived at the separator, where they were cooled to room temperature and the unreacted methanol and water vapor were condensed. The space velocity of the output flow of dry gas was measured using an AWM43300VH gas flow meter (Honeywell Inc.), and the composition of this gas was analyzed using Kristall-2000 and LKhM-8 chromatographs with thermal conductivity detectors. The detection of H_2 was performed using a NaX-packed column (argon as the carrier gas), and CO and CO_2 were determined in a column packed with SKT carbon (helium as the carrier gas). All measurements were taken at atmospheric pressure.

The activity of the catalyst deposited on microchannel plates was experimentally studied in the following manner: After loading the microchannel plates into the microreactor, the catalyst was activated by purging with a mixture of 10 mol % hydrogen and 90 mol % argon at 450°C for 2 h. Next, the starting reactants, a water–methanol mixture with a 1 : 1 molar ratio between water and methanol ($\beta = 1$), were supplied to the microreactor inlet. At the separator outlet, the flow rate of dry gas (v_{out}, cm^3/min) was measured and the concentrations of CO, CO_2, and H_2 were determined. The conversion of methanol was calculated in accordance with a procedure described elsewhere [16]. The con-

centrations of CH_3OH and H_2O were calculated from the material balance. As a result of the experiment, the dependence of the conversion of methanol (x) on the reciprocal of the normalized molar rate of the input flow of methanol ($g/F^0_{CH_3OH}$) over the temperature range of 350– 450°C, where g is the weight of the catalyst deposited on a microchannel plate, was found. Preliminary control experiments demonstrated that the microchannel plates without deposited catalysts did not exhibit catalytic activity in methanol steam reforming.

RESULTS

Figure 1 shows the dependences of x on $g/F^0_{CH_3OH}$ obtained in the tests of microchannel plates MCP1–MCP3 over the temperature range of 350–450°C. It can be seen that, in all cases, as the temperature was increased, the full conversion of methanol was reached at lower values of $g/F^0_{CH_3OH}$; this suggests an increase in the activity of the catalyst. The catalyst deposited on MCP1, which was made of copper foam, exhibited the best results. Table 2 summarizes the residence times of the reactants (τ), the full hydrogen production of the microreactor (U_{H_2}), the specific production per unit weight of the catalyst ($U_{H_2/g}$), and the specific production per unit volume of the block of microchannel plates ($U_{H_2/V}$) for the microchannel plates. The hydrogen production (U_{H_2}, l/h) of the microreactor with MCP1 of copper foam was 78.6 l/h at 450°C. This value is larger than the analogous parameters for MCP2 and MCP3 by a factor of 1.6 and 2.4, respectively. Note that the specific hydrogen production of the microreactor ($U_{H_2/V}$) changed analogously to the fill production. However, the specific hydrogen production per unit weight of the catalyst ($U_{H_2/g}$) calculated for MCP3 of corrugated brass foil was higher than the analogous value for MCP2 of nickel foam and lower than that for MCP1 of copper foam by a factor of only 1.2. This is because the access of reactants to all of the active sites of the catalyst is better in a thin catalyst film deposited on corrugated brass foil, as compared with the situation in which a large catalyst amount is pressed into metal foam. In the latter case, the reaction can be limited by diffusion in the catalyst bed. However, the low total hydrogen production of the microreactor with MCP3 suggests that the amount of the catalyst remained insufficient, although the catalyst was used more efficiently.

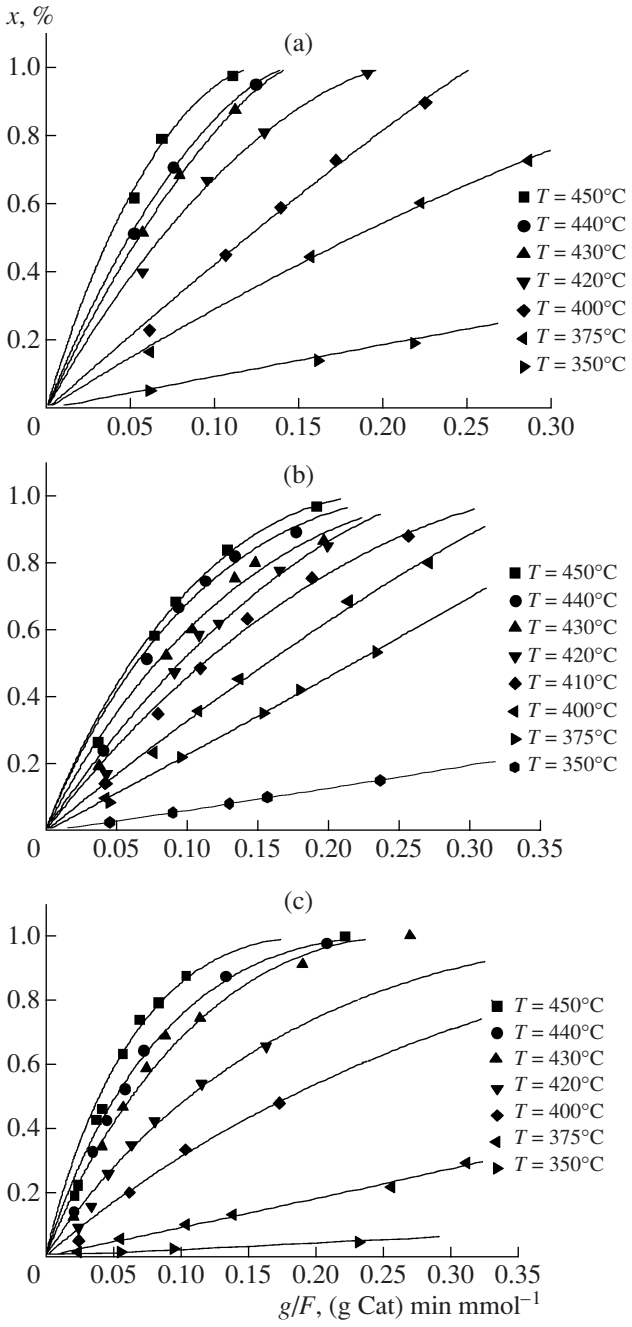

Fig. 1. Dependence of methanol conversion on g/F at various temperatures for a microreactor with (a) MCP1, (b) MCP2, and (c) MCP3. Solid lines and points refer to calculated and experimental data, respectively.

Table 2. Dependence of the production of the microreactor on the material of microchannel plates at 80% methanol conversion and 450°C*

Microchannel plates	$g/F^0_{CH_3OH}$, (g Cat) min mol^{-1}	$\tau \times 10^3$, s	U_{H_2}, l/h	$U_{H_2/g}$, l (g Cat)$^{-1}$ h^{-1}	$U_{H_2/V}$, l cm^{-3} h^{-1}
MCP1	0.068	29.1	78.6	52.1	21.8
MCP2	0.110	47.2	48.6	32.2	13.5
MCP3	0.083	127	32.8	42.6	9.1

* See the text for comments.

Figure 2 shows the experimental temperature dependences of the conversion of methanol in the microreactor with MCP1–MCP3 at a methanol feed flow rate of $F^0_{CH_3OH}$ = 0.158 mmol/min for MCP1 and MCP2 and $F^0_{CH_3OH}$ = 0.073 mmol/min for MCP3. In this experiment, the feed flow rates were chosen so that the conversion of methanol at 450°C was close to 100%. In Fig. 2, it can be seen that methanol steam reforming on MCP1 started at 330°C, unlike reforming on the other microchannel plates, for which this temperature was as high as 360°C. It is likely that this difference is due to the high thermal conductivity of copper, as compared with those of nickel and brass; because of this, heat transfer to the reaction zone was more efficient. This is also supported by the fact that the curve of the temperature dependence of methanol conversion for MCP1 lies higher than the other curves.

To analyze the efficiency of operation of microchannel plates, we measured the temperature dependences of the gas composition at the reactor outlet. We found that the gas composition was independent of the type of microchannel plates. Figure 3 shows the experimental temperature dependences of the concentrations of methanol steam reforming products (CO, CO_2, and H_2) and starting components (H_2O and CH_3OH) at the microreactor outlet at a fixed input flow rate of the water–methanol mixture. The thermodynamic equilibrium concentrations of all of the substances that participate in methanol steam reforming, which were calculated using tabulated thermodynamic constants for reactions (I) and (II), are also given in Fig. 3. In Fig. 3, it can be seen that methanol steam reforming almost did not occur on the given catalyst at 320°C. The concentration of the initial components decreased with temperature, and almost complete methanol conversion was observed at a temperature higher than 440°C. In

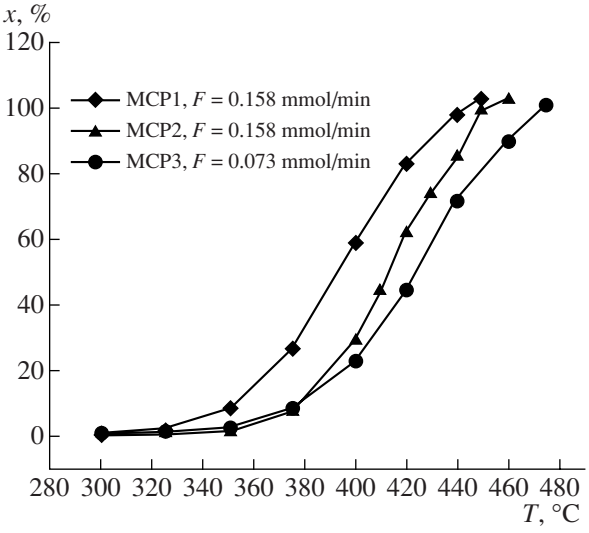

Fig. 2. Temperature dependence of methanol conversion for microreactors with various microchannel plates.

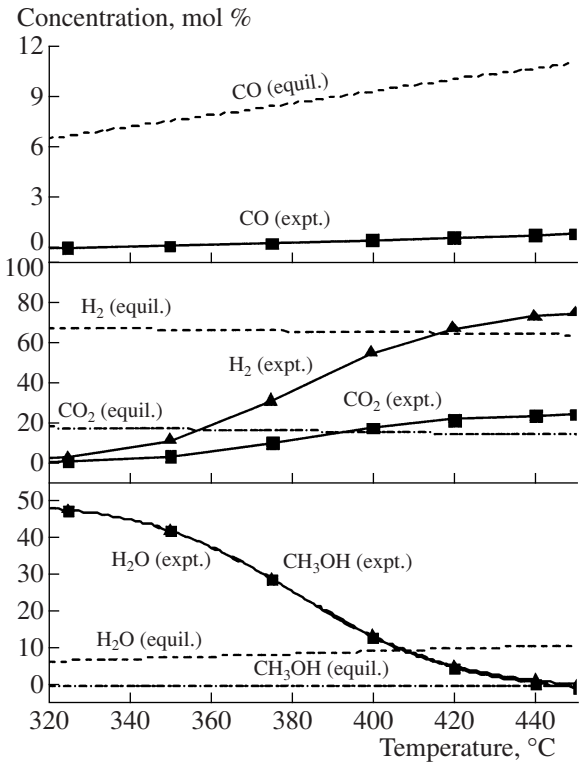

Fig. 3. Temperature dependence of the experimental and equilibrium concentrations of reaction products at the outlet of a microreactor with MCP1. Points and dashed lines represent experimental data and equilibrium values, respectively.

this case, the concentrations of H_2 and CO_2 at the microreactor outlet reached stoichiometric values for reaction (I). The concentration of CO at the microreactor outlet was much lower than the equilibrium value over the entire temperature range. An analogous situation was observed previously [3, 6], and it can be related to diffusion and adsorption processes in the catalyst bed. The low concentrations of CO at the microreactor outlet over the entire temperature range, as compared with the equilibrium value, suggest that CO is a secondary product rather than one formed in the decomposition of methanol into hydrogen and carbon monoxide [17]. Indeed, if reaction (II) on the catalyst is suppressed and does not reach equilibrium, this explains the appearance of superequilibrium concentrations of H_2 and CO_2 and the decrease in the concentration of H_2O below the equilibrium value at temperatures higher than 420°C, when the conversion of methanol approaches 100%.

Experimental Data Processing

Methanol steam reforming is an endothermic process that occurs in the presence of a catalyst above 200°C with the formation of hydrogen, carbon dioxide, and carbon monoxide. This process can be described by the following two linearly independent overall reactions:

$$\begin{aligned} &CH_3OH + H_2O = CO_2 + 3H_2 \\ &(\Delta_r H^0_{298} = 49.3\ \text{kJ/mol}), \end{aligned} \quad \text{(I)}$$

$$\begin{aligned} &CO_2 + H_2 = CO + H_2O \\ &(\Delta_r H^0_{298} = 41.2\ \text{kJ/mol}). \end{aligned} \quad \text{(II)}$$

The former reaction is the main reaction of methanol steam reforming, in the course of which 3 mol of hydrogen and 1 mol of carbon dioxide are produced from 1 mol of methanol. The latter is the reversed water-gas shift reaction, which leads to the formation of carbon monoxide. The temperature dependence of the equilibrium concentrations of products for a given total pressure of the mixture can be calculated using material balance equations for the elements at the microreactor inlet and outlet and tabulated thermodynamic constants for reactions (I) and (II) [18, 19]. The gas flow at the microreactor outlet contained both unreacted starting substances (methanol and water) and reaction products (hydrogen, carbon dioxide, and carbon monoxide). Based on material balance equations, the molar flow rates of these substances at the microreactor outlet (F_{CH_3OH}, F_{H_2O}, F_{CO_2}, F_{H_2}, and F_{CO}) were related to the input molar flow rate of methanol $F^0_{CH_3OH}$ by the following equations:

$$\begin{aligned} F_{CH_3OH} &= (1-x)F^0_{CH_3OH}, \\ F_{H_2O} &= (\beta - x + \eta)F^0_{CH_3OH}, \\ F_{CO_2} &= (x-\eta)F^0_{CH_3OH}, \\ F_{H_2} &= (3x-\eta)F^0_{CH_3OH}, \\ F_{CO} &= \eta F^0_{CH_3OH}. \end{aligned} \quad \text{(1)}$$

Here, $x = \dfrac{F^0_{CH_3OH} - F_{CH_3OH}}{F^0_{CH_3OH}}$ is the conversion of methanol; $\eta = \dfrac{F_{CO}}{F^0_{CH_3OH}}$ is the fraction of methanol converted into carbon monoxide; and $\beta = \dfrac{F_{H_2O}}{F^0_{CH_3OH}}$ is the molar ratio between water and methanol in the water–methanol mixture at the microreactor inlet. Using the expression for the equilibrium constant of the reaction, $K_p = \prod_i \left(\dfrac{P_i}{P_0}\right)^{\nu_i}$, and the relationship between molar flows and the partial pressure, $P_i = \dfrac{F_i}{\sum_i F_i} P_0$, we find equilibrium conditions for reactions (I) and (II) in terms of the dimensionless parameters x, η, and β (henceforth, we assume that $P_0 = 1$ bar):

$$\begin{aligned} \frac{(x-\eta)(3x-\eta)^3}{(1-x)(\beta - x + \eta)(1+2x+\beta)^2} &= K_{p_1}(T), \\ \frac{\eta(\beta - x + \eta)}{(3x-\eta)(x-\eta)^2} &= K_{p_2}(T). \end{aligned} \quad \text{(2)}$$

On the other hand, based on thermodynamic relationships, the equilibrium constant is related to the standard change in the Gibbs energy $\Delta G^0 = \sum_i \nu_i \Delta_f H^0_i(A_i, T) - T\sum_i \nu_i S^0_i(A_i, T)$ by the following equation: $K_p = e^{-\frac{\Delta_r G^0}{RT}}$. The set of Eqs. (2) was solved using the MathCad program package at $\beta = 1$ with the use of tabulated heats of formation $\Delta_f H^0_i(A_i, T)$ of the substances and reaction entropies $S^0_i(A_i, T)$ [6]. As a result, the temperature dependences of x and η were calculated. Substituting these values into Eq. (1), we can calculate the equilibrium gas composition at the microreactor outlet as a function of temperature (Fig. 3). A special feature of reaction (I) is that the thermodynamic equilibrium is shifted to the formation of reaction products even at room temperature. However, the reaction did not occur because of the high activation energy. The reaction occured only in the presence of the catalyst at elevated temperatures.

The microreactor containing microchannel plates with channels < 0.5 mm in cross section and 20 mm in

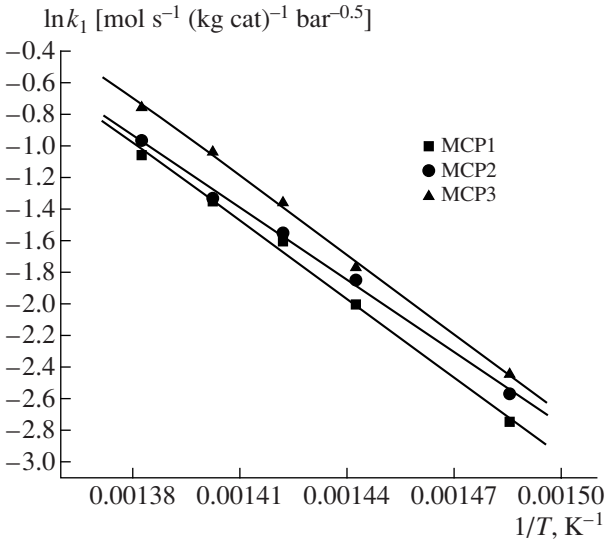

Fig. 4. Arrhenius plots of the formal rate constants of reaction (I) for the microchannel plates over the temperature range of 400–450°C. Points and solid lines represent experimental data and linear fits, respectively.

length can be considered as a plug-flow reactor because the ratio of the channel diameter to the channel length is greater than 10. In this sense, it is analogous to a tube reactor with a fixed catalyst bed. Moreover, as a first approximation, it is believed that methanol steam reforming occurs under isothermal conditions at an average temperature because the temperature gradient along the microreactor was small. With the use of corresponding equations for a plug-flow reactor, we obtain a relationship to describe the dependence of methanol conversion x on $g/F^0_{CH_3OH}$ for our case. As noted above, equilibrium in reaction (I) is completely shifted toward the formation of products, whereas reaction (II) can be ignored; that is, $\eta = 0$. Then, the expression for the rate of methanol steam reforming takes the simple form of

$$w_1 = k_1 P^m_{CH_3OH} P^n_{H_2O}. \quad (3)$$

Using the relationships obtained by Froment and Bichoff [20] and taking into consideration Eqs. (1) and (3), we write the following differential equation to describe methanol steam reforming in a plug-flow reactor:

$$\frac{dx}{d(g/F^0_{CH_3OH})} = k_1 \frac{(1-x)^m(\beta - x)^n}{(1+2x+\beta)^{m+n}} P_0^{m+n}. \quad (4)$$

The solution of Eq. (4) for our case ($\beta = 1$) is

$$\frac{g}{F^0_{CH_3OH}} = \frac{1}{k_1 0.5^a} \int_0^{x(g/F^0_{CH_3OH})} \left(\frac{1+z}{1-z}\right) dz. \quad (5)$$

Here, z is the integration variable and $\alpha = m + n$ is the overall order of reaction (I). This equation was solved numerically using the MathCad program package. The unknown parameters—the rate constant of reaction (I) k_1 and the quantity α—were determined by finding the best fit between experimental data and calculated curves using standard error minimization by the successive gradient method. Figure 1 shows the experimental points and calculated dependences of methanol conversion (x) on $g/F^0_{CH_3OH}$ for MCP1–MCP3. In Fig. 1, it can be seen that the proposed model adequately describes experimental data. However, in the temperature range from 350 to 400°C, the overall order of reaction (1) (α) increased from 0 to 0.5 and then remained unchanged to 450°C. In the high-temperature range from 400 to 450°C, we can use the Arrhenius function $k_1 = k_0 \exp(-E_a/RT)$ for the temperature dependence of the rate constant of the reaction and determine the activation energy of reaction (E_a) on the microchannel plates. Figure 4 shows the Arrhenius anamorphoses of the formal rate constant k_1 obtained over the temperature range from 400 to 450°C. It can be seen that these anamorphoses can be adequately approximated by a linear function. For the catalyst deposited on the microchannel plates, the activation energy of methanol steam reforming was the same within the limits of experimental error and amounted to 132 kJ/mol.

DISCUSSION

The Zn/TiO_2 catalyst deposited on microchannel plates of metal foams and corrugated brass foil exhibited high efficiency in the methanol steam reforming process. The maximum hydrogen production of the microreactor with the microchannel plates of copper foam with a volume of 3.6 cm^3 was 78.6 l/h at 450°C and a methanol conversion of 80%. The hydrogen production of the microreactor with the microchannel plates of nickel foam or corrugated brass foil was lower than that with the microchannel plates of copper foam by a factor of 1.6 and 2.4, respectively.

It was found that methanol steam reforming on the catalyst mainly occurred in accordance with reaction (I). In this case, the contribution of reversed water-gas shift reaction (II) was small. At the microreactor outlet, two products (hydrogen and carbon dioxide) mainly occurred in concentrations close to a stoichiometric ratio. The concentration of carbon monoxide at 450°C was lower than 1.0 mol %, which is much lower than the equilibrium value (11 mol %).

We used a plug-flow reactor model to obtain the kinetic parameters of methanol steam reforming. The formal activation energies of reaction (I) on the catalyst deposited on the microchannel plates made of various materials were calculated from the experimental data. It was found that the Arrhenius dependence of the rate constant adequately describes only the high-temperature region (400–450°C) of methanol steam reforming, where the order of reaction (I) does not depend on temperature. In the low-temperature region (350–400°C), the proposed exponential kinetic model did not allow us

to correctly treat experimental data. The resulting formal activation energy (132 kJ/mol) and the overall order of the reaction ($\alpha = 0.5$) were independent of the material of microchannel plates. Hence, we can conclude that the physical properties such as thermal conductivity rather than the chemical nature of the microchannel plate material affected the efficiency of catalyst operation in the methanol steam reforming process.

The specific hydrogen production of the microreactor per unit weight of the catalyst can be considered as a catalyst performance criterion. It reached a maximum of 52.1 l (g Cat)$^{-1}$ h^{-1} with the use of microchannel plates of copper foam. With the use of microchannel plates of corrugated brass foil or nickel foam, the production decreased by a factor of 1.2 and 1.6, respectively. It is likely that this phenomenon was related to different efficiencies of heat transfer from the heater arranged at the outer wall of the microreactor through the microchannel plates immediately to the catalyst. Indeed, the thermal conductivity decreased in the order MCP1 (copper) > MCP3 (brass) > MCP2 (nickel) and the operational efficiency of the catalyst deposited on them decreased in the same order (see Tables 1, 2). In addition, because of the great difference between the efficiencies of catalyst operation on various microchannel plates, we can conclude that the analysis of microreactor operation made in this work as a first approximation without considering the occurrence of temperature gradients is not entirely adequate. However, it allowed us to use simple equations and clear views of the occurrence of methanol steam reforming in the microreactor. The consideration of the temperature gradient along the microreactor will result in an unreasonable increase in the parameters used for the treatment of experimental data, the determination of which is an independent problem.

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