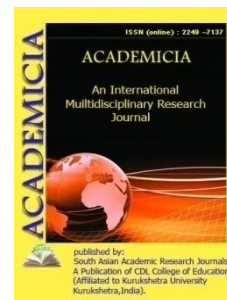




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Multidisciplinary  
Research Journal**  
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**DOI: 10.5958/2249-7137.2021.02137.6**

## **SCIENTIFIC BASIS OF CATALYST REGENERATION OF METHANE OXYCONDENSATION PROCESS**

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### **ABSTRACT**

*In the study, the coking mechanism of the methane oxycondensation reaction catalyst was developed and the optimal conditions for catalyst regeneration were selected. Based on the results obtained, the process of catalyst regeneration of the methane oxycondensation reaction was modelled and the rate constant and activation energy of the coke formation process was evaluated based on experimental data.*

**KEYWORDS:** *Catalyst, Coke, Regeneration, IR Spectrum, Thermogravimetry, The Velocity Constant, Activation Energy, Mathematical Modelling.*

### **INTRODUCTION**

At a time when oil reserves are declining, natural gas is of great interest as an alternative fuel in petrochemical production. The current traditional method of converting natural gas to liquid fuels is multi-stage, going under high temperature and high pressure. At present, the only sensible way to process natural gas is by its oxycondensation reaction. This process is a one-step process that takes place at normal atmospheric pressure [1-6].

The main target products in the catalytic oxycondensation of methane are ethane and ethylene. Currently, 156 million tons of ethylene is produced worldwide, and the growth in demand for ethylene requires 5-6% per year. Ethylene is an important product of petroleum and gas chemistry and is used in the production of polyethene, polyvinyl chloride, polystyrene, alkylbenzenes, ethylene oxide and others [7-10].

The efficiency of any petrochemical heterogeneous-catalytic process is primarily determined by the activity, selectivity and stability of the catalyst. Deterioration of the recorded characteristics

is observed during the use of the catalyst. The main reason for the deterioration of these parameters is the formation of coke on the active surface of the catalyst. As a result of coke loss, the catalytic properties of the catalyst are restored. A common method of restoring the catalytic properties of a catalyst is oxidative regeneration [11-16].

## EXPERIMENTAL PART

The catalyst for the synthesis of C<sub>2</sub>-hydrocarbons was prepared by two methods of precipitation and absorption. High-silicon zeolite, which was thermally and chemically treated with bentonite, was used in our laboratory as a binder [17-20]. Aqueous solutions of manganese acetate and sodium molybdate were used to prepare the catalyst by the precipitation method. The precipitate was filtered, dried at 130 °C, and baked in an oven at 800–1100 °C for 5 h. The required amount of zirconyl nitrate solution was then added to the resulting mass. The catalyst was then filtered, dried, and fired in the above sequence.

In the absorption method, the catalyst was prepared in the following two steps. In the first stage, a solution of manganese acetate was injected into the expanded clay heated to 550-600 °C. The mixture was then fired at 900 °C for 3 h at 150 rpm until a homogeneous mass was obtained. In the second stage, an aqueous solution of sodium acetate, ammonium molybdate, was added. Subsequent drying and firing steps were continued as above.

The amorphous structures of the catalysts were determined by X-ray phase analysis, the porous structure was determined by the analysis of adsorption curves obtained by the method of thermodesorption of nitrogen, the surface area of the samples ( $S_{sol}$ ) was determined by the BET method, the volume of micropores and mesopores was determined by BJH method.

The specific surface area of the catalyst was determined by the adsorption-desorption method of nitrogen at -77 °C Micro metrics Sorptometer Tristar 3000 using the BET method. Examination of the catalyst was performed by scanning electron microscopy (SEM) on an analytical auto emission wave electron microscope (ULTRA 55 Carlziss, Germany).

The spatial composition of the catalytic systems was tested on a Shimadzu XRD 7000 X-ray diffractometer.

The catalytic oxycondensation reaction of methane was carried out in a flow reactor under differential reactor conditions. The gaseous products of the reaction were analyzed chromatographically on the chromatograph "Gazochrome 3101" with a thermochemical detector connected to an additional thermostat under the following conditions: column thermostat temperature-100 °C, carrier gas (air) flow rate -35 ml/min, column length filled with activated carbon - 1m, inner diameter - 3 mm. Quantitative analysis was performed using the absolute grading method [21-23].

The catalytic activity of the catalysts was studied in a flow differential reactor, at normal atmospheric pressure, at 750–850 °C, and under a volume ratio of methane: oxygen = 1.5 ÷ 5: 1 [24-29].

The reactor is a quartz tube with an inside diameter of 8 mm and a length of 650 mm. Methane and pure oxygen with 99.9% purity were used for the reaction. The gases were mixed before entering the reactor. The contact gas coming out of the reactor was cooled in an aqueous refrigerator-separator.

This work aims to construct a mathematical model of oxidative regeneration. The kinetic model is the sum of the quantities that characterize the relationship between the reaction parameters of the rate of chemical change (pressure, temperature, reagent concentration, etc.) and the elementary stages, reactions, equations. This relationship is determined based on experimental data in the field of change of reaction parameters.

Manganese-based oxide catalysts prepared by the absorption method for the oxidative dimerization reaction of methane have high catalytic activity and efficiency, and the best results were obtained in the presence of the  $(\text{Mn}_2\text{O}_3)_x \cdot (\text{Na}_2\text{MoO}_4)_y \cdot (\text{ZrO}_2)_z$  complex. Glide was used as a carrier. Methane conversion in the presence of catalysts obtained by the above methods was 56.8%, selectivity for target products was 62.3%, selectivity for ethylene was 65.8% and  $\text{C}_2$ -hydrocarbon yield was 35.4%.

Regeneration of coking catalysts to restore their activity and selectivity is an important part of the technological process. Oxidative regeneration of coked catalysts is a potent exothermic process. Overheating of the catalyst can lead to a loss of irreversible catalytic activity: rounding of porous structures, crystallization and recrystallization, as well as leakage of active components. In this case, the maximum temperature of the catalyst is determined depending on its composition and structure. Coke formation follows the following scheme:

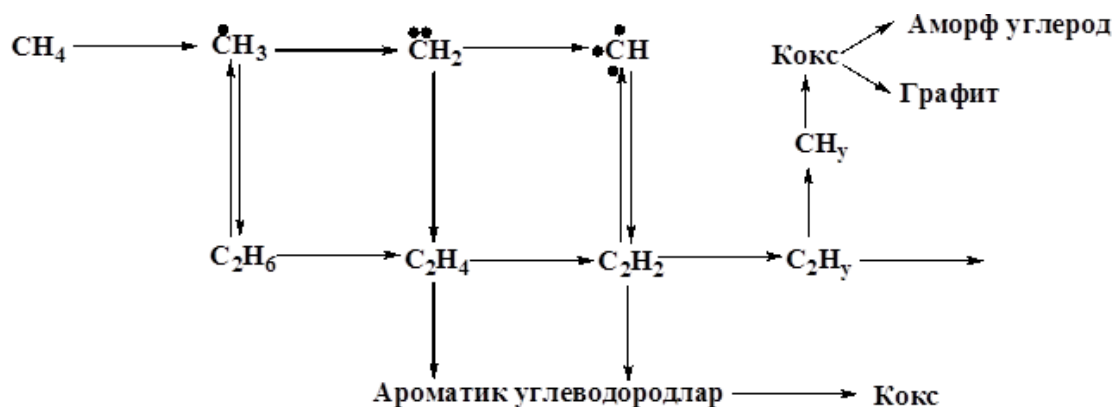


Figure 1. Scheme of coke formation during methane oxycondensation

## RESULTS AND DISCUSSION

It is known that in the oxycondensation reaction of methane, the activity and productivity of the catalyst are reduced due to the formation of coke precipitate containing  $\text{CH}_x$  ( $1 \geq x \geq 0$ ). Oxidative regeneration was used to restore the activity of the catalyst. To determine the structure of the resulting coke (graphitized or amorphous), the experimental results were found to have an error  $\pm 3\%$  when compared with the results obtained by the derivatographic analysis method (Fig. 2). The size of the catalyst pores and the specific surface area determine the susceptibility to coking, so the method of physical adsorption of nitrogen was used to determine the surface area of the catalyst, the size and volume of the pores.

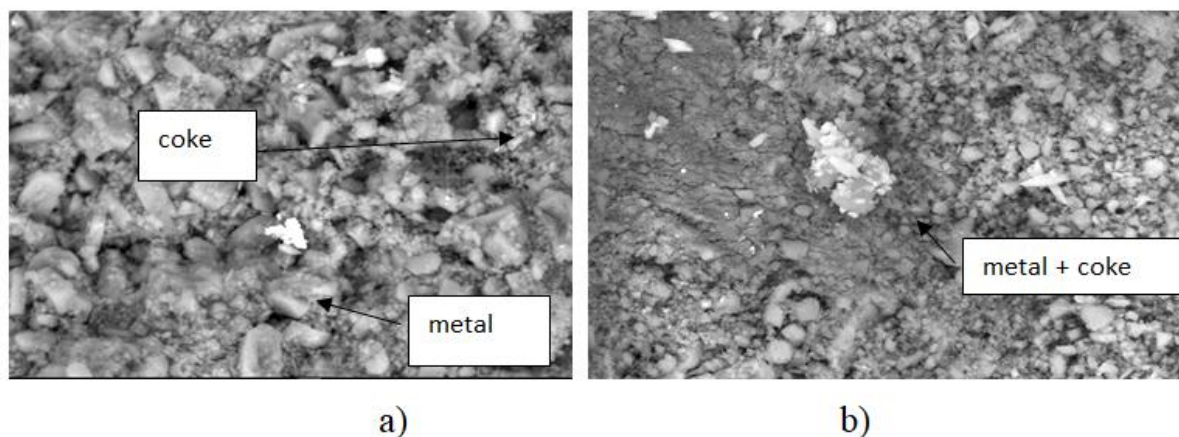
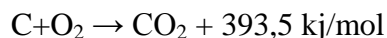


Figure 2. Coke catalyst micrograph (5000 magnification)

The larger the specific surface area of the catalyst, the higher its activity. The formation of coke on the active surface of the catalyst leads to a deterioration of the performance of the regime of catalytic processes. The laws of regeneration of the coking of catalyst particles were realized using a diffusion mathematical model. The amount of coke in the catalysts was determined by the difference between the masses before and after heating in the open air. To do this, the catalyst was heated in air at 110 °C and the mass was measured, then fired in an oven at 800 °C. After 1 h, its mass was measured again and the amount of coke was determined. Catalyst inactivation is reversible (coke sediment is formed) and irreversible (spatial change of the active component, sticking of the active centres of the catalyst under the influence of heat, decomposition, poisoning, etc.). In reactivation, the initial activity of the catalyst can be partially or completely restored. The following reactions can take place between coke and oxygen:



The approximate composition of the coke sediment corresponds to the  $\text{CH}_x$  formula as noted above. In this case, the combustion of coke  $x=0\div 1$  is characterized by the following total reaction:



The coked catalyst sample was placed in a reactor and washed with an inert gas-argon (volumetric velocity of argon 500 h<sup>-1</sup>) at 650 °C for 20 min. After that, gradually increasing the volume fraction of oxygen, the catalyst was chemically treated at 650 °C in a mixture of inert gas and oxygen. For 2.5 hours, the oxygen concentration in the regeneration mixture was increased to 25%. In this case, the chemical treatment was continued for 1.5 hours. The temperature was then raised to 750 °C for 3 h and chemically treated under an airflow rate of 500 h<sup>-1</sup>. At the end of the catalyst regeneration cycle, the catalyst was washed at 750 °C in an argon atmosphere with a volumetric velocity of 500 h<sup>-1</sup> and cooled in an argon stream. The temperature range of oxidation treatment of catalysts was 200-1200 °C, the heating rate in the air was 10 °C / min. The

amount of coke released was studied in the range of 50–850 °C using a combination of thermogravimetry and differential thermal analysis methods. The absolute error in temperature measurement was  $\pm 5$  °C and in mass measurement  $\pm 0.5\%$ .

For IR spectroscopic examination, 10 g of coked catalyst was taken and 25 ml of chloroform was added. After 2 h, the resulting extract was placed on a plate and placed on an IK-Fure spectrophotometer after the chloroform had evaporated. Spectra were then recorded for 1 h at room temperature in the  $600 \div 4,000$   $\text{cm}^{-1}$  wavelength range. For quantitative analysis of inactivating components, their extract was prepared on a Soxhlet instrument: catalyst mass - 10 g, extragenic (acetone) volume - 40 ml, extraction time - 1 hour.

The number of extract components was analyzed by the gas-liquid chromatographic method: flame-ionization detector, carrier-gas (hydrogen) flow rate-1 ml/min; the Heating rate in the temperature range  $40 \div 200$  °C  $10$  °C/min; capillary column length 50 m, column diameter 0.32 mm, stationary phase-polyethene glycol (thickness  $1.2$   $\mu\text{m}$ ). Determining the microstructure of the catalysts was carried out on a JEM-2010 instrument using irradiated electron microscopy. Coke formation was assessed according to DTA-TG data.

For laboratory regeneration of the methane oxycondensation reaction catalyst under laboratory conditions, experimental studies were carried out in a flow isothermal reactor by adding  $0.3 \div 1.0$  g of catalyst to a reactor with a diameter of 3 mm. The  $(\text{Na}_2\text{MoO}_4)_x \cdot (\text{Mn}_2\text{O}_3)_y \cdot (\text{ZrO}_2)_z$  catalyst was used in the experiments. As a result of the study, it was found that the specific surface area of the catalyst according to the BET method is  $\sim 65\text{m}^2/\text{g}$ . Experimental experiments on catalyst regeneration were carried out at  $450\text{-}500$  °C under conditions of air consumption  $10 \div 30\text{ml}$  / min. The catalyst was heated in a nitrogen stream to the required temperature, then an airstream was connected. The catalyst ( $0.3 \div 0.5$  mm fractions) was mixed with quartz to increase surface heat absorption. Changes in the concentration of oxygen leaving the  $(\text{Na}_2\text{MoO}_4)_x \cdot (\text{Mn}_2\text{O}_3)_y \cdot (\text{ZrO}_2)_z$  catalyst regeneration reactor were detected by gas chromatography. Figure 3 shows the results of the change in the oxygen concentration leaving the  $(\text{Na}_2\text{MoO}_4)_x \cdot (\text{Mn}_2\text{O}_3)_y \cdot (\text{ZrO}_2)_z$  catalyst regeneration reactor over time at different temperatures.

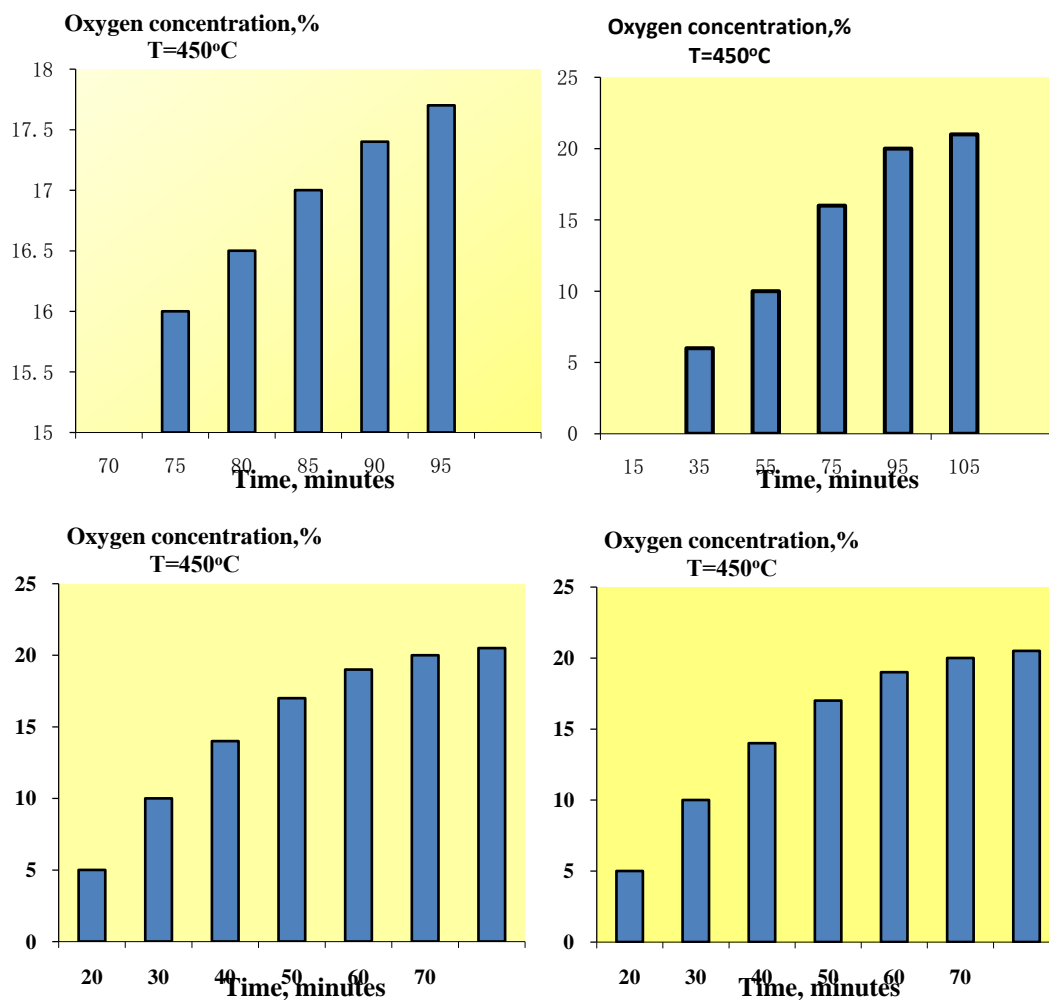


Figure 3. Graph of the change in the concentration of oxygen leaving the reactor over time at different temperatures

Using the formula  $-\frac{1}{y} \ln\left(\frac{y_0}{y_1}\right) = k \cdot t + A$ , it was studied that the experimental data of the oxygen concentration at the exit of the catalyst regeneration reactor containing  $(\text{Na}_2\text{MoO}_4)_x \cdot (\text{Mn}_2\text{O}_3)_y \cdot (\text{ZrO}_2)_z$  depend on the regeneration time. The results obtained are shown in Figure 4 below.

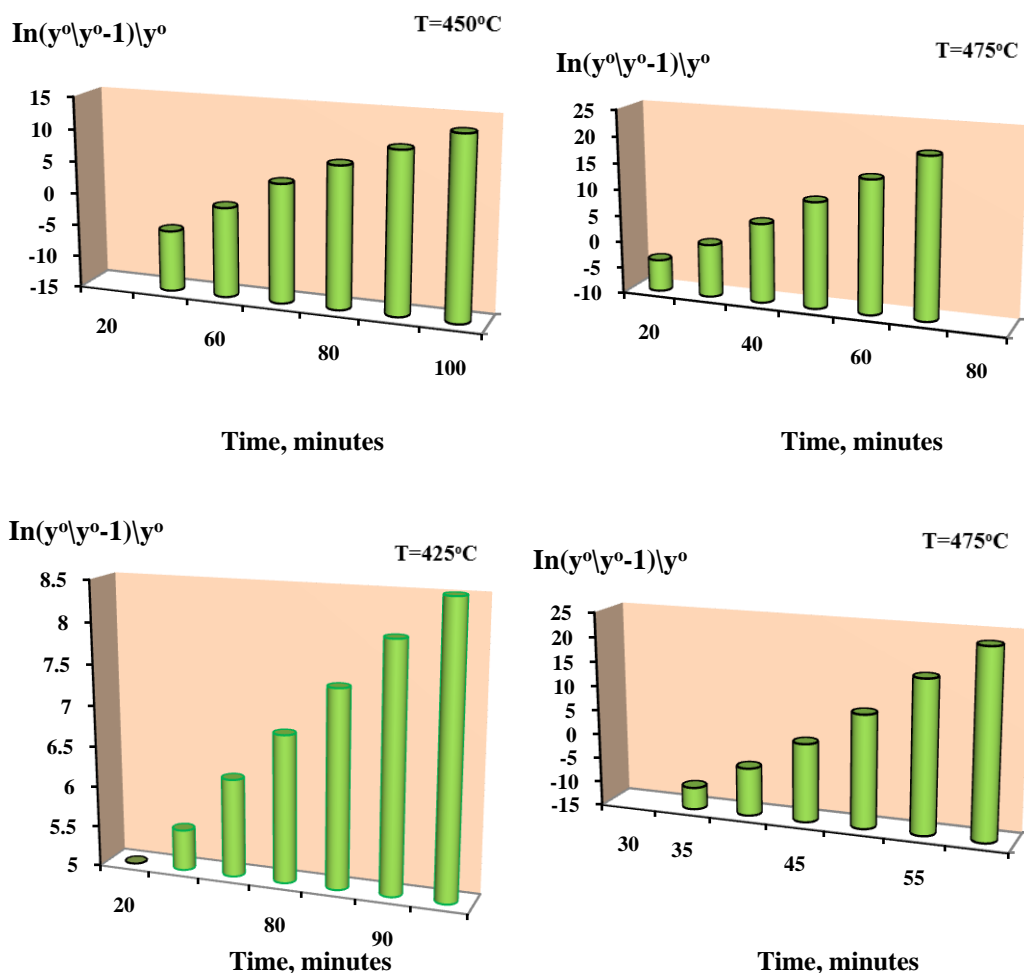


Figure 4. The dependence of the oxygen concentration leaving the reactor on the regeneration time

To determine the value of the reaction rate constant at different temperatures, the relationship between the concentration of carbon dioxide at the exit of the reactor and the regeneration time was linearly formed by the coordinates of the equation  $-\frac{1}{y} \ln \left( \frac{y_0}{y_1} \right) = k \cdot t + A$ . The results are shown in the figure below (Figure 5).

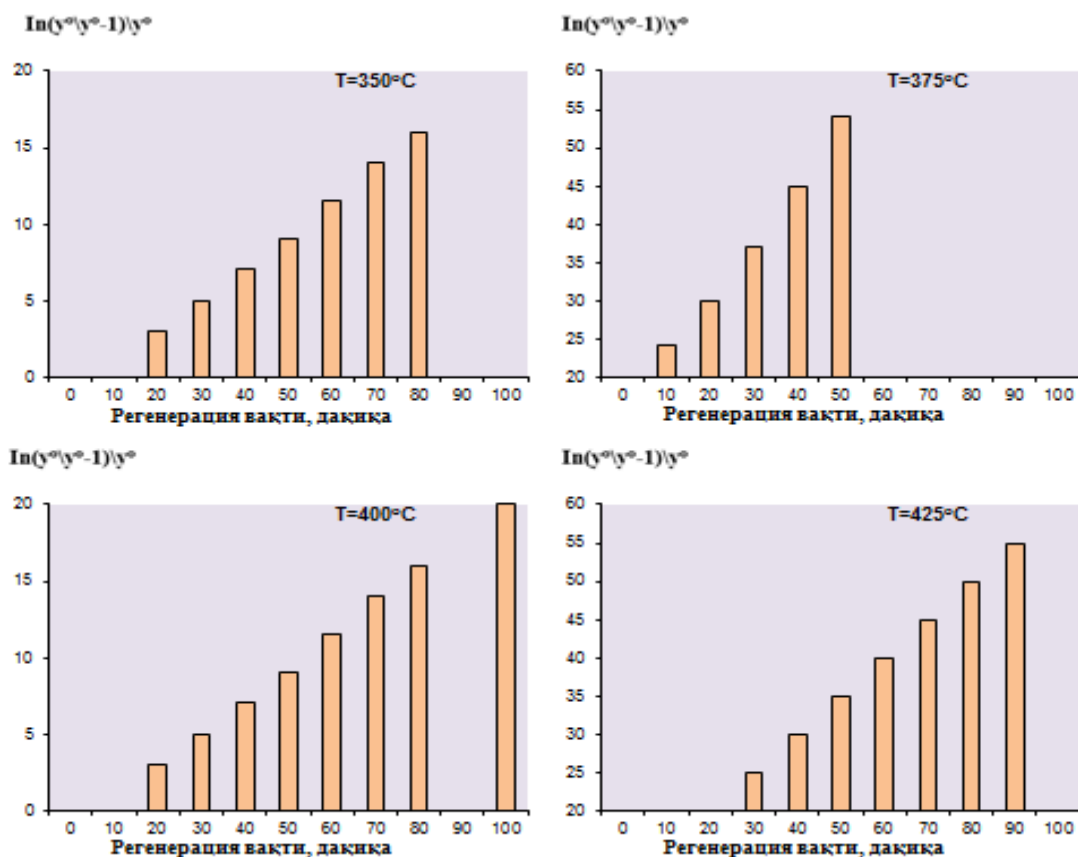


Figure 5. the relationship between the concentration of carbon dioxide at the exit of the reactor and the regeneration time

Based on the calculation of the rate constants of the oxidation reaction of coke in a catalyst containing  $(\text{Na}_2\text{MoO}_4)_x \cdot (\text{Mn}_2\text{O}_3)_y \cdot (\text{ZrO}_2)_z$  at different temperatures, the activation energy of the complete oxidation reaction of coke was determined. For this, a correlation graph between  $2 + \ln(k)$  and  $1000/T$  was constructed and the activation energy was determined based on the value of the slope angle tangent. Based on the results obtained, it was proved that the activation energy of the coke combustion reaction is  $75.8 \pm 5 \text{ kJ/mol}$ .

Figure 6 below shows a micro photo of a coking catalyst containing  $(\text{Na}_2\text{MoO}_4)_x \cdot (\text{Mn}_2\text{O}_3)_y \cdot (\text{ZrO}_2)_z$  after use at different time values at  $800^\circ\text{C}$ . As can be seen from the figure, the volume of graphite aggregates accumulated in the catalyst sludge and their volume increase significantly with increasing operating time.



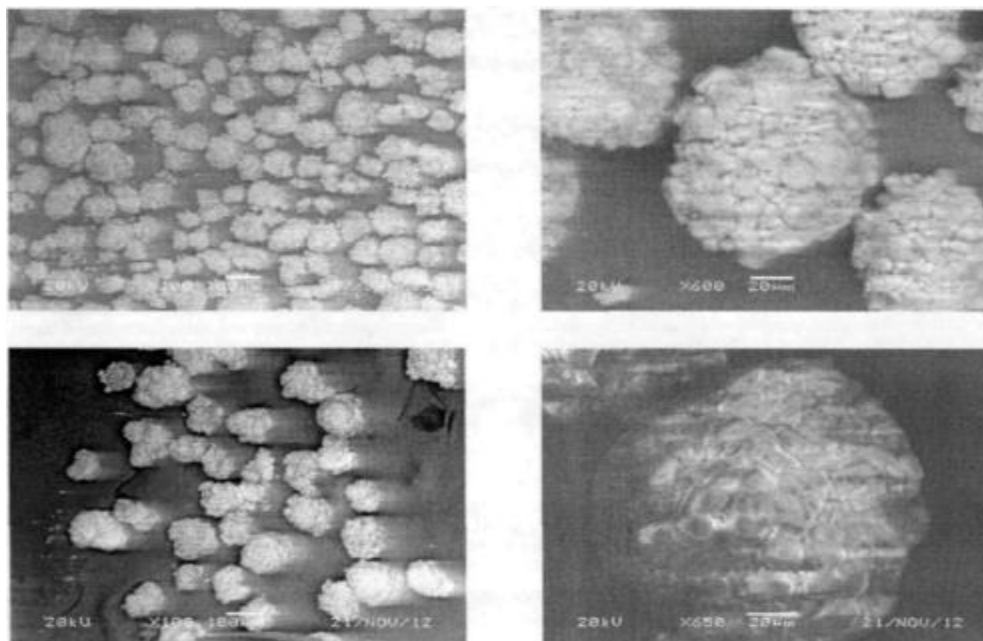


Figure 6. Micro photo image of catalyst surface after 240 hours (A), 480 hours (V), 720 hours (S), 960 hours (D) at 80 °C

The concentration of oxygen at the outlet of the reactor was determined chromatographically. The relationship between the oxygen concentration at the outlet of the reactor and the regeneration time was calculated according to the following formula:

$$-\frac{1}{y_0} \ln \left( \frac{y_0}{y_1} - 1 \right) = k \cdot t + A$$

To fully evaluate the rate and energy of the coke formation process, the reaction rate and activation energy were determined.

The velocity constant and activation energy were calculated based on the experimental data given in the following table:

**TABLE 1. VELOCITY CONSTANT AND ACTIVATION ENERGY**

Temperature, K	$\tau$ , sec	$m_0$ , r	$m$ , r
973	900	1,0128	0,9138
1073	900	1,0390	0,8595

The process of coke formation is a 1-order reaction. The rate equation for a first-order reaction is:

$$\frac{dx}{d\tau} = k(a - x)$$

The calculation of the velocity constant is performed according to the following equation:

$$k = \frac{2,303}{\tau} \lg \frac{m_0}{m}$$

The activation energy was calculated according to the following equation:

$$\lg \frac{k_2}{k_1} = \frac{E_a}{2,303R} \left( \frac{T_2 - T_1}{T_2 * T_1} \right)$$

Speed constant:

$$T_2 = 1073$$

$$k_2 = \frac{2,303}{900} \lg \frac{1,039}{0,8595} = 2,11 \cdot 10^{-4} c^{-1}$$

$$T = 873K$$

$$k_2 = \frac{2,303}{900} \lg \frac{1,0128}{0,9138} = 1,14 \cdot 10^{-4} c^{-1}$$

Activation energy:

$$\lg \frac{2,11 \cdot 10^{-4}}{1,14 \cdot 10^{-4}} = \frac{E_a}{2,303 \cdot 8,314} \cdot \frac{200}{936729}$$

$$\lg 1,851 = \frac{E_a}{2,303 \cdot 8,314} \cdot \frac{200}{936729}$$

$$0,267 = \frac{E_a}{2,303 \cdot 8,314} \cdot \frac{200}{936729}$$

$$E_a = \frac{0,267 \cdot 19,15 \cdot 936729}{200} = 23,95 \text{ кЖ/моль}$$

## CONCLUSION

1. The coking mechanism of the methane oxycondensation reaction catalyst has been developed.
2. Optimal conditions for methane oxycondensation reaction catalyst regeneration were selected.
3. The process of regeneration of the methane oxycondensation reaction catalyst was modeled.
4. The rate constant and activation energy of the coke formation process were calculated on the basis of experimental data.

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