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Authors: L.L. Makarshin, D.V. Andreev, A.G. Gribovskiy, V.N. Parmon

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CATALYTIC PARTIAL OXIDATION OF METHANE IN MICROCHANNEL REACTORS WITH CO-CURRENT AND COUNTERCURRENT REAGENT FLOWS: AN EXPERIMENTAL COMPARISON

L.L. Makarshin\textsuperscript{a,b}, D.V. Andreev\textsuperscript{a}, A.G. Gribovsky\textsuperscript{a,b} and V.N. Parmon\textsuperscript{a,b}

\textsuperscript{a}Bioreskov Institute of Catalysis, pr. acad. Lavrentieva 5, Novosibirsk 630090, Russia

\textsuperscript{b}Novosibirsk State University, ul. Pirogova 2, Novosibirsk 630090, Russia

Abstract

Microchannel catalytic reactors have repeatedly proved their high efficiency in the process of partial oxidation of methane (POM) as compared to traditional fixed-bed catalytic reactors. However, a serious problem of the microchannel reactor operation at this process appears to be high thermal power evolved on the narrow front edge of the microchannel (MC) plates. As a result, the front edge of the plates may undergo thermal corrosion and destruction during the POM process. The way out is to develop microchannel plates, which design would provide a countercurrent reagents flow inside the reactors. A comparison of the operation of microchannel reactors using co-current and countercurrent reagent flows shows substantial advantages of the latter. At high and prolong heating load, a microchannel reactor with the countercurrent reagent flow (MCR-Z) outperforms a reactor with the co-current reagent flow (MCR-P) both in the methane conversion and carbon monoxide selectivity. This is associated with the lower temperature of the front edge of the microchannel plate as well as the lower inner temperature gradient in the MCR-Z in comparison to the MCR-P. Thus, the countercurrent flow scheme allows solving some serious problems of corrosion and destruction of the microchannel plate front edge at high heat loads during the POM process.

Keywords: catalytic microreactor; microchannel plate; methane partial oxidation; syngas; hydrogen production

1. Introduction

Catalytic partial oxidation of methane or natural gas (POM) is known to be able to provide both high conversion of methane and high output of syngas. The commonly used catalytic reactors for POM employ usually the fixed catalyst bed, the inlet of which is fed...
with a methane (natural gas)-air mixture in the ratio that meets stoichiometry of partial oxidation of methane reaction globally written as:

\[
\text{CH}_4 + 0.5\text{O}_2 = \text{CO} + 2\text{H}_2, \quad \Delta_r H_{298}^0 = -45 \text{ kJ/mol} \quad (I)
\]

The reaction pathway include main parallel reactions:

\[
\begin{align*}
\text{CH}_4 + 2\text{O}_2 &= \text{CO}_2 + 2\text{H}_2\text{O}, \quad \Delta_r H_{298}^0 = -802 \text{ kJ/mol} \quad (II) \\
\text{CH}_4 + \text{H}_2\text{O} &= 3\text{H}_2 + \text{CO}_2, \quad \Delta_r H_{298}^0 = +206 \text{ kJ/mol} \quad (III) \\
\text{CO}_2 + \text{CH}_4 &= 2\text{CO} + 2\text{H}_2, \quad \Delta_r H_{298}^0 = +247 \text{ kJ/mol} \quad (IV)
\end{align*}
\]

The reaction (II) is a fast and highly exothermal reaction of complete methane oxidation, the rest two reactions of the steam (III) and carbon dioxide (IV) reforming of methane are endothermic. Comprehensive studies on the POM process in a pilot plant in the presence of a Pt-Pd monolith catalyst [1] showed that the reaction of complete methane oxidation (II) proceeds mostly in the front edge of the monolith, while reactions (III) and (IV) proceed in the subsequent parts along the monolith. This cause a high temperature gradient of 200 – 400°C along the monolith, which can result in intensive corrosion and destruction of the front catalyst layer. To prevent the danger of large overheating, a catalyst support should possess high heat conductivity to arrange an efficient heat transfer from the zone of exothermal methane oxidation to the zone of endothermic methane reforming.

Microchannel chemical reactors are a new type of structured reactors. The common feature of such reactors is small single or many parallel channels with submillimeter cross-section. The small cross-section of microchannels permits one to obtain also a high surface-to-volume ratio and high mass-and-heat transfer rates, which can be 1-2 orders of magnitude higher than those observed for the systems with the fixed catalyst bed. As the result, microchannel reactors can provide nearly isothermal conditions even for extremely exothermic or endothermic reactions. In case the microchannel reactors are directed to use heterogeneously catalyzed reactions, the catalyst is generally deposited onto the walls of the microchannels [2,3].

The MC plates for the POM reactors are traditionally made of the FeCrAl alloy, the surface of which is covered with a thin catalyst layer using sol-gel methods [4,5]. Although heat conductivity of FeCrAl is rather high as compared to bulk oxide catalysts, the front edge of the MC plates at their operation in POM can also suffer a sufficient overheating (100-200°C) regarding the inlet gas flow temperature [5]. This results in severe corrosion of the front edge of the FeCrAl MC plates. Thus, a primary problem at designing the microchannel
catalytic reactors for POM is to develop a configuration of MC plates enabling to decrease temperature gradient between the front edge and the rest part of the MC plates.

The present work was aimed at studying the operation of a MC reactor during the process of POM with the use of specially designed MC plates providing a countercurrent flow of reagents.

2. Experimental

We used two types of MC plates manufactured from the FeCrAl foil of 50 µm thick. The both types of plates contained flat linear channels of width 6 mm and of depth 0.2 mm. However, the first type plates had a standard flat form 23×23 mm in the size. To prepare the second type, a plate (23×75 mm) was shaped similar to letter “Z”.

Before coating the MC plates with the catalyst, the plate were annealed at 1000°C in calm air for 4 h to obtain a thin oxide layer on the surface, which improves adhesion between the plate surface and the catalyst.

The catalyst coatings were prepared via the following procedure. After mechanochemical activation of the γ-Al2O3 powder (Fluka, specific surface area 230 m²/g), it was used to prepare a 5 mass.% suspension in a 0.3M nitric acid solution upon continuous stirring during 72 hours. Simultaneously, we prepared an aqueous suspension (5 mass.%) of pseudoboehmite AlOOH (Disperal P2, SASOL, Germany) using the same procedure. The both suspensions were mixed in the volume ratio γ-Al2O3/AlOOH = 2:1, then crystalline hydrates Ni(NO3)2⋅6H2O and Mg(NO3)2⋅6H2O were added in the amount to obtain a catalyst corresponding to average formula Ni0.5Mg1Al1(O). The resulting mixture was stirred for 4 h and then layer-by-layer brushed on the plate. Each deposited layer was annealed at 450°C for 30 min. The coating procedure was repeated for 6 times. The as-prepared MC plate was annealed at 860°C for 6 h in a furnace in a calm air. Platinum was deposited by the incipient wetness impregnation from an aqueous solution of H2PtCl6, to which triethanolamine was preliminary added to keep pH=7. The concentrations of platinum in the solution were chosen so as to provide the required platinum concentration in the catalyst during three impregnation procedures. After each impregnation, the MC plate was dried at 300°C and finally calcined at 860°C for 6 h in air. As a result, the weight of the catalyst supported on both sides of the plate was approximately 5.7 mg/cm².

The microchannel reactor (36×26×9 mm) was made of high-temperature stainless steel. A welded seam along the reactor perimeter provided its hermecity. In the MCR-P (co-current reagent flow) we placed 16 MC plates of the first type. In the MCR-Z (countercurrent
reagent flow) we placed five Z-shaped plates of the second type. To provide temperature control, four chromel-allimel thermocouples were placed into thin-wall stainless steel tubes which are situated inside the reactor. The lay-out of the thermocouples is schematically shown in Fig. 1. Thermocouples \( T_{\text{Cin}} \) and \( T_{\text{Cout}} \) are situated at the MCR inlet and outlet to monitor the temperature of inlet and outlet gas flows, respectively. Thermocouples \( T_{\text{Cf}} \) and \( T_{\text{Cb}} \) monitor the temperature on the front and back edge of the MC plates, respectively. Figure 2 shows a cross-section view of a MC plate array in which the co-current and countercurrent reagent flows are performed. In spite of the fact that the number of channels in the MCR-P is three times higher than that in the MCR-Z, the total microchannel volume and, as a consequence of this, the residence time of the reagents and the catalyst layer were equal in the both types of MC reactors.

The reactor was placed into a muffle furnace with temperature control by a RIF-101 (Russia) automatic controller within a range of 20–960°C, the accuracy was 1°C. Data from the thermocouples were transferred to a computer via the ADAM-4018 analog-digital converter. Gas flow controllers RRG1 and RRG2 (Russia) were used to control the rates of methane and air feedings into a mixer. The air-methane mixture (the dioxygen-to-methane volume ratio 0.5) was heated in a special heat exchanger situated in the separated muffle furnace and directed into the MC reactor. The inlet flow of the mixture was varied from 6.9 to 135 ml/s, which corresponds to the gas hourly space velocity (GHSV) of 18000-400000 h⁻¹, calculated for the total volume of the microchannels. Recording of temperature in different parts of the MC reactor as well as the concentrations of the reaction products in the outlet flow (at a preset inlet flow) was performed the heat equilibrium between the MCR and muffle furnace is established. The above procedure was repeated for five times in the temperature range 600-830°C. During the run, the concentration of reaction products \( \text{O}_2 \), \( \text{N}_2 \), \( \text{CH}_4 \) and \( \text{CO} \) were registered in dry and cooled to room temperature outlet mixtures using a LHM-8MD chromatograph (Russia) supplied with a thermal conductivity detector and a column with zeolite CaA. For registering \( \text{CO}_2 \), a Porapaq Q column was used (the gas carrier was helium in both cases).

The conversion of methane, \( X_{\text{CH}_4} \), was calculated with the use of the material balance equation (1).

\[
F_{\text{in}} \cdot N_2^0 = F_{\text{out}} \cdot N_2, \tag{1}
\]

where \( F_{\text{in}} \) and \( F_{\text{out}} \) are inlet and outlet reagent flows (ml/s), respectively, \( N_2^0 \) and \( N_2 \) are the corresponding concentration of inert nitrogen in the gas mixture.
Considering that \( \frac{F_{\text{in}}}{F_{\text{out}}} = \frac{N_2}{N_2^o} \), the methane conversion is:

\[
X_{\text{CH}_4} = 100\% \cdot \frac{CH_4^o \cdot N_2^o \cdot CH_4}{CH_4^o} ,
\]

here \( CH_4^o \) is the concentration of methane in the inlet gas flow and \( CH_4 \) is the concentration of methane at the outlet. Selectivity to carbon monoxide, \( S_{CO} \) is:

\[
S_{CO} = 100\% \cdot \frac{CO}{CO + CO_2} ,
\]

where \( CO \) and \( CO_2 \) are the concentrations of carbon monoxide and carbon dioxide in the outlet gas flow. The concentration of hydrogen (dry basis, vol. %) at the MCR outlet was calculated from a difference of concentrations of the rest gases determined by chromatography:

\[
H_2 = 100\% \cdot N_2 \cdot O_2 \cdot CO_2 \cdot CH_4 \cdot CO .
\]

Yield of hydrogen was calculated as:

\[
Y_{H_2} = H_2 \cdot F_{\text{in}} \cdot \frac{N_2^o}{N_2} ,
\]

and selectivity to hydrogen as:

\[
S_{H_2} = 100\% \cdot \frac{Y_{H_2}}{2 \cdot CH_4^o \cdot F_{\text{in}} \cdot X_{\text{CH}_4}} .
\]

Yield of carbon monoxide was calculated as:

\[
Y_{CO} = CO \cdot F_{\text{in}} \cdot \frac{N_2^o}{N_2} .
\]

3. Temperature profile of the operating MCR

Figure 3 shows the temperature profile along the MCR-P at the co-current reagent flow in the regions of low (650°C) and high (780°C) temperatures \( T_{in} \) in the range of the studied inlet flow rates. One can see, the temperature \( T_f \) of the front edge of MC plates increases with increasing the rate of an inlet flow, as compared to the temperature of the inlet gas flow \( T_{in} \). The similar situation is observed for the MCR-Z with the countercurrent reagent flow (Fig. 4). The very important characteristics of the MC reactors operation are the temperature of the front edge, \( T_f \), and temperature gradient along the MC plate, \( \Delta T/L \).
Тb, where L is length of the MC plate). Table 1 compiles the temperature data for both types of the MC reactors operating at low and high inlet flow rates.

Figures 3 and 4 evidence that the temperature profiles are different for the reactors operating at the similar external conditions. As the process of POM is performed in the MCR-P with the co-current reagent flow, both Тf and ΔТ/L are higher compared to those in the MCR-Z. For high inlet temperature, Тin = 780°C, the temperature gradient along the MC plate in the MCR-P is 2.4 times higher than that in the MCR-Z at the inlet flow rate of 6.9 ml/s; it is 3.3 times higher at the inlet flow rate of 135 ml/s. At Тin = 650°C, the temperature gradients differ by a factor of about 2 irrespective of the inlet flow rate. These data evidence that heat is actively generated at the front edge of the MC plate, which is observed for the MCR-P. In the MCR-Z, the countercurrent reagent flow results in a decrease in both the temperature difference and temperature of the front edge of the plate. In MCR-P at Тin = 650°C and high rates of the inlet flow, Фin = 135 ml/s, the difference between the gas temperature at the inlet and the temperature at the front edge of MC plates is 130°C. For the MCR-Z this value is 90°C under the similar conditions. Consequently, one can suggest that the conditions of the MC plates operation in the MCR-Z appear to be “milder” than those in the MCR-P.

It should be noted that the experimentally measured temperature of the front edge may be underestimated because of a number of external reasons associated with the provision of a good contact between the thermocouple and the front edge of MC plates. In addition, there is also the existence of a parasitic heat flow along the thermocouples, as well as an effect of radiation heat losses. All this can worsen the accuracy in the thermocouple measurements. However, a general regularity is preserved and the main conclusion is that the overheating of the front edge of MC plates in the MCR-Z with a countercurrent reagent flow is lower than that in the MCR-P. As follows from ref. [5], overheating of the front edge of MC plates is associated with a two-stage performance of POM in the MC reactor. At the first stage, a part of methane undergoes complete oxidation on the front edge of the MC plate to yield H2O and CO2. This is accompanied by almost complete conversion of dioxygen. At the second stage, the rest portion of methane is subjected to endothermic processes of steam and carbon dioxide reforming to yield CO and H2. Assuming that the reaction of complete methane oxidation proceeds in the outer diffusion mode, one can calculate the dioxygen concentration along the MC plate length and, consequently, the rate of the heat evolution. In our case, the specific rate of complete methane oxidation per unit of the surface-to-volume ratio MC plate is much higher than the coefficient of mass exchange [6]. Then, if a MC reactor works at the plug-
flow mode without change of the mole numbers in the course of the reaction (II) [7], the degree of dioxygen conversion can be described as:

\[ X_{O_2}(x) = 1 - \exp(-\beta \cdot S \cdot \frac{x}{u}) \]  

where \( x \) is the distance along the length of the MC plate, \( S = 330 \text{ m}^2/\text{m}^3 \) is the surface-to-volume ratio for the MC plates, \( u_0 = \frac{F_{CH_4}^{in}}{w} \) is the linear velocity of the inlet methane flow related to STP (Standard temperature and pressure – 273.15 K and 101325 Pa), \( F_{CH_4}^{in} = F_{in} \cdot CH_4^0 / 100 \) is the volumetric flow rate of methane at the MC reactor inlet, \( w \) is the total geometrical cross-section of the channels in the MC plates, \( \beta = Sh \cdot D/d \) is the coefficient of mass transfer, which depends on the gas flow mode, \( Sh \) – Sherwood number, \( d \) - equivalent diameter of a microchannel and \( D \) - coefficient of dioxygen diffusion at the preset temperature \( T_{in} \). To evaluate \( \beta \), we used the following tabulated values and experimental parameters: \( D = 1.43 \cdot 10^{-4} \, \text{m}^2/\text{s} \), \( d = 4 \cdot 10^{-4} \, \text{m} \), \( \nu = 3.8 \cdot 10^{-5} \, \text{m}^2/\text{s} \) (kinematic viscosity) [8] and \( u_0 = 7.2 \, \text{m/s} \) (maximal linear rate of the inlet flow). If we take the value of porosity \( \varepsilon = 0.412 \) for our case, the Reynolds number will be \( Re = u_0 \cdot d/(
u \cdot \varepsilon) = 190 \). This value suggests the existence of the laminar flow in the MC reactor. Then, for our microchannels with rectangular cross-section of \( 0.2 \times 6 \, \text{mm}^2 \), the Sherwood number is 6.2 [9]. Hence, \( \beta = 2.3 \, \text{m/s} \). The heating power \( E(x) \) released from the complete methane oxidation is determined by formula:

\[ E(x) = \Delta H_T^0 \cdot X_{O_2}(x) \cdot F_{CH_4}^{in}, \]  

where \( \Delta H_T^0 \) is enthalpy of the reaction of complete methane oxidation (II) at the given temperature. Since \( \Delta H_T^0 \approx \Delta H_{298}^0 \) and using the above parameter, one can calculate the value of heat power generated on the front edge of MC plates in MCR-P and MCR-Z. To compare the calculated and experimental data, one should use the difference of the heat power release in MCR-P and MCR-Z (\( E_P \) and \( E_Z \), respectively), which is the most important feature. For this purpose we use a parameter \( G(x) \), which characterizes the heat power release differences normalized to the maximal heat power release at the 100% conversion of dioxygen:

\[ G(x) = (E_P(x) - E_Z(x))/E_{max}, \]  

where \( E_{max} = \Delta H_T^0 \cdot F_{in}^{CH_4} \) is the maximal heat power release at the 100% dioxygen conversion. \( E_P(x) \) and \( E_Z(x) \) – the heating power for co-current and countercurrent reagent flow, respectively. By substituting (7) and (8) in (9), we obtain a resultant expression for the calculations of \( G(x) \):
\[ G(x) = \exp\left(-\beta \cdot S \cdot \frac{x}{u_0^p}\right) - \exp\left(-\beta \cdot S \cdot \frac{x}{u_0^Z}\right), \]

where \( u_0^p = \frac{F_{in}^{CH_4}}{w_P} \) and \( u_0^Z = \frac{F_{in}^{CH_4}}{w_Z} \) are the linear rates of the inlet methane flow, \( w_P = 0.58 \text{ cm}^2 \) and \( w_Z = 0.18 \text{ cm}^2 \) are the total cross-sections of microchannels in the MCR-P and MCR-Z, respectively.

Figure 5 presents the calculated relationship between \( G(x_0) \) and \( F_{in} \) in the studied range of inlet flows \( F_{in} = 6 - 140 \text{ cm}^3/\text{s} \). Here we took \( x_0 = 0.05 \text{ cm} \) - the size of the near-surface region of the MC plate front edge (equal to the thickness of the MC plate), where the main part of the dioxygen conversion seems to occur. As follows from Fig. 5, parameter \( G(x_0) \) increases with increasing the rate of the inlet reagent flow. This constitutes evidence that in the MCR-P the rate of heat release on the MC plate front edge depends on \( F_{in} \) more strongly than that in the MCR-Z.

It is evident that the temperature, to which the MC plate front edge is heated, has to be, to a first approximation, linearly dependent on the power of heat release.

Fig. 5 also shows the temperature difference \( \Delta T \) between the front edge temperatures of P- and Z-type MC plates as the function of the inlet reagent flow rate at \( T_{in} = 650^\circ\text{C} \) and \( 780^\circ\text{C} \). \( \Delta T = T_f^P - T_f^Z \), where \( T_f^P \) and \( T_f^Z \) are experimental temperatures of the front edge of MC plates of P- and F-types. As the inlet flow rate increases, the temperature difference increases and correlates with parameter \( G(x_0) \). Our analysis evidences that the MC front edge is overheated due to sufficiently high heat release, associated with the processes of the methane complete oxidation and almost complete conversion of dioxygen, occurring in a small region on the front edge of the MC plates. Note that the values of the heat power release and temperature increase are higher in the MCR-P than that in the MCR-Z.

4. Comparison of the operation of MC reactors with the co-current and countercurrent reagent flows

Figures 6 and 7 present experimental data on the methane conversion, selectivity to carbon monoxide and hydrogen, production of hydrogen and carbon monoxide from MCR-P and MCR-Z at inlet flow temperate \( 780^\circ\text{C} \). In spite of different temperature profiles registered in the above reactors (Figs. 3, 4), at low flow rates the data on the methane conversion, selectivity to carbon monoxide differ insignificantly, while the values of selectivity to hydrogen for MCR-P is higher compared to MCR-Z at all GHSV values. In the range of \( \text{GHSV} > 10^5 \text{ h}^{-1} \), for MCR-Z the conversion of methane and selectivity to carbon monoxide
decreases compared to MCR-P. E.g., at GHSV $\approx 4 \cdot 10^5$ h$^{-1}$, the methane conversion is 90% in the MCR-P and 78% in the MCR-Z. The value of the hydrogen production, $Y_{H_2} = H_2 F_{out}$, calculated from eq. (5), shows that $Y_{H_2}$ decreases proportionally with decreasing the degree of the methane conversion in the MCR-Z. Thus, at GHSV $\approx 4 \cdot 10^5$ h$^{-1}$, the hydrogen production is 250 l/h in the MCR-P versus 220 l/h in the MCR-Z. A slight decrease in the methane conversion observed for the MCR-Z seems to be associated with the different nature of gas dynamic flows in MC reactors: the linear rate of reagents flow in the MCR-Z is three times higher than in MCR-P.

A bottleneck in the operation of MC reactors is a practically uncontrolled increase of the temperature of the front edge of MC plates, resulting in their corrosion and following destruction. To study the problem, we increased thermal loads for both reactors after their operation for 30 hours (MCR-Z) and 22 hours (MCR-P). The test parameters for the elevated heat loads were: the inlet flow rate 100 ml/s, furnace temperature 920°C, test within 8 hours. After that the conversion of methane, selectivity to carbon monoxide and production of hydrogen and carbon monoxide were determined at lower thermal loads as in our previous experiments. This experimental procedure provided information on the degradation of MC plates in both MC reactors. Table 2 presents experimental data on the operation of both reactors after the elevated heat loads.

As follows from Table 2, the degree of the methane conversion in the MCR-Z did not practically change after high heat loadings. For the MCR-P, the degree of the methane conversion decreased and became lower than that for the MCR-Z before the elevated thermal loads.

Provided that the MCR-P initially surpassed the MCR-Z in the production of hydrogen and carbon monoxide, the performance of MCR-P significantly degraded after the testing. This indicates severe damages of MC plates in the MCR-P, which is confirmed by a visual inspection of the plates withdrawn from the reactor. In some places, the front edge can be destroyed on 2 mm, that is, about 10% of the total length of a plate (23 mm). It should be noted that the MC plates in the MCR-Z appeared to be not destroyed.

5. Conclusions

The work of two kinds of MC reactors, in which the specially designed microchannel plates provided co-current and countercurrent reagent flows, was studied. In both microreactors the total volume of channels was equal, which provided the similar residence
time of the reagents. The operation of both reactors was compared via analysis of temperature profiles and parameters of the methane partial oxidation, such as the methane conversion, selectivity to carbon monoxide and hydrogen, and hydrogen and carbon monoxide production.

The data on the temperature profiles of the MC plates evidenced that difference between the temperatures of the inlet flow and the MC plate front edge increased with increasing the inlet flow rate. The maximum temperature difference at inlet flow temperature 780 °C appears to be 95 and 60°C for the MCR-P and MCR-Z, respectively, and the temperature difference between the front and back edge of the MC plate is 3.3 times higher in the MCR-P than that in the MCR-Z. Thus, the conditions of the MC plates operation in MCR-Z are much “milder” than in MCR-P.

In the MCR-Z countercurrent flows partially remove the heat excess at the beginning of the reactor, averaging the temperature profile along the MC plates and a little bit decreasing the overall performance of the system.

There is a good correlation between the experimental temperature differences of the front and back edges of MC plates in MCR-P and MCR-Z and the calculated heat release versus the rate of inlet reagent flows due to the partial methane oxidation and almost complete conversion of the dioxygen in the narrow frontal layer of the MC plates.

As the MC reactors operate at convenient POM conditions and the temperature of the inlet reagent flow is not higher than 780°C, both the methane conversion and selectivity to carbon monoxide and hydrogen the for MCR-P were higher by few percent in comparison to MCR-Z. However, after elevating the heat loads, a decrease in the methane partial oxidation characteristics is observed being much higher in the MCR-P. Moreover, the front edge of the MC plates is destroyed under the action of high heat loads only in the MCR-P, which confirms advantages of countercurrent reagent flows in MC reactors.

6. Acknowledgements

The work was supported by Russian Fund of Basic Researches, Grant No 09-08-01047.

7. References


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Fig. 3. The temperature profile along the microchannel plates as a function an inlet flow rate with the co-current reagent flow in the regions of low (650°C) and high (780°C) temperatures.

Fig. 4. The temperature profile along the microchannel plates as a function an inlet flow rate with the countercurrent reagent flow in the regions of low (650°C) and high (780°C) inlet flow temperatures.
Fig. 5. Comparison for estimated parameter $G(x)$ and the experimental temperature difference $\Delta T = T_{fP}^\circ - T_{fZ}^\circ$ between the front edge temperatures of P- and Z-type MC plates as the function of the inlet reagent flow rate at $T_{\text{in}} = 650^\circ\text{C}$ and $T_{\text{in}} = 780^\circ\text{C}$.

Fig. 6. Conversion of methane, selectivity of CO, selectivity of H$_2$ and yield of CO and H$_2$ in the MC reactor as the function of GHSV for MCR-P.

Fig. 7. Conversion of methane, selectivity of CO, selectivity of H$_2$ and yield of CO and H$_2$ in the MC reactor as the function of GHSV for MCR-Z.

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We study POM process in reactors with co-current and countercurrent reagent flows. Increasing GHSV increase temperature gradient along microchannel plates. For MC plates with co-current flows temperature gradient is severely higher. Countercurrent flows remove heat excess at reactor beginning, averaging temperature. This prevents destroying of microchannel plates in partial oxidation of methane.
Table 1. The temperature $T_f$ at the front edge of the MC plates and the temperature gradient $\Delta T/L$ along the MC plates.

<table>
<thead>
<tr>
<th>$T_{in}$, °C</th>
<th>$T_f$, °C</th>
<th>$\Delta T/L$, °C/cm</th>
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<tbody>
<tr>
<td></td>
<td>$F_{in} = 4$ ml/s</td>
<td>$F_{in} = 135$ ml/s</td>
</tr>
<tr>
<td>MCR-P</td>
<td>MCR-Z</td>
<td>MCR-P</td>
</tr>
<tr>
<td>650</td>
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<td>670</td>
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<tr>
<td>780</td>
<td>810</td>
<td>795</td>
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Table 2. Data on the operation of MC reactors before and after elevated thermal loads.

<table>
<thead>
<tr>
<th>Microchannel reactor</th>
<th>Working conditions of MCR before and after the experiment run</th>
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<tr>
<td></td>
<td>X, %</td>
<td>S ( \text{CO} ), %</td>
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<tr>
<td></td>
<td>Before</td>
<td>After</td>
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<tr>
<td>MCR-P</td>
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<td>77.2</td>
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Figure 1
Figure 2
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Figure(s)