Synthesis of methanol in microchannel

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Abstract. Systematic experimental data have been obtained on the results of catalytic chemical reactions in a microchannel reactor for the synthesis of methanol from synthesis gas. Synthesis gas contains hydrogen, carbon monoxide and dioxide, as well as nitrogen in the ratio 58/29/5/8. The experiments were carried out at different flow rates in the temperature range 190-260°C. Experiments were also carried out for methanol synthesis in fixed bed reactor at different synthesis pressures.

1. Introduction
Methanol, CH₃OH, is a simple oxygen-containing hydrocarbon, one of the widely sold gas chemistry products in the world [1, 2], traditionally used for the production of adhesives, paints, LCD screens, silicones, pharmaceuticals. Methanol is a versatile fuel as it can be used directly in combustion engines or as feed for fuel cells, either for a direct methanol fuel cell (DMFCs), or as on-board hydrogen storage for downstream proton exchange membrane fuel cells (PEMFCs). Methanol is important intermediate in the chemical industry for a variety of feedstocks and applications.

Traditional methanol production usually involves the production of synthesis gas (a mixture of hydrogen and carbon monoxide) from natural gas and the actual methanol synthesis process [3]. In the production of synthesis gas, part of the natural gas is burned for steam reforming of methane (the main component of natural gas). This process is carried out at high temperature with excess steam to prevent coke formation on the nickel catalyst. Methanol is formed by hydrogenation of CO and/or CO₂, and the overall reaction is highly exothermic and equilibrium limited under industrial conditions.

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CO + 2H₂ \rightarrow CH₃OH \quad \Delta H^{0}_{298} = -90.8kJ/mole \quad (1)
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\[
CO₂ + 3H₂ \rightarrow CH₃OH + H₂O \quad \Delta H^{0}_{298} = -132kJ/mole \quad (2)
\]

Low-temperature synthesis of methanol is carried out at temperatures of 220-260°C and pressures of more than 5 MPa. This process is carried out using Cu-Zn-Al oxide catalysts developed by ICI back in the 60s [4,5]. The composition and production technology of the catalyst has remained practically unchanged over the past time [4,5].

During the production of methanol from synthesis gas, heat is released (see 1-2), which causes an increase in the temperature of the reactor, a deterioration in the degree of conversion, and a faster deactivation of the catalyst.

The use of microchannel reactors for methanol synthesis makes it possible to create more isothermal process conditions [6-9]. The small dimensions of the channel provide a high surface-to-volume ratio of the reactor, which significantly improves heat and mass transfer. For gas-phase reactions, narrow
distributions of residence times in the reactor are usually obtained due to the rapid heat and mass transfer of substances due to diffusion in small lateral dimensions. Microchannel reactors can be of two types: channels filled with catalyst granules [6-7], channels with a catalyst deposited on their surface [8-11].

The purposes of this work are to investigate methanol synthesis of an industrial catalyst CHM1 in a microchannel reactor with channels filled with catalyst granules and fixed bed reactor.

2. Experiment

The experiments were carried out for a multichannel reactor with a channel gap of 1 mm, filled with a finely dispersed catalyst SNM-1 with a fraction of 240-360 μm, at various contact times in the temperature range 190-260 °C and a pressure of 48 atm. The walls of the channels were made of fechral 0.5 mm thick, which led to the equalization of the temperature inside the reactor. The reactor temperature was measured with an insulated thermocouple in a special groove in the central plate, which was 1.5 mm thick. The temperature was also measured on the outer surface of the reactor. The temperature in the working section was created by an external electric heater [10-11]. Before the experiments, the CHM-1 (CuO / ZnO / Al2O3) catalyst was reduced in situ at atmospheric pressure in a premixed hydrogen-nitrogen mixture (H2 / N2 = 10/90) at a flow rate of 350 Nml / (min gcat) and a temperature of 250°C for 5 hours. After the reduction, the reactor temperature was lowered and the premixed synthesis gas was supplied and the reactor temperature was adjusted to the desired experimental temperature. The reaction gas mixture containing H2: CO: CO2: N2 in the ratio 58/29/5/8, respectively, was fed into the reactor using Bronkhorst HI-TECH flow controllers. The reactor pressure was controlled by a back pressure valve. Most of the experiments carried out were carried out at a pressure of 48 bar. Liquid reaction products were separated in a condenser downstream of the reactor, which were regularly withdrawn through a valve system. The volumetric flow rate of the dried gas mixture at the reactor outlet was measured with an OMEGA flow meter. The component composition of the dried mixture was analyzed using a Maestro gas chromatograph and an Agilent 5975C gas chromatograph-mass spectrometer.

The effect of pressure on the synthesis of methanol was determined in the fixed bed reactors with catalyst with a fraction of 240-360 μm in a square tube with a side of 12 mm. In this case, only the upper part of the working section 2 cm long was filled with the catalyst, and the rest was filled with silica of the same size fraction. The experiments were carried out at pressures of 48.40 and 30 bar. Fixed bed temperature was measured in the center of the catalytic pack.

Figure 1. Microchannel reactor for methanol synthesis. The callout shows a photo of the channels when viewed from above, as well as catalyst granules.
3. Experimental Results

Since the synthesis reaction proceeds slowly with a single passage of the reagents, the change in the concentrations of hydrogen and carbon monoxide changes slightly. An important ingredient in methanol synthesis is the presence of carbon dioxide in the feed mixture. According to [5], the synthesis of methanol is carried out through the reaction (2). Preliminary experiments on the synthesis of methanol from synthesis gas without carbon dioxide gave a negative result on the yield of methanol.

![Figure 2](image1.png)

**Figure 2.** Concentrations of the output gases of methanol synthesis in microchannel reactor at 3000 h\(^{-1}\) inlet flow rate.

In fig. 2 shows the volumetric concentration of the outlet gas after the reactor as a function of the temperature of the microchannel reactor for a space velocity of 3000 h\(^{-1}\).

An important parameter of the ongoing synthesis reactions is the degree of conversion of carbon monoxide depending on the temperature and contact time \(X_i = (n_{i,in} - n_{i,out}) / n_{i,in}\), where \(n_i\) is the molar flow rate of carbon monoxide.

![Figure 3](image2.png)

**Figure 3.** The degree of conversion of carbon monoxide for two flow rates of synthesis gas depending on temperature for a microchannel reactor.

In fig. 3 shows the degree of conversion of carbon monoxide CO depending on the temperature of the reactor for two flow rates of synthesis gas in a microchannel reactor.
Figure 4 shows the degree of CO conversion at different pressures during the synthesis in the fixed bed reactor for the most effective synthesis temperature of 240°C for a given catalyst. It has been shown experimentally that an increase in pressure from 30 to 48 bar leads to a more than 80% increase in the degree of conversion of carbon monoxide. Probably, at a higher synthesis pressure, higher degrees of conversion of carbon monoxide can be achieved.

Temperature measurements on the outer wall of the reactor and inside it showed that during synthesis in a microchannel reactor with a packed bed, compared with a fixed bed reactor, a significant equalization of the reactor temperature occurs. This led to a decrease in the temperature difference between the outer wall and the inside of the reactor by more than two times.

Figure 4. CO conversion in methanol synthesis at different pressures in fixed-bed reactors with Cu-Zn-Al₂O₃ catalyst at the same temperature (240 °C).

4. Summary
The synthesis of methanol in a microchannel reactor at different temperatures and gas flow rates at a process pressure of 48 bars was experimentally studied using SNM-1 catalyst granules. The effect of the synthesis mode and residence time on the conversion rate reaching 0.43 at a synthesis gas flow rate of 3000 h⁻¹ was revealed; it was found that the highest conversion is achieved at a temperature of 240 °C. It was determined the degree of conversion of carbon monoxide in the synthesis of methanol for different pressures, obtained on the fixed-bed reactor.

Acknowledgement
The study was performed in the framework of the state contract IT SB RAS 121031800215-4.

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