Abstract. A catalyst with high catalytic activity has been developed for the methane carbonate conversion reaction. Various factors (ratio CO₂:CH₄, temperature, initial volume rate and other factors, the yield of the desired product, process conversion and selectivity, as well as the effect of various promoters on catalyst activity in the presence of the selected catalyst in the methane carbonate conversion reaction rate) have been studied. As a result of the study, the following optimal reaction conditions were selected: CO₂:CH₄ = 1.5, T = 820°C, V_methane = 1000 h⁻¹. Based on the obtained results, a process mechanism is proposed. The reasons for the inactivation of the methane carbonate conversion reaction catalyst and its regeneration are discussed.

Introduction. Today, around the world, 25 billion tons of carbon dioxide are emitted into the atmosphere every year. As a result of such a sharp increase in the amount of carbon dioxide in the atmosphere, an increase in temperature on Earth is predicted by 0.35 degrees over the next 15-20 years and by 1.5-2 degrees over 100-120 years. This creates global environmental and economic problems [1-3].

The most promising way to solve this environmental problem is to synthesize gas by converting carbon dioxide into methane and producing methanol based on it [4-6]. The process of converting methane to carbon dioxide and producing "synthesis gas" has not yet been introduced into the industry due to the lack of a long-term stable catalyst, but it is important in terms of CO₂ losses. Methane carbonate conversion is also a promising method with the simultaneous use of two different gases (methane and carbon dioxide), which cause a "greenhouse effect" and are of important environmental and economic importance. The methane carbonate conversion reaction is most important among synthesis gas (H₂ and CO) production reactions. This process is an important reaction for the production of hydrogen in industry and is of great importance in the production of high molecular weight hydrocarbons, methanol, oxygen-containing organic substances and important products of the chemical industry according to the Fischer-Tropsch method [9-22].

The general equation of the methane carbonate conversion reaction is:

\[ \text{CH}_4 + \text{CO}_2 \leftrightarrow 2\text{CO} + 2\text{H}_2, \Delta H_{298K}^0 = +247 \text{ kJ/mol} \]

Additional reactions that may occur when methane is converted to carbonate:

1. \[ \text{CO}_2 + \text{H}_2 \leftrightarrow \text{CO} + \text{H}_2\text{O}, \Delta H_{298K}^0 = -41,1 \text{ kJ/mol} \]
2. \[ \text{CH}_4 \rightarrow \text{C} + 2\text{H}_2, \Delta H_{298K}^0 = +74,8 \text{ kJ/mol} \]
3. \[ \text{CO}_2 + 4\text{H}_2 \leftrightarrow \text{CH}_4 + 2\text{H}_2\text{O}, \Delta H_{298K}^0 = -165,0 \text{ kJ/mol} \]
4. \[ \text{CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO} + 3\text{H}_2, \Delta H_{298K}^0 = +206,0 \text{ kJ/mol} \]
5. \[ 2\text{CO} \leftrightarrow \text{C} + \text{CO}_2, \Delta H_{298K}^0 = -72,5 \text{ kJ/mol} \]
Reaction diagrams show that coke is formed as a by-product of the methane carbonate conversion reaction. Coke formation causes decontamination of the catalyst by filling the pores and active sites of the catalyst. In view of the above, the object of this work is to provide a catalyst with high catalytic activity, characterized by a decrease in the coking rate for the catalytic carbonation reaction of methane, and to study the kinetic patterns of the reaction in the presence of this catalyst.

**Experimental part.** The methane carbonate conversion reaction was carried out in a flow reactor at normal atmospheric pressure, a space velocity of 1000 h\(^{-1}\) and a temperature of 750-1000 °C. The composition of the starting and final materials was analyzed by gas chromatography. The catalyst volume was 6 ml and the process duration was 180-240 hours. The amount of methane and carbon dioxide entering the reactor was monitored by means of a sequentially connected rheometer and gas clock. The methane carbonate conversion reaction catalyst was prepared as follows: Before use, expanded clay is divided into fractions of 2-3 mm. For the preparation of the catalyst used Al(NO\(_3\))\(_3\) \(\cdot\)12H\(_2\)O, Ni(NO\(_3\))\(_2\) \(\cdot\)6H\(_2\)O, ZrO(NO\(_3\))\(_2\) \(\cdot\)2H\(_2\)O, Co(NO\(_3\))\(_2\) \(\cdot\)6H\(_2\)O. A 30% solution of the above salts was prepared and soaked in expanded clay for 10 hours. The sample was then heated in an airstream at 300 °C for 1 hour and then at 700 °C for 4 hours. Qualitative and quantitative analysis of gaseous and liquid products of the catalytic methane carbonization reaction was carried out by gas chromatography. All gas chromatography measurements were performed on the “Gazochrom 3101” and “Light 100 Model 165” chromatographs [8].

Catalytic carbonation of methane gives a mixture of gases consisting of nitrogen, hydrogen, oxygen, carbon monoxide and methane. Artificial mixtures of gases were prepared to select optimal separation conditions for this mixture. Activated carbon and polysorbate were used as sorbents for their separation in a chromatographic column. The size of the column is \(x_1\) (from 1 m to 3 m), the flow rate of the moving phase is \(x_2\) (from 20 to 50 ml/min), the particle size of the sorbent is \(x_3\) (as influencing factors for choosing optimal separation conditions) 0.150-0.500 mm), the temperature of the column thermostat is \(x_4\) (from room temperature to 120 °C), and the size is the degree of separation (RS), which indicates the degree of mutual separation of the components. Based on the results of the experiment, the following regression equation was formed, which shows that the degree of separation (RS) depends on the factors affecting the separation:

\[
R_S = a_0 + a_1x_1 + a_2x_2 + a_3x_3 + a_4x_4 + a_1x_1 + a_44x_4^2
\]

and the adequacy of the equation was assessed. The optimal values of factors providing a high degree of separation of the components of the mixture are implemented by a simplex optimization method based on an adequate regression equation.

**Results and discussion.** Studies have shown that the maximum hydrogen yield is CO\(_2\):CH\(_4\) =1,45. When the ratio of carbon dioxide to methane exceeds this value, the hydrogen yield decreases and the amount of carbon dioxide in the reaction products increases. The amount of carbon monoxide in the reaction products was 1.50. At this time, the yield of carbon dioxide with respect to carbon dioxide is 70%. The peak conversion of the reagent is achieved when CO\(_2\) : CH\(_4\) = 1,15. The effect of temperature on the yield and selectivity of the methane carbonate conversion reaction products was studied under the conditions of carbon dioxide: methane 1.51. Because at a ratio of 1.51, coke formation has the lowest value.
The effect of temperature was examined in the range of 700-900 °C (Figures 1). When the temperature rises above 700 °C, the hydrogen yield increases. Maximum working gas yield is observed at temperature 850 °C. After that, gas emissions will decrease. This can be explained by the thermal dissociation of methane to carbon and hydrogen as the temperature rises. Hydrogen selectivity increases with thermal dissociation of methane to methane and decreases with respect to carbon dioxide due to additional processes. The selectivity of the working gas is close to 100% at 850 °C. When the temperature rises again, the CO selectivity decreases.

Carbon dioxide: The study of the influence of the volume ratios of methane and temperature made it possible to choose the optimal conditions for the methane carbonate conversion reaction.
A number of studies have been conducted to investigate the effect of methane space velocity on the yield of methane carbonate conversion reaction products, the selectivity of their formation and the conversion of reagents. As shown in Figure 2, the optimum volume flow rate of methane is 950-1000 hours\(^{-1}\). Based on the relationship between the conversion of methane and carbon dioxide and the space velocity of methane (Figure 3), it can be said that in all cases the conversion of methane remains unchanged and is 100%. We compared the literature data on the study of kinetic patterns of carbonate conversion of methane with the results of experiments and concluded that they have common patterns. As the partial pressures of methane and carbon dioxide in the feed increase, the yield of synthesis gas increases. Based on this conclusion, it can be assumed that the formation of synthesis gas occurs according to a single mechanism, despite the differences in the composition of the catalysts used.

**Conclusion.**

1) A catalyst with high catalytic activity was created for the reaction of carbonate conversion of methane. In the presence of the selected catalyst, the effect of various factors on the reaction rate, product yield and selectivity was studied.

2) Based on the study of the influence of various factors on the reaction rate, product yield, selectivity, kinetic regularities of the process were determined.

3) Based on the results obtained, a process mechanism was proposed. The reasons for the inactivation of the methane carbonate conversion reaction catalyst and its regeneration were discussed.

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