KINETIC REGULARITIES OF METHANE DIMERIZATION REACTION

**Abstract.** The article studies the factors affecting the rate of methane dimethylation reaction with catalytic oxidation, the kinetic laws of the reaction in a flow differential quartz reactor \((P = 0.1 \, \text{MPa}, \, V_{\text{cat}} = 0.5 \, \text{ml} + 2 \, \text{ml}, \, \text{CH}_4 : \text{O}_2 = 2 : 4, \, \text{contact time} \, 0.1-0.09 \, \text{sec})\) in the temperature range 750-850 °C. Based on the study of such factors as the effect of temperature on methane conversion and product selectivity, the effect of oxygen and hydrogen additives on methane conversion and product selectivity, the effect of temperature on ethane selectivity, \(\text{CH}_4 : \text{O}_2 = 3:1\) on acetylene selectivity for various concentrations of methane in the mixture, a mechanism for the formation of ethane, ethylene, acetylene, and carbon dioxide reactions was proposed and a kinetic model was created.

**Introduction.** Currently, the demand for petroleum products around the world is growing. Vinyl chloride, polyethylene, ethylene oxide, vinyl acetate, lavsan and others are in great demand. The main feedstock for all of the above substances is ethylene. Currently, ethylene is mainly thermally decomposed into gasoline. The...
dynamic growth of demand for motor fuel stimulates the search for another innovative way to obtain the main product of organic synthesis. One such innovative method is catalytic dimerization of methane to ethylene [1-6]. At present, ethylene production from methane is not allowed. The main reason for this is that the equipment of the devices for conducting the process has not been implemented and the optimal mode has not been chosen. To determine the optimal mode and equipment of the devices, it is necessary to study the kinetic patterns of the reaction. Several papers on catalytic oxidative changes of methane [7-11] have been published, proposing various absorbent catalysts for the production of ethylene and ethane from methane. The peculiarity of the redox-condensation reaction of methane is that in all known catalysts the reaction takes place at a high temperature, and the process is highly exothermic.

In addition, the mixture CH$_4$ + O$_2$ has a strong explosive property. The activity and selectivity of the catalysts is low. Besides, in all studied literatures Kinetics of reaction of dimerization of methane in Bi$_2$O$_3$:9% K$_2$CO$_3$/Al$_2$O$_3$; 34% PbO/Al$_2$O$_3$; 4% Na$_2$MoO$_4$*10%Mn-O/SiO$_2$ of % it wasn’t completely investigated without processes with participation of Mn-O/SiO2 catalysts. In reactions involving these catalysts, formal equations for kinetic expression of the process are also used. In all studies ethylene [12-19] was obtained as the end product. Prospects for the practical application of the methane catalytic dimerization process. The C2 hydrocarbon flour reaction mixture is highly dependent on the oxygen content of CH$_4$ +.

To obtain high productivity C$_2$ hydrocarbons, an insoluble reaction mixture must be used. It is desirable that CH$_4$/O$_2$=4-5 be in a volume ratio. The following difficulties exist in the practical application of the catalytic methane dimerization reaction: 1) the reaction produces ethane, ethylene and a small amount of propane and propylene with high reactivity to methane. The resulting products are completely oxidized to CO$_2$ in the presence of a catalyst. 2) reaction products react easily with oxygen than with methane in the gas phase. Therefore, a portion of the oxygen is required or the reaction products are rapidly removed from the reaction zone. 3) the catalytic dimerization of methane produces a large amount of heat, which requires the efficient use of heat [21-27].

Experimental part. The reactor is a quartz tube, length 650 mm, inner diameter 8 mm. To reduce the size of the catalyst by 0.25-0.5 mm, quartz glasses are laid on the bottom and on top of the catalyst. Catalytic activity of the catalyst was studied in a flow differential quartz reactor (P = 0.1 МПа, V$_{kat}$ = 0.5 мл + 2 мл, CH$_4$ : O$_2$ = 2 \div 4$, contact time 0.1-0.09 sec) with a temperature range of 750-850 °C [23, 21-26].

The temperature ranged from 700 to 850 °C. Under the specified conditions, the conversion of methane ranges from 1 to 35%, the conversion of oxygen from 4 to 98%. Selectivity to reaction products ranges from 30 to 70%. Methane and pure oxygen at 99.9% purity were used for the reaction. The gases were mixed before entering the reactor. To study the kinetic patterns of the methane oxidation reaction, a laboratory device with a flow differential reactor was created. The gas products of the reaction were analysed by chromatography on the Gazochrom 3101 chromatograph with a thermochemical detector, to which an additional thermostat is connected, under optimal conditions: column thermostat temperature-100 °C, carrier gas (air) flow rate -35 ml/min, Column length filled with activated carbon - 1 m, inner diameter - 3mm. quantitative analysis was performed by absolute graduation [20, 21-24].

Results and discussion of the experiment. The effect of some parameters on the reaction rate of catalytic methane dimerization was studied. The results are shown in Figure 1.
Figure 1 shows the temperature relationships between methane (X) conversion and the selectivity of reaction product formation. As shown in Figure 2, methane conversion begins at 600 °C. The first product of the methane oxidative dimerization reaction is ethane and a small amount of ethylene. With a further increase in temperature, the selectivity of the formation of ethane and ethylene increases, and the selectivity of ethane reaches a maximum at 800 °C. The selectivity of ethane at 800 °C is about 2 times higher than the selectivity of ethylene. However, at 820-8300 °C, the selectivity for all products drops sharply. When the temperature exceeds 800 °C, peaks (bulges) characteristic of acetylene appears on the chromatograms. When the temperature exceeds 850 °C, its selectivity increases dramatically.

Also, the selectivity of the formation of ethane and ethylene reaches a second maximum at 900 °C. Figure 2 below shows the effect of oxygen and hydrogen additives on methane conversion and acetylene selectivity.

With oxidative dimerization, the conversion of methane to the reaction mixture of the desired composition begins at 600 °C and increases with increasing temperature. Methane conversion increases with increasing oxygen concentration in the initial reaction mixture.
The conversion of methane is substantially unchanged with the addition of hydrogen to the initial reaction mixture. The formation of ethane, the first reaction product at this time, is independent of the reaction conditions. When the reaction is carried out in the absence of oxygen (line 3), ethane begins to form at 680-700 °C.

In the presence of oxygen (CH₄: O₂ = 3:1 vs CH₄:O₂ = 2:1; lines 4 and 5) it is formed by 650 °C. When CH₄:H₂ = 1:1 vs CH₄:H₂ = 1:2 are taken in proportions (rows 2 and 1), the formation of 700 °C begins. Under these conditions, the selectivity to ethane is maximum at 750 °C.

As can be seen from the figure, when choosing the effect of temperature on acetylene selectivity for 15%, 30. 45. 60% methane concentrations in the mixture CH₄:O₂=3:1 acetylene selectivity increases with decreasing methane concentration in the mixture.

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