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Effect of Reaction Conditions on the Formation of the Products of Oxidative Pyrolysis of Methane on the Resistive Fechrall Catalyst

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Abstract

The effect of reaction conditions (methane concentration, flow rate, catalyst position, gas dynamic mode) on methane pyrolysis within temperature range 700–1200 °C on preliminarily annealed Fechrall wire heated with electric current, at a ratio $\text{CH}_4/\text{O}_2 = 15 : 1$ was investigated. It was shown that independently of conditions the process runs in two temperature regions differing in the selectivity of the formation of major products – C_2 hydrocarbons. Reaction conditions have a substantial effect on methane conversion and selectivity with respect to reaction products. The maximal selectivity with respect to C_2 products can be achieved with the transversal coil position to the gas flow and with the use of flow-circulation set-up instead of flow one. An increase in methane concentration in the initial mixture has ambiguous effect on the selectivity with respect to C_2 hydrocarbons within different temperature ranges: for temperature not higher than 1000 °C, this causes an increase in selectivity with respect to ethylene and acetylene, while at 1000 °C and above this causes a decrease in selectivity with respect to these components.

Key words: catalytic pyrolysis, methane, Fechrall, resistive catalysts

INTRODUCTION

Development of the technology of natural gas processing into valuable products remains a very important problem [1]. One of the most well mastered technologies at present is considered the technology of synthesis gas on catalysts [2, 3] and its subsequent transformation into alkanes (mainly C_{6+}) according to Fischer–Tropsch or into methanol [4]. Another promising direction in methane processing is high-temperature (1500–1600 °C) oxidative pyrolysis of natural gas with the formation of gas mixture containing up to 8–12 % acetylene, subsequent selective hydrogenation of acetylene into ethylene and oligomerization of the latter to obtain motor fuel [5].

It should be stressed that in some works metal coils and meshes heated with electric cur-

rent were used to initiate methane transformation reactions. It was demonstrated in [6] that the radicals formed on the surface of these catalysts pass into the volume and continue the process in the gas phase. The authors of [7] studied methane pyrolysis on a platinum filament 0.2 mm in diameter, heated with electric current. The time of contact was about 100 ms. At 1310 °C the degree of methane transformation was 19.7 %, and selectivity with respect to C_2 hydrocarbons was 51 %.

The authors of [10–12] carried out pyrolysis and oxidative pyrolysis on nickel meshes and on a mesh made of Monel (65 % Ni, 33 % Cu and 2 % Fe). A mesh fragment was heated with the help of electric current to 950 °C. In the opinion of the authors, at low flow rates the gas film around the wires of the mesh is distinguished by the large thickness, which hin-

ders the diffusion of radicals through it. After desorption, CH_3 and H^\bullet radicals recombine inside the film with repeated formation of methane, while the formed ethane can easily undergo decomposition in the presence of H^\bullet . Under increased flow rate, the thickness of gas film around catalyst wires decreases, which simplifies the transition of radicals through the surface gas film. As a result, ethane is formed due to rapid cooling (quenching) of recombination products.

Taking the above considerations into account, we studied current-heated Fechrals as the catalysts of oxygen-free and oxidative pyrolysis [13]. A cold gas mixture was fed to the catalyst in the experiments. This allowed us to quench and conserve pyrolysis products less thermally stable than methane due to breakthrough of a part of gold gas. It was established that oxygen-free pyrolysis of methane on Fechrals proceeds within two temperature ranges: at 600–950 °C, with predominant formation of ethane and ethylene, while at temperatures above 950 °C the formation of ethane and ethylene decreases, and a sharp increase in selectivity with respect to acetylene is observed with temperature rise. During the transition from one temperature region to the other, around 950–1000 °C, mainly carbon and the products of compaction are formed.

Oxidative pyrolysis of methane also proceeds in two temperature regions but they are shifted to higher temperatures. A transition between temperature ranges is characterized by the maximal formation of carbon deposition on the catalyst and the maximal selectivity with respect to CO.

The goal of the present work was to study previously detected regularities with broader ranges of pyrolysis conditions (flow rate, concentration, and catalyst position) within temperature range 700–1300 °C.

EXPERIMENTAL

A wire made of Fechrals alloy of Kh23Yu5T grade (GOST 12766 1–90) 0.25 and 1 mm in diameter was used as the catalyst. Preparation of Fechrals wire [14] included several operations. The wire was coiled, degreased by washing in acetone, baked in the air in a muffle furnace at a tempera-

ture of 1000 °C for 12 h. As a result of oxidative thermal treatment, an oxide layer is formed on the surface of the alloy; it is composed mainly of γ aluminium oxide and hematite.

Thus prepared coil was placed in a flow quartz reactor 20 mm in diameter, as a rule, in the transverse direction to the gas flow. Coils were made of wire 0.25 or 1 mm in diameter, 800 and 200 mm long, and the diameter of coils was 5.5 and 7 mm, respectively. Voltage was supplied to the coil to heat it within the required temperature range from 700 to ≥ 1200 °C. Temperature was measured with the help of a PD-7 optical pyrometer (Etalon JSC, Russia) with laser guidance at the coil. For this purpose, the reactor was equipped with a window made of optical-grade quartz. Local temperature in the centre of the coil at the point of laser beam was determined with the accuracy of ± 1 °C. Reaction mixture composed of methane (15–76 vol. %), nitrogen and addition of air (oxygen) was supplied to the heated wire.

The samples of gas mixture at the outlet of the reactor were analysed using a Tsvet-500M chromatograph (Russia). Residual methane, products – ethane, ethylene and acetylene – were determined with a flame ionisation detector and a capillary column 15 m long with SiO_2 as immobile phase (pressure of carrier gas – nitrogen – was 1 kgf/cm², air flow rate 300 mL/min, hydrogen flow rate 30 mL/min, column temperature 50 °C). The concentrations of the formed CVO and residual oxygen were determined with the help of heat conduction detector at the packed column 1.5 m long filled with CaA zeolite (the flow rate of carrier gas: 30 mL/min, current at the detector: 164 mA, column temperature: 50 °C).

RESULTS AND DISCUSSION

The effect of such parameters as the position of the coil with respect to the gas flow, methane concentration in the mixture and the flow rate of initial mixture was investigated. The following parameters were accepted as the initial ones: transverse position of the coil with respect to the gas flow, the ratio of methane/oxygen = 15 : 1, methane concentration 15 vol. %, flow rate 80 cm³/min.

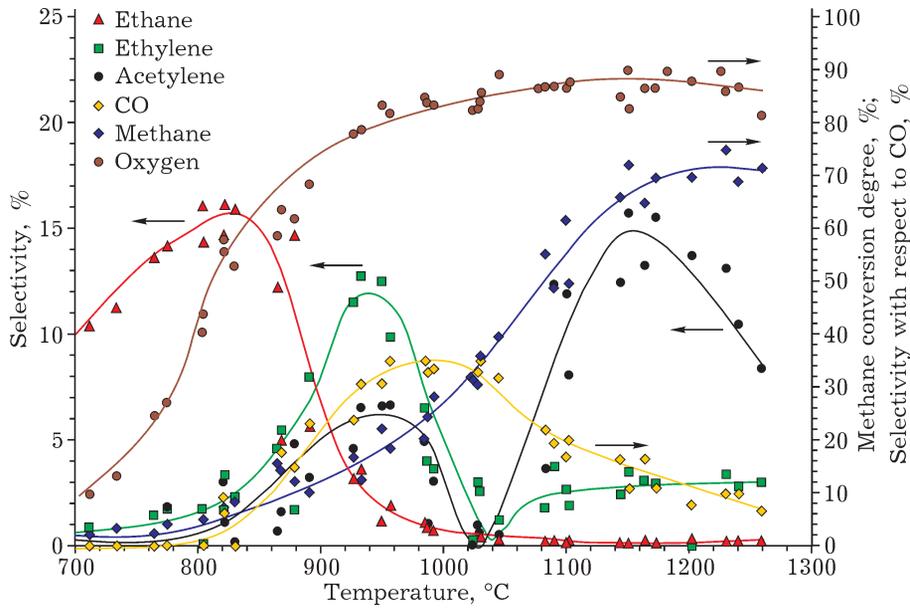


Fig. 1. Dependencies of methane and oxygen conversion, and selectivity of the formation of ethane, ethylene, acetylene and CO on temperature in the oxidative pyrolysis of methane. Process conditions: wire diameter, 1 mm; $\text{CH}_4/\text{O}_2 = 15 : 1$; mixture flow rate: $80 \text{ cm}^3/\text{min}$.

The general view of the dependencies of methane conversion and selectivity of product formation on temperature for oxidative pyrolysis of methane in the presence of oxygen is shown in Fig. 1.

Effect of catalyst (coil) position in the reactor on process parameters

It was established that the behaviour of the curves does not exhibit principal changes when

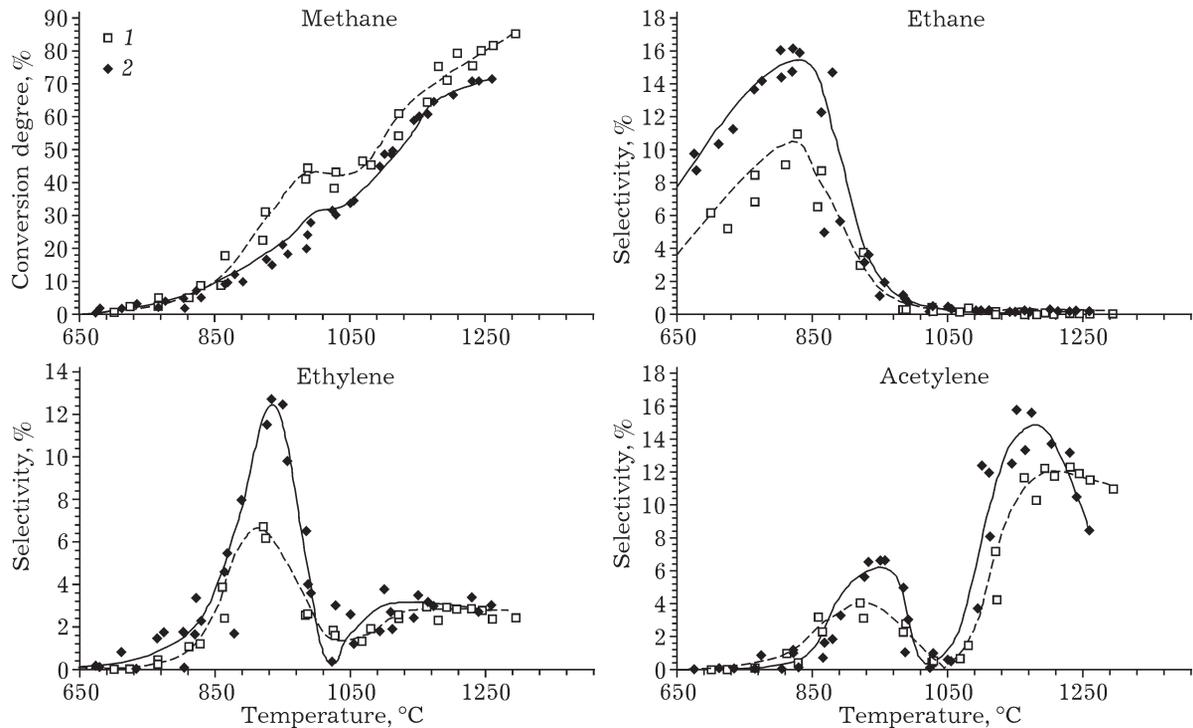


Fig. 2. Effect of gas flow direction on methane conversion and selectivity with respect to products (wire diameter: 1 mm, $\text{CH}_4/\text{O}_2 = 15 : 1$; gas flow rate: $80 \text{ cm}^3/\text{min}$): 1 - along the coil, 2 - across the coil.

the coil position is changed from transverse to longitudinal. At the same time, coil position in the gas flow has a substantial effect on methane conversion and selectivity with respect to the products (Fig. 2). One can see that for the longitudinal flow (along the coil) methane conversion degree increases in comparison with transverse flow. However, selectivity with respect to C_2 products is lower for longitudinal flow than for transverse one, which can be connected with worsening of quenching conditions in the case of longitudinal flow. For transverse flow, the major part of cold gas does not get in contact with the coil, which promotes better quenching of the products. During the experiments, we observed intense carbonisation of coil surface at high temperatures and the deposition of carbon on reactor wall. In the reactor with the transverse flow, the zone of carbonised surface on reactor wall was formed directly around the coil and broadened gradually along the reactor, according to the direction of

the gas flow. In the reactor with longitudinal flow along the coil, we observed more intense carbonisation of the coil and of reactor surface. Only transverse flow of gas mixture flow was used in subsequent experiments.

Dependence of process parameters on methane concentration in the initial gas mixture

The dependence of methane transformation degree and selectivity with respect to C_2 products on methane concentration in initial mixture is shown in Fig. 3. One can see that the degree of methane transformation within the whole temperature range is weakly dependent on methane concentration in initial gas mixture, which may be the evidence of the first order to reaction with respect to methane. It should be noted that the reaction order should be the first also for diffusion-controlled reaction. Change in methane concentration has almost no effect on selectivity with respect to ethane.

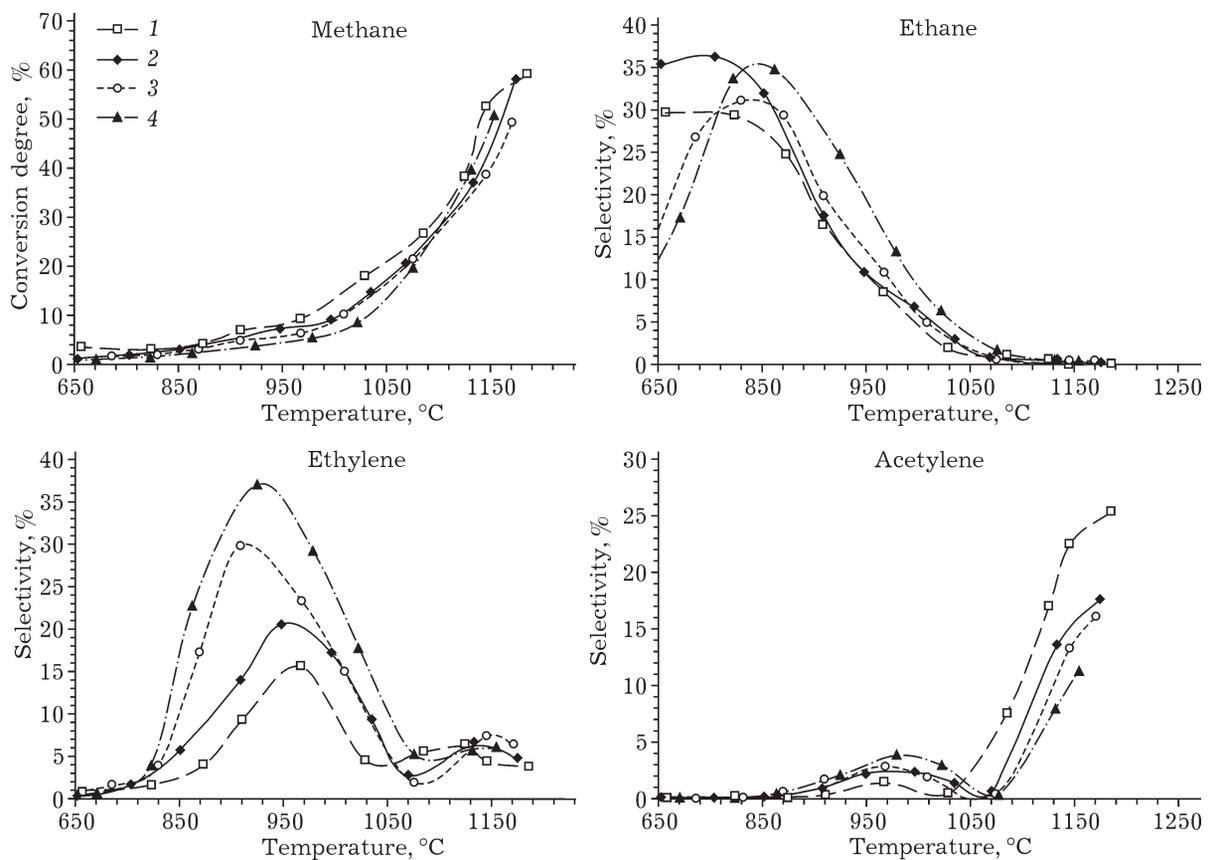


Fig. 3. Dependence of methane conversion degree and selectivity with respect to products on temperature and methane concentration (wire diameter: 0.25 mm, wire length: 800 mm; coil diameter: 5.5 mm; $CH_4/O_2 = 15 : 1$; gas flow rate: $80 \text{ cm}^3/\text{min}$). Methane content in the gas mixture (%): 15 (1), 30 (2), 50 (3), 78 (4).

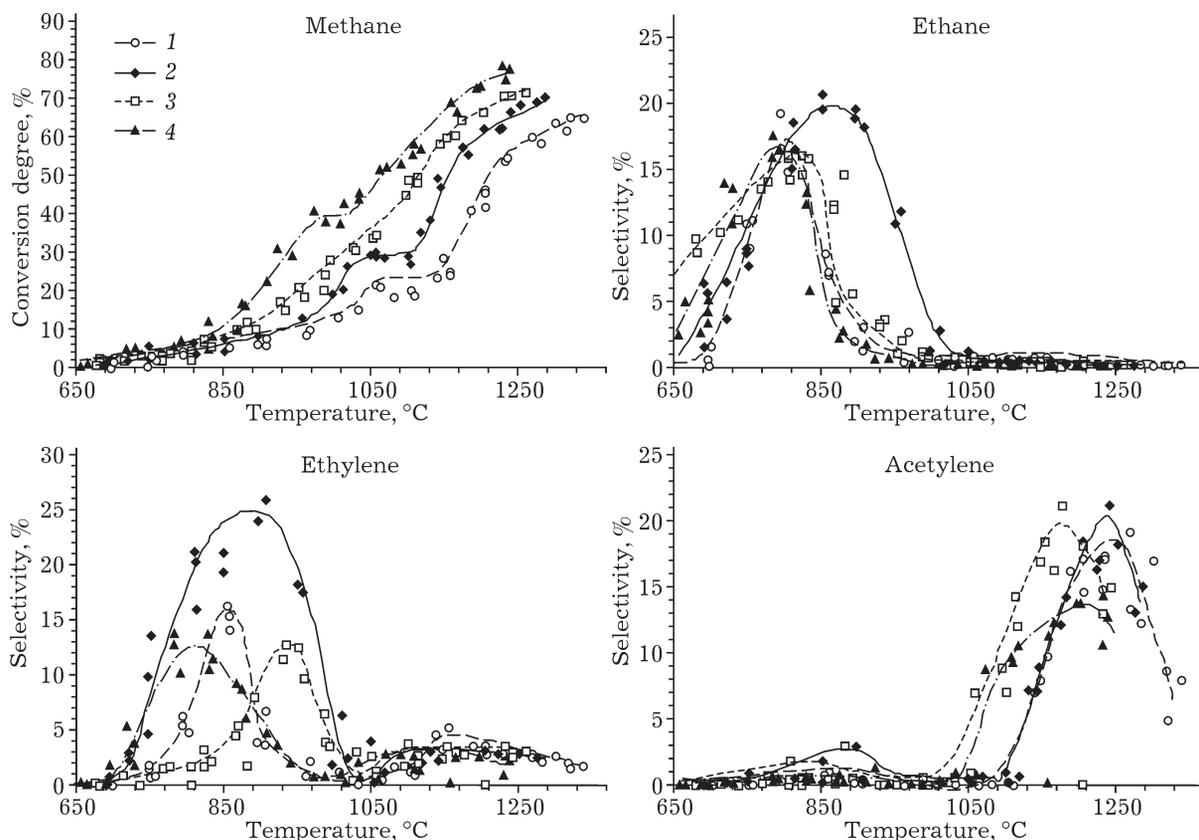


Fig. 4. Effect of the volume flow rate of the mixture on methane conversion and selectivity with respect to products for Fechral (wire diameter: 1 mm, wire length: 200 mm; coil diameter: 7 mm, $\text{CH}_4/\text{O}_2 = 15 : 1$; $C_{\text{CH}_4} = 15$ vol. %). Volume flow rate of the mixture (cm^3/min): 150 (1), 100 (2), 80 (3), 60 (4).

However, in the region of low temperatures, an increase in methane concentration in the gas mixture causes substantial increase in selectivity with respect to ethylene; the higher is methane concentration in initial mixture, the higher is the peak of selectivity with respect to ethylene and the stronger is its shift to the region of lower temperatures. Selectivity with respect to acetylene within this temperature range also increases with an increase in methane concentration but the peak of selectivity with respect to acetylene shifts to higher temperatures. It should be noted that within the high-temperature region the maximal selectivity with respect to acetylene is observed for the lowest methane concentration in the mixture: 15 %.

Effect of volume flow rate of gas mixture on process parameters

The dependencies of methane conversion and selectivity with respect to products (ethane, eth-

ylene, acetylene) on the Fechral catalyst on the volume gas mixture flow rate are shown in Fig. 4. One can see that with an increase in flow rate the curve of methane conversion shifts to higher temperature region, that is, methane conversion at a definite temperature decreases because the time of contact decreases. According to the data reported in [13–15], an increase in the linear rate of gas flow causes a decrease in the thickness of gas layer adjacent to coil surface and promotes the transition of pyrolysis-generated radicals into the gas phase thus leading to the changes in methane transformation degree and selectivity with respect to products. However, in our experiments the change of flow rate was too small in comparison with experiments described in [13–15] and did not cause sharp changes of the conditions under which the radicals are released into the gas layer.

At the same time, the changes of selectivity with respect to ethylene in the low-temperature region are very essential and can be connected with the changes of the conditions of

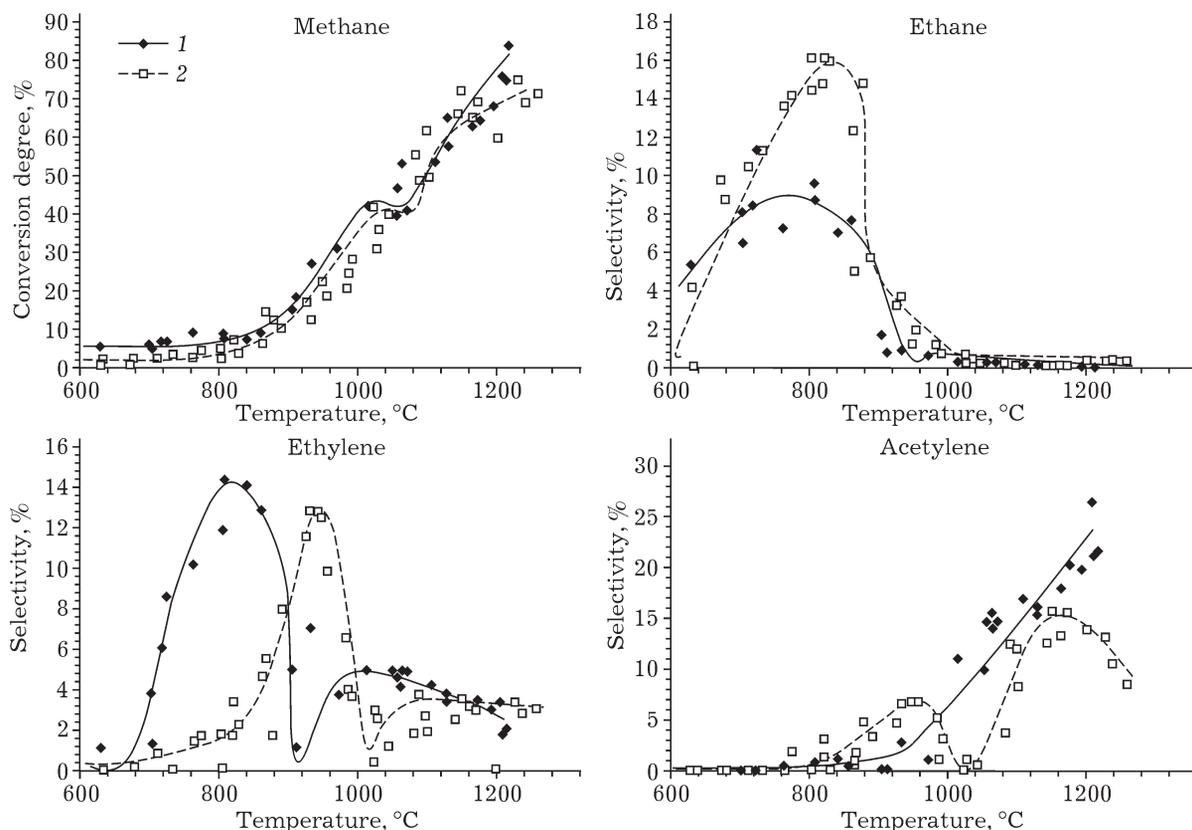


Fig. 5. Effect of gas dynamic conditions on the oxidative pyrolysis of methane ($\text{CH}_4/\text{O}_2 = 15 : 1$, wire diameter: 1 mm, $C_{\text{CH}_4} = 15$ vol. %): 1 - flow circulation mode, 2 - flow mode.

quenching and the effect of the cold reactor wall, which is especially important for the case of the minimal flow rate.

Pyrolysis in the flow circulation mode

The effect of a sharp increase in the linear flow rate was studied using a flow circulation set-up instead of the flow one in some experiments. With the same rate of reaction mixture supply into the set-up (80 cm³/min) circulation rate was about 11.3 L/min, that is, about 140 times higher. It was established that a change of the flow mode to the flow circulation one has almost no effect on methane conversion but affects the selectivity with respect to reaction products (Fig. 5). Thus, selectivity with respect to ethane in the flow circulation set-up is lower in comparison with that in the flow set-up. Quite contrary, selectivity with respect to ethylene and acetylene are higher. It is necessary to stress that the points of selectivity minima with re-

spect to C₂ products are shifted to lower temperatures in comparison with the flow set-up.

An increase in the rate of gas mixture admission with the conservation of gas circulation rate (11.3 L/min) causes a substantial decrease in methane conversion rate within the whole temperature range under investigation due to a decrease in the time of contact (Fig. 6). In this situation, inflection of conversion curve is not shifted to higher temperatures with an increase in the rate of reaction mixture admission into the set-up, unlike for the flow set-up, but it becomes less pronounced (a decrease in the temperature range of inflection region). In addition, with an increase in the rate of gas mixture admission into the flow circulation set-up, selectivity with respect to all C₂ reaction products increases substantially, which is accompanied by a decrease in the rate of carbon deposition on the catalyst.

To explain the data obtained, further studies are necessary.

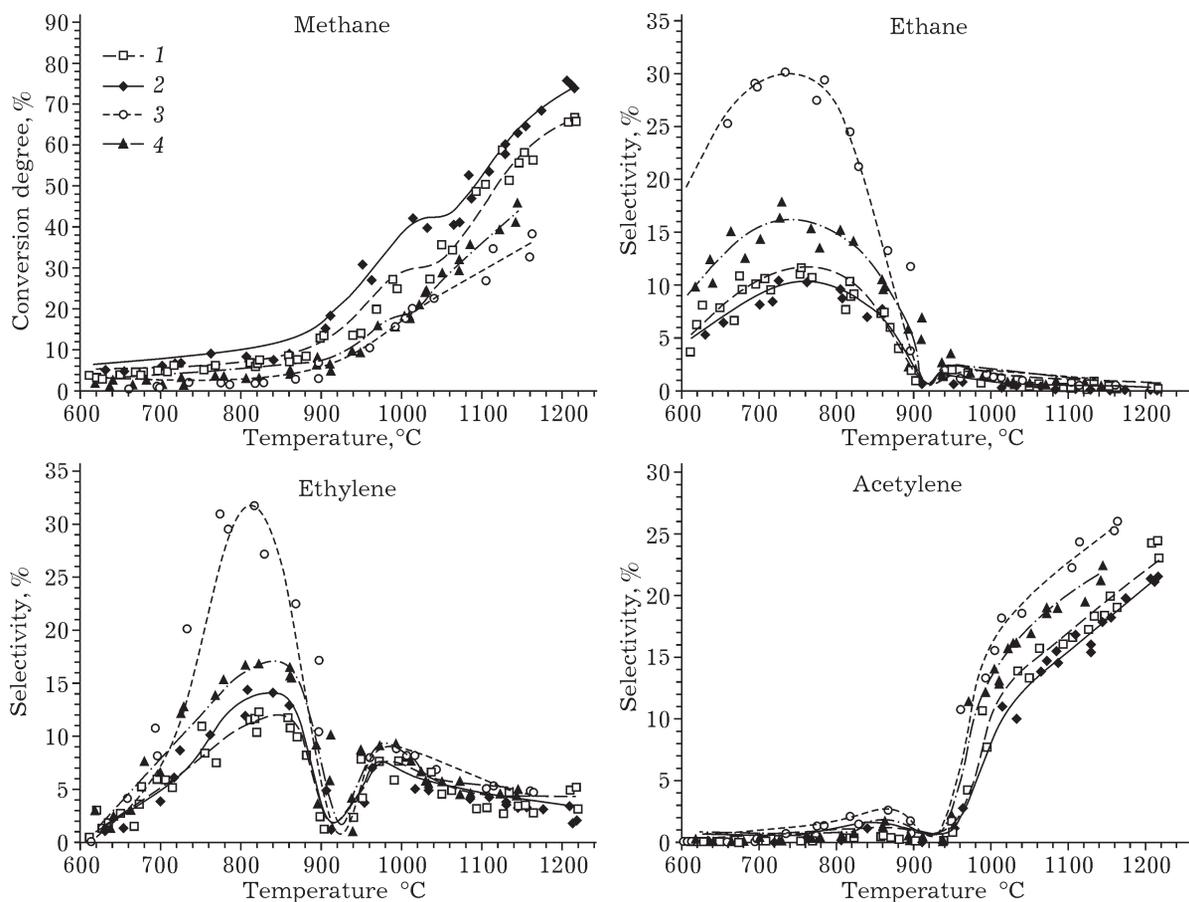


Fig. 6. Effect of the rate of gas mixture admission into the flow circulation set-up on the degree of methane conversion and selectivity with respect to reaction products ($\text{CH}_4/\text{O}_2 = 15 : 1$, $C_{\text{CH}_4} = 15$ vol. %, wire diameter: 1 mm). Admission rate (cm^3/min): 80 (1), 160 (2), 240 (3), 320 (4).

CONCLUSION

A substantial effect of methane pyrolysis conditions on conversion and selectivity with respect to products is demonstrated. The maximal selectivity with respect to C_2 products was obtained in the reactor with the transverse position of the coil with respect to the gas flow direction, but methane conversion was lower in this case in comparison with longitudinal position. It was demonstrated that during the oxidative pyrolysis of methane in the region of low temperatures an increase in methane concentration leads to a substantial increase in selectivity with respect to ethylene with almost unchanged degree of methane conversion. Quite contrary, in the region of high temperatures an increase in methane concentration leads to a strong decrease in selectivity with respect to C_2 products.

In other words, low temperature and high methane concentration in the raw material is necessary to obtain ethylene, while, quite contrary, higher temperatures and low methane concentrations are necessary to obtain acetylene.

It was discovered that with a decrease in gas mixture flow rate the experimental curve of the dependence of transformation degree on temperature passes higher, and inflection connected with carbon deposition on the catalyst shifts to lower temperatures. The flow circulation mode does not cause principal changes of the dependence of methane transformation degree on temperature but has a strong influence on selectivity with respect to products, especially in the low-temperature region, which is likely to be connected with changes in the conditions of heterogeneous-homogeneous process in comparison with the flow mode.

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