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A PROMISING METHOD FOR PROCESSING NATURAL GAS

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Annotation. *The effect of internal diffusion braking during methane oxycondensation was analyzed. The influence of various factors on the reaction rate of ethylene recovery from methane was studied. Based on the obtained results, a reaction mechanism for the formation of ethylene from methane is proposed, a kinetic equation characterizing the whole process is selected, and its adequacy is evaluated.*

Introduction. Proved reserves of natural gas in our country amount to almost 2 trillion m^3, oil - 350 million tons. Currently, the level of oil reserves in Uzbekistan is 31-32%. In the world, 1.5-2.0% of methane is chemically processed. This aims to increase the production of valuable methane-based products in natural gas and expand research on the synthesis of substances necessary for the national economy. Saving material and thermal energy resources are one of the important tasks of modern technology. The development of energy-saving technologies is one of the main areas of chemical technology and scientific and technological progress. In many chemical industries, energy consumption is the main source of waste. Also, it is necessary to create technologies that allow the integrated use of thermal resources (oil, coal, natural gas) - several chemical synthesis products both as raw materials and as an energy source [1-3]. The only and promising way to process natural gas is through an oxycondensation reaction that proceeds in one step and at normal atmospheric pressure. More than 30 years have passed since the opening of the methane oxycondensation reaction, but this reaction has not yet been introduced into the industry due to the lack of a stable catalyst with high activity and efficiency.

Therefore, it is important to create highly efficient catalysts and optimize the operating parameters of the devices to obtain the desired products with maximum efficiency [4-10].

Experimental part. Based on the analysis of the starting materials and reaction products, the following process parameters were determined:

1. Conversion of hydrocarbons:

$$X_{YB} = \frac{\sum_i c_i^{maxc} \cdot \mathrm{n}_\mathrm{i}^\mathrm{c}}{\sum_i c_i^{maxc} \cdot n_i^c + c_i^{YB}} \cdot 100\%$$

2. Oxygen conversion:

$$X_{O_2} = \frac{\left(C_{O_2}^0 - C_{O_2}^i \cdot K_N\right)}{C_{O_2}^0} \cdot 100\%$$

3. Selectivity in relation to reaction products:

$$S_i = \frac{C_i^{макс} \cdot n_i^c}{\sum_i C_i^{макс} \cdot n_i^c} \cdot 100\%$$

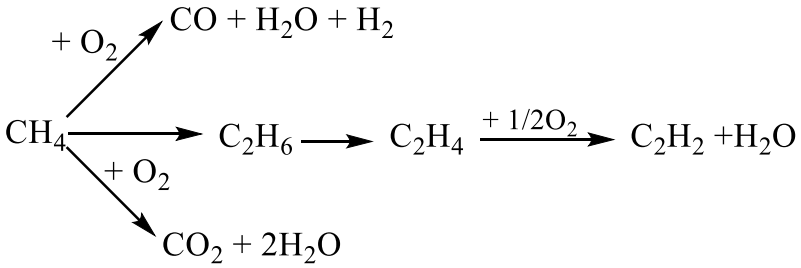
4. Productivity of reaction products:

$$Y_i = \frac{C_i^{макс} \cdot n_i^c}{\sum_i c_i^{макс} \cdot n_i^c + C_i^{УВ}} \cdot 100\%$$

in this $C_i^{УВ}$ - the appropriate hydrocarbon concentration at the reactor exit (mol.%); $C_i^{макс}$ - in the gas at the outlet of the reactor *i*- the concentration of the product (mol.%); n_i^c - the number of carbon atoms in the product molecule; $C_{O_2}^0$ - oxygen concentration in the starting mixture (mol%); $K_N = \frac{N_2^0}{N_2^i}$ - coefficient that takes into account the change in total volume during the reaction, N_2^i - nitrogen concentration at the reactor entrance; N_2^i - Nitrogen concentration at the reactor outlet.

Results and discussion. The kinetic regularities of the methane oxycondensation process in the presence of an acceptable catalyst containing $(Mn_2O_3)_x * (Na_2MoO_4)_y * (ZrO_2)_z$ were studied under differential reactor conditions at different values of partial pressures and temperatures of the starting materials, and a kinetic model of the process was developed.

It is known that during the oxidation of methane, 3 reactions occur in parallel:



we consider the mechanisms and kinetic models of reactions that occur along the chain. The reliable mechanism of ethane formation from methane can be summarized as follows:

$$2Z + O_2 \xrightarrow{k_1} 2ZO;\ 2ZO + CH_4 \xrightarrow{k_2} ZOCH_3 + ZOH;\ ZOCH_3 + CH_4 \xrightarrow{k_3} C_2H_6 + ZOH$$

$$2ZOH \xrightarrow{k_4} H_2O + ZO + Z$$

$$0{,}5O_2 + 2CH_4 \rightarrow C_2H_6 + H_2O$$

In a stationary state $W_1 = W_2 = W_3 = W_4$ and the total number of surface areas is constant ($\sum\theta_i = 1$), the equation for the rate of ethane formation by the above mechanism is as follows:

$$W_{C_2H_6} = \frac{k_3^2 P_{CH_4}}{4k_2}\left(\sqrt{\frac{k_2 P_{CH_4}}{k_1 P_{O_2}} + \sqrt{\frac{k_2 P_{CH_4}}{k_4}}} + 1\right) + \sqrt{(\sqrt{\frac{k_2 P_{CH_4}}{k_1 P_{O_2}} + \sqrt{\frac{k_2 P_{CH_4}}{k_4}}} + 1)^2 + 4\frac{k_2}{k_3}}$$

The chain mechanism for the formation of ethylene from ethane:

$$C_2H_6 \xrightarrow{k_5} 2CH_3^{\blacksquare};\ CH_3^{\blacksquare} + C_2H_6 \xrightarrow{k_6} CH_4 + C_2H_5^{\blacksquare};\ C_2H_5^{\blacksquare} \xrightarrow{k_7} C_2H_4 + H_2$$

$$H^{\blacksquare} + C_2H_6 \xrightarrow{k_8} C_2H_5^{\blacksquare} + H_2;\ 2\,C_2H_5^{\blacksquare} \xrightarrow{k_9} C_2H_4 + C_2H_6;\ 2\,C_2H_5^{\blacksquare} \xrightarrow{k_{10}} C_4H_{10}$$

$$2CH_3^{\blacksquare} \xrightarrow{k_{11}} C_2H_6;\ C_2H_6 \rightarrow C_2H_4 + H_2$$

The reaction equation for the formation of ethylene according to the above mechanism:

$$W_{C_2H_4} = 3k_6 P_{C_2H_6}\left(1 - \frac{0.33}{1 + \frac{K_8}{k_9}}\right) + \frac{k_5(\frac{k_7}{k_9})^{1/2}}{(1 + \frac{k_8}{k_9})^{1/2}} P_{C_2H_6}^{1/2}$$

CO_2 has also been found in contact gases. CO_2 is mainly formed by the interaction of a weakly adsorbed oxygen molecule with methane:

$$O_2 + Z \xrightarrow{k_1^*} O_2Z;\ CH_4 + Z \xrightarrow{k_2^*} CH_4Z;\ ZCH_4 + 2ZO_2 \xrightarrow{k_{12}} 2CO_2 + 2H_2O + 3Z$$

CO_2 ҳосил бўлиш реакцияси тезлиги:

$$W_{CO_2} = \frac{2k_{12}K_1^* P_{O_2} K_2^* \cdot P_{CH_4}}{(1 + K_1^* \cdot P_{O_2} + K_2^* \cdot P_{CH_4})^2}$$

The interaction between a methane molecule and dissociatively adsorbed oxygen gives a working gas:

$$2Z + O_2 \xrightarrow{K_1} 2ZO;\ 2ZO + CH_4 \xrightarrow{k_{13}} CO + 2Z + H_2 + H_2O;$$

$$O_2 + 2CH_4 \rightarrow 2CO + 3H_2 + H_2O$$

The equation for the rate of formation of CO:

$$W_{CO} = k_{13} P_{CH_4}\left(\frac{1}{1 + \sqrt{\frac{k_{13} P_{CH_4}}{K_1 P_{O_2}}}}\right)^2$$

The calculation of the reaction rate constants was performed based on the experimental results given in Table 1.

Table 1

Experimental results

Temperature, ^{0}C	Component concentration,% mol							
	H_2	CH_4	O_2	N_2	CO_2	C_2H_4	C_2H_6	CO
	Contact time-2 s							
700	1,9	24,8	0,8	56,8	2,4	8,7	1,3	0,4
730	0,8	25,6	1,1	57,3	3,6	8,0	1,2	0,3
735	1,8	24,6	1,8	57,4	2,8	8,0	1,2	0,3
750	4,6	26,2	1,7	53,3	3,4	8,5	0,7	1,3
750	3,8	22,4	1,5	58,6	3,9	8,0	0,8	1,1
800	8,4	24,0	0,3	49,8	3,5	8,0	0,2	3,8
850	14,8	23,7	0,2	42,0	2,2	6,9	0,0	8,1

Continuation of tab. 1

Contact time-1 s								
600	0,4	30,4	0,1	55,7	1,2	8,3	1,4	0,5
660	1,7	27,1	0,0	56,6	2,1	8,4	1,1	1,0
665	2,7	28,1	0,0	54,7	2,0	8,4	1,1	1,0
700	2,2	29,1	0,0	54,3	1,9	8,4	1,3	0,7
750	2,3	27,6	0,0	55,5	2,2	8,5	1,2	0,7
770	2,2	28,6	0,0	54,4	2,1	8,8	1,3	0,7
800	6,2	28,0	0,0	50,2	2,6	8,2	0,7	2,1
Contact time-0.5 s								
615	2,8	26,1	1,0	56,1	1,3	5,8	0,8	2,0
650	3,9	27,2	0,0	54,1	1,7	6,0	0,6	2,6
700	3,2	27,6	0,0	54,6	1,4	5,9	0,6	2,3
750	2,8	27,2	0,0	55,6	1,5	6,0	0,6	2,3
800	5,1	28,9	0,0	51,3	1,9	5,9	0,6	2,4
800	3,7	24,9	0,0	56,1	1,5	5,8	0,5	3,3
850	4,3	24,6	0,0	55,7	1,6	5,8	0,4	2,5

In the catalytic dimerization of methane, acetylene is formed as a result of the oxidative dehydrogenation of ethylene. At this time, the dissociatively adsorbed oxygen molecule interacts with the ethylene molecule to form the ZOC_2H_4 complex. It splits into acetylene and water molecules, respectively:

$$2Z + O_2 \xrightarrow{k_1} 2ZO;\ ZO + C_2H_4 \xrightarrow{k_{14}} ZOC_2H_4;\ ZOC_2H_4 \xrightarrow{k_{15}} C_2H_2 + H_2O + Z$$
$$0.5O_2 + C_2H_4 \rightarrow C_2H_2 + H_2O$$

The rate of formation of acetylene by this mechanism:

$$W_{C_2H_2=k_1P_{O_2}}\left[\frac{-1+\sqrt{1+4\left(\frac{k_1P_{O_2}}{k_{14}P_{C_2H_4}}+\frac{K_1P_{O_2}}{k_{15}}\right)}}{2\left(\frac{k_1P_{O_2}}{k_{14}P_{C_2H_4}}+\frac{k_1P_{O_2}}{k_{15}}\right)}\right]^2$$

The above equations form a kinetic model of the process.

The parameters of the kinetic models were determined based on the experimental results using the following objective function:

$$F(x)=\sum_1^N\left[\frac{A_{эксп}-A_{хисоб}}{A_{эксп}}\right]^2$$

here *x* is the kinetic parameter of the model under consideration; $A_{эксп}$; $A_{хисоб}$ - Experimental and calculated values of the yield of the reaction products; Number of *N*-components.

The generated kinetic model of the methane oxidation condensation reaction adequately represents the experimental values (the relative error of the experimental and calculated values does not exceed 10%).

Conclusion. Thus, the factors affecting the rate of the reaction of catalytic oxidation and dimerization of methane, the kinetic laws of the reaction in a current differential quartz reactor (P = 0,1 МПа, V_{kat} = 0,5 мл ÷ 2 мл, CH_4: O_2 = 2 ÷ 4, time contacts 0,1–0.09 s) were investigated in the temperature range 750–8500 ^{0}C.

Based on the study of factors such as the effect of temperature on the

conversion of methane and the selectivity of the product, the effect of oxygen and hydrogen additions on the conversion of methane and the selectivity to acetylene, the temperature dependence of the selectivity to ethane, the effect of temperature on the selectivity to acetylene for various methane concentrations in CH_4:O_2=3:1 the mechanism of reactions of formation of ethylene, acetylene, carbon dioxide is proposed and a kinetic model is created.

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