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Kinetic of Oil Sludge Thermolysis Process in Presence of Nickel, Cobalt and Iron-Supported Microsilicate

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The article is devoted to the experimental determination of thermokinetic parameters of oil sludge thermal degradation using the model-free Ozawa-Flynn-Wall method in the presence of a nanocatalyst (nickel, cobalt and iron-supported microsilicate) by calculating Arrhenius kinetic parameters (activation energy and pre-exponential factor). The phase composition of the reflex microsilicate was established – 4.12; 2.51 Å – SiO_2, nickel-supported microsilicate reflexes: 2.09; 1.48 Å – NiO, reflexes: 4.25 Å – SiO_2 and acid numbers of microsilicate – 64 μmol/g of prepared nanocatalysts. Using the method of Brunauer, Emmett and Teller, the specific surface area of the microsilicate was established – 18.3 ± 0.3 m^2/g, the microsilicate with nickel applied – 20.9 ± 0.2 m^2/g and the adsorption isotherm of the prepared nanocatalysts (microsilicate with nickel, cobalt and iron). Thermokinetic parameters of thermal decomposition of oil sludge without a catalyst and with a catalyst at an increment of 0.9 are 99.0 and 93.3 kJ/mol nickel-supported microsilicate, 51.9 kJ/mol cobalt-supported microsilicate, 111.3 kJ/mol iron-supported microsilicate and non-metal-supported microsilicate 173.7 kJ/mol, respectively. The study of the kinetic parameters of pyrolysis of oil sludge using various catalysts makes it possible to assess their influence on the process of decomposition of organic components. The results of the experiments showed that the use of catalysts significantly affects the destruction of oil sludge. Dynamic thermal analysis at different heating rates studied the dynamics of oil sludge decomposition. The study of the effect of catalysts on the kinetic parameters of oil sludge pyrolysis is an important step in the development of new methods for the disposal of petroleum products and the reduction of their negative impact on the environment. The obtained experimental data on thermal degradation kinetics of oil sludge will find application in designing a reactor for the process of destructive hydrogenation of heavy hydrocarbon raw materials.

Keywords: thermokinetic parameters, thermogravimetry, kinetics, nanocatalyst, microsilicate, oil sludge, iron, nickel, cobalt.

INTRODUCTION

Currently, the urgent task is the problems of rational use of natural resources, a huge amount of which is lost in the form of industrial waste, for example, oil sludge generated during transportation through pipes containing valuable components – hydrocarbons[1, 2].

Every year, the global oil industry produces more than one billion tons of oil sludge[3]. This poses a serious threat to the environment and human health, since oil sludge is a complex mixture of organic and inorganic residues containing in their composition, disease-causing bacteria, parasites, heavy metals, as well as inert solids

The choice of the method of processing and neutralizing oil waste mainly depends on the amount and nature of oil products contained in them. Processing to produce gaseous and liquid fuels by thermal processing is more economically advantageous. In addition, the rational use of oil waste could be a significant step in creating resource-saving technology based on the integrated use of oil raw materials[4–8]. Work[9] shows that there is a high rate of energy consumption of heavy oil residues (vacuum residues, oil sludge and others). In recent years, the world community has developed various methods for processing oil sludge[8]. However, mathematical planning methods have not been developed involving many interconnected physicochemical processes, such as the chemical decomposition of oil sludge to form volatile substances, and the effect of a heterogeneous catalyst on the thermal destruction of the organic mass of oil sludge.

The relationship between catalyst synthesis and thermal analysis kinetics is to understand and control the properties and behavior of catalytic materials.

Catalysts play a fundamental role in many chemical processes and industries, including energy production, pharmaceuticals, and environmental protection. The performance and efficiency of the catalysts are closely related to their physical and chemical properties such as composition, crystal structure, surface area and pore size distribution.

Catalyst synthesis involves various preparation methods to adapt these properties to specific applications. However, the synthesis process itself can affect the structure and properties of the catalyst, which in turn can affect its performance.

Thermal analysis methods such as differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) provide valuable information on the thermal behavior of catalytic materials. This includes their temperature stability, thermal degradation, phase transitions, and reactions with various gases or analytes.

In addition, the relationship between catalyst synthesis and thermal analysis kinetics may also help in the development of new catalytic materials. By studying the thermal behavior of different precursor mixtures, researchers can identify suitable synthesis pathways and optimize reaction conditions to achieve specific catalyst properties.

Thus, establishing a link between catalyst synthesis and the kinetics of thermal analysis is critical to gain a comprehensive understanding of catalytic materials. This knowledge paves the way for the design and development of more efficient, stable and selective catalysts for various applications.

The development of a mathematical model of complex physicochemical processes, such as the chemical decomposition of oil sludge and the influence of heterogeneous catalysts on the thermal destruction of an organic mass, can have a number of significant advantages.

Firstly, it will help in the development and optimization of industrial processes related to the processing and disposal of oil sludge, which will lead to increased efficiency, lower costs and more sustainable methods.

Secondly, the mathematical model can predict the results of various scenarios and help in decision-making processes. This can be especially valuable in situations where empirical data are limited or unavailable and predictions need to be made based on theoretical calculations.

Thus, the development of a mathematical model of complex physicochemical processes can improve understanding, increase efficiency, assist in decision-making and lead to new discoveries and decisions. For numerical modeling, it is necessary to have values of thermokinetic parameters of oil sludge thermal degradation. Kinetic studies of oil sludge in the presence of catalysts containing active nanoparticles of nickel, cobalt and iron metals are slightly presented in the literature[10]: the particle size of the starting microsilicate (sample 5) is from 73.96 to 123.27 nm. On the surface of the supported catalysts, NiO particles (sample 2) of 85.70, 94.84 and CoO particles (sample 3) of 140.5, 159.4 and 211.7 nm and 106.32 nm, FeO particles (sample 4) of 157.2, 160.8 and 178.4 nm.

Studies to determine the thermokinetic parameters of thermal destruction of oil sludge in the presence of a nanocatalyst have several advantages. Some of these include:

1. Improved understanding of oil sludge degradation: The study provides valuable information on the thermal decomposition of oil sludge in the presence of a nanocatalyst. This knowledge can be used to develop better strategies for managing and disposing of this type of waste.
2. Environmental friendliness: The use of nanocatalysts in the process of thermal decomposition can increase the environmental friendliness of the process. With a sustainable approach to waste management, environmental harm is reduced, and soil and water resources of the environment are less polluted.
3. Cost-effectiveness: The use of nanocatalysts can make the process of decomposition of oil sludge more economical. With nanocatalysts, it may be possible to complete the process more efficiently, thereby saving time and reducing the total cost of the procedure.
4. The scalability of the results of this study can be used in the development of large-scale industrial processes for the decomposition of oil sludge, making this process scalable.

Overall, the study highlights the potential of nanocatalysts in oil sludge degradation and the significant advantages they can provide over traditional methods. This could pave the way for developing more sustainable strategies, thereby reducing the environmental impact of oil drilling and contributing to a more sustainable future.

The organic mass of oil sludge contains various aromatic and heterocyclic compounds[10]. Due to the complex composition of oil sludge, it is difficult to select an effective and selective catalyst for processing oil sludge[10]. Thermal gravimetry of oil sludge degradation process allows to selection of an effective catalyst or catalyst additive. When studying the kinetics of pyrolysis of organic substances, the thermogravimetric analysis method (TGA) is widely used[11, 12]. Various methods for determining the kinetic parameters of non-isothermal pyrolysis are known in the literature[13–15], which can be divided into model-fitting and model-free or isoconversion. One of them is a model-free method of calculating Ozawa-Flynn-Wall kinetic parameters[16, 17] which requires the construction of kinetic curves at different heating rates.

The purpose of the work is the experimental determination of kinetic parameters of oil sludge thermal degradation in the presence of elements of the VIII group of the periodic system by thermal analysis, determination of specific surface area, acid number and adsorption isotherm of three prepared nanocatalysts.

MATERIALS AND METHODS

Oil sludge obtained in the process of oil transportation through the pipeline and the Kazstransoil enterprise of the West Kazakhstan oils of the Republic of Kazakhstan were used as study objects. The physical and chemical characteristics of oil sludge and the elemental composition of oil sludge are presented in[14].

The product of the Karaganda silicon plant Tau-Ken. temir LLP (microsilicate) was used as a carrier and catalyst for the conversion of oil sludge.

The starting microsilicate was pre-ground, and then samples with a particle size of 0.1 mm were taken by sieve analysis.

The initial microsilicate was leached using a 20% hydrochloric acid solution to remove alkali and alkaline-earth metals. Table 1 shows the chemical composition of the starting microsilicate and after leaching. The qualitative, individual and quantitative chemical composition of the starting microsilicate and the leached starting microsilicate was determined by X-ray spectral analysis.

The data presented in Table 1 showed that acid treatment of the microsilicate did not result in significant changes in the chemical composition of the starting microsilicate.

EXPERIMENTAL

For the preparation of nanocatalysts, we used the method of impregnating the catalyst support with the active substance followed by calcination. The impregna-

Table 1. Composition of starting microsilicate after leaching

	Content of components, %									
Chemical composition	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	MnO	P_2O_5	K_2O	Na_2O
Microsilicate	95.5	0.02	<0.95	<1.0	0.5	0.4	0.04	0.06	<0.1	0.3
Leached Starting Microsilicate	97.439	0.023	<0.95	<1.0	0.414	0.304	0.033	0.057	<0.1	0.276

tion was carried out by immersing the support (leached microsilicate) in a 1% salt solution: $Ni(NO_3)_2 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 6H_2O$. The impregnated support (microsilicate) was heated for 120 minutes with solutions of nickel nitrate, cobalt nitrate and iron nitrate of microsilicate (20 g) at 80–90°C temperature, then the obtained samples were dried at 105°C temperature for 120 minutes. Then, the catalyst samples were calcined in a muffle furnace at 650°C temperature for 120 minutes. To study the effect on thermal decomposition of oil sludge, 5 samples were prepared: Sample 1 – oil sludge without catalyst addition, Sample 2 – oil sludge mixture supported on 1% nickel microsilicate (0.1 mm microsilicate), Sample 3 – oil sludge mixture with 1% cobalt applied to the microsilicate (0.1 mm microsilicate), Sample 4 – mixture of oil sludge with 1% applied to the microsilicate, iron (0.1 mm microsilicate), Sample 5 – mixture of oil sludge with microsilicate without metal application (0.1 mm microsilicate).

Previously, we have carried out work[15] with nanocatalysts obtained by wet impregnation, the particle size of the initial microsilicate – 232 nm and prepared samples of catalysts (sample 2 particle size of nickel – 324.2 nm, sample 3 particle size of cobalt – 139.4 nm, sample 4 particle size of iron – 196.3 nm), the particle sizes of metals were determined using a laser particle size detector Nano-S90. According to the hierarchy of catalyst systems in a heterogeneous catalyst, catalysts having a size of 10 to 1000 nm can be classified as nanocatalysts[18].

The conditions for conducting thermogravimetric study of oil sludge thermal degradation kinetics in the presence of a catalyst are presented in[10]. Thermogravimetric testing was performed using a Labsys Evo TG-DTA/DSC 1600 derivatograph (Setaram, France) in corundum crucibles in the temperature range of 30 to 600°C in the nitrogen stream (the flow rate of the protective and purge gases was 30 ml/min^{-1}, respectively).When calculating the kinetic parameters (speed, activation energy and pre-exponential factor) of the thermal degradation of the oil sludge mixture in the presence of a catalyst, the Ozawa-Flynn-Wall (OFW) model-free method was used[15, 16]. Kinetic characteristics were determined based on TG data at three different heating rates of 10, 20 and 30 deg min^{-1}. Measurement results were processed using the OriginLab software package and the Python Anaconda3 distribution kit.

The method of determining the activation energy is based on the dependence of the velocity constant on the inverse temperature, which is calculated from the Arrhenius equation[10].

The adsorption isotherm, specific surface area, and micropore volume of the prepared catalyst samples were determined using the Brunauer – Emmett – Teller (BET) method. The Brunauer, Emmett, Teller (BET) method is one of the most adequate methods for determining the specific surface area for adsorbents having a certain kind of adsorption isotherm. Adsorption surveys of the prepared catalyst samples were performed on SoftSorbi-II ver.1.0. Figure 1 shows the adsorption isotherm of the starting microsilicate and Table 2 shows the specific surface area of the starting microsilicate and the nickel-supported microsilicate determined by the BET method.

Table 2 shows the specific surface area of the starting microsilicate and nickel-supported microsilicate as determined by the BET method.

Based on the conducted experimental research, the following optimal conditions were established:

a) Yield of the middle fraction of oil sludge: amount of added nanocatalyst 1 – 1.2–1.5%; initial hydrogen pressure 2.5–3 MPa; temperature 400–410°C; process duration 50–60 minutes.

b) Change in the kinematic viscosity of the middle fraction obtained from oil sludge: amount of added nanocatalyst 1 – 0.5%; initial hydrogen pressure 4.5 MPa; temperature 370°C; process duration 45 minutes; amount of added catalyst 2 – 2.0%.

During hydrogenation of oil sludge, the maximum total yield of light fractions of 62.1% and a decrease

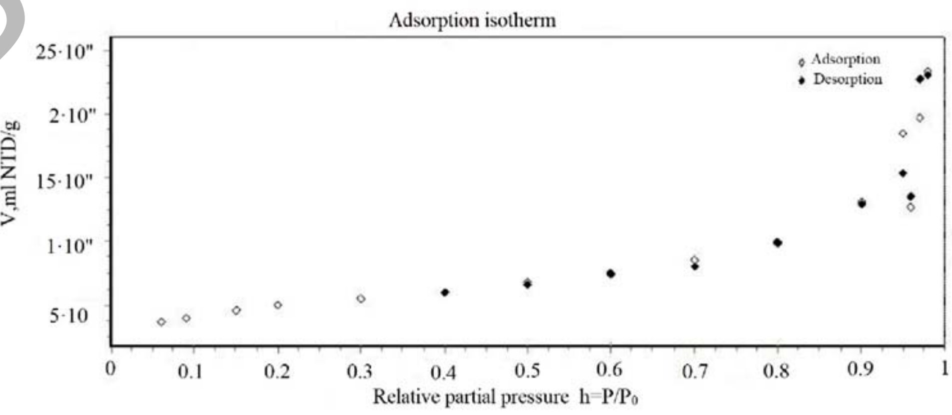

Figure 1. Adsorption isotherm (along the ordinate axis, we place the absolute adsorption value related to the adsorbent mass unit: ml of NTD/g (NTD – normal temperature and pressure: 00S, 760 mm. Hg. art., and along the abscissa axis we deposit the pressure of the adsorbate gas in relative units (absolute pressure referred to the pressure of saturated vapors, for nitrogen P0 = 760 mm Hg)

Table 2. Surface area of the starting microsilicate and nickel-supported microsilicate

Name	Sample 5 (starting microsilicate)	Sample 2 (nickel-supported microsilicate)
Specific surface area	18.3 ± 0.3 m^2/g	20.9 ± 0.2 m^2/g
Specific volume of monolayer	4.20 ml HTD/g	4.79 ml HTD/g
BET constant	68	85
Slope **k** of straight line f=k*h+b	$2.3\cdot10^{-1} \pm 3.3\cdot10^{-3}$ g/ml HTD	$2.1\cdot10^{-1} \pm 2.4\cdot10^{-3}$ g/mlHTD
Cut-off segment **b** straight f=k*h+b	$3.5\cdot10^{-3} \pm 4.6\cdot10^{-4}$ g/ml HTD	$2.4\cdot10^{-3} \pm 3.2\cdot10^{-3}$ g/ml HTD
Correlation coefficient	0.9997	0.9998
Attention! Total Sample Surface goes beyond the measuring limits of the instrument	(1.755 m^2) (from 4 to 12 m^2)	(1.963 m^2) (from 4 to 12 m^2)

in the kinematic viscosity value from 2.2 to 1.2 mm^2/s were achieved.

This is explained by changing the content of aromatic hydrocarbons in the initial fraction to 350°C – 14.08% (individual chemical composition is presented: toluene – 3.07% and others), paraffinic hydrocarbons – 57.6 (individual chemical composition is presented: heptane – 3.02, 1-nonadecene – 1.52%, decane –7.59, dodecane – 4.51, heptadecane – 3.19, hexadecane – 2.37, nonane – 5.96, octadecane – 6.87 and others), unsaturated hydrocarbons –15.7% (individual chemical composition is presented: 1-decene – 1.09, 1-hexadecene -1.1and others), naphthenic hydrocarbons – 35.97% (individual chemical composition is presented: 1.3-dimethylcyclohexane – 2.57%, 1-ethyl-3-methylcyclohexane – 1.25%, cyclododecane – 0.56%, cyclohexane, (1-methylpropyl) – 4.89% and others), polyaromatic hydrocarbons – 9.56% (individual chemical composition is presented: naphthalene, 1,4,6-trimethyl-1.33, naphthalene, 2,7-dimethyl – 2.59%, naphthalene, decahydro-2-methyl – 1.8% and others).

The group and individual chemical composition of the hydrogenate of the fraction with the end of boiling 350°C obtained during catalytic hydrogenation from oil sludge is characterized by the following composition: aromatic hydrocarbons – 12.94% (individual chemical composition is represented by: toluene – 1.97%, benzene, 1-ethyl-3-methyl – 1.68% and others); paraffinic hydrocarbons – 80.72% (individual chemical composition is represented by: 1-heptadecene – 0.36%, 2-Bromo dodecane – 0.22%, Decane – 9.89%, Dodecane – 11.47%, Heptadecane – 5.27%, Heptane – 2.65%, Hexadecane – 5.36% and others); unsaturated hydrocarbons – 9.31% (individual chemical composition is represented by: 1-Decene, 5-methyl- – 0.19%, 1-Tridecene – 0.65%, 2,4-Hexadiene – 2.33%, 2-Heptene – 0.14%, 2-Tetradecene – 0.66%, 3-Dodecene – 1.16% and others); naphthenic hydrocarbons – 34.48% (individual chemical composition is presented: Cyclodecane – 0.4%, Cyclodecane – 1.18%, 0.33 Cyclododecane, ethyl- – 0.8%, Cyclohexane, (1-methylpropyl)- – 0.12%, Cyclohexane, (2-methylpropyl)- – 1.36%, Cyclohexane, 1,1,2,3-tetramethyl- – 0.34%, Cyclohexane, 1,2,3-trimethyl- – 2.18% and others); polyaromatic hydrocarbons – 4.27% (individual chemical composition is represented by: Naphthalene, 1,2,3,4-tetrahydro-6- – 0.25%, Naphthalene, 1,4-dimethyl- – 0.26%, Naphthalene, 2,3,6-trimethyl- – 0.39%, Naphthalene, 2,7-dimethyl- – 0.84%, Naphthalene, decahydro-2-methyl- – 2.58% and others); iso-Alkanes – 41.19% (individual chemical composition is presented: Octane, 2,6-dimethyl- – 0.23%, Nonane, 4-methyl- – 0.22%, Nonane, 2,6-dimethyl- – 0.57%, Decane, 5-methyl- – 0.33%, Decane, 4-methyl- – 0.18%, Decane, 2-methyl- – 0.41%, Heptane, 3-ethyl-2-methyl- – 0.58%, Undecane, 2-methyl- – 1.78%, Undecane, 2,6-dimethyl- – 1.87%, Tridecane, 2-methyl- – 1.23% and others).

The obtained fraction composition of the fraction hydrogenate up to 350°C shows that the use of the nanocatalyst 1 in small amounts of 1.2–1.5% makes it possible to increase the yield of the fraction to 350°C and components of the diesel fraction.

From the data obtained in Figure 1 and Table 2, it can be seen that the adsorption isotherm according to work**[19]** on non-porous adsorbents is described by the III type of concave shape isotherm. The specific surface area of the starting microsilicate is 18.3 m2/g and the nickel-supported microsilicate is 20.9 m2/g, respectively.

The acidic properties of the microsilicate samples and prepared catalyst samples were examined by thermal programmed desorption (TPD) using ammonia molecules as a probe. The TPD method allows recording the energy spectrum of the catalyst by adsorption of probe substances and quantifying the concentrations of active centers in various forms of desorption. The choice of ammonia is due to its high basicity, which makes it possible to determine not only strong acid centers but also weak centers, as well as the small size of the molecule and ease of dosage. The chromatographic version of programmed thermal desorption consists in the fact that a sample of the catalyst with pre-adsorbed on its molecules of the probe substance is heated at a certain constant rate in the current of the carrier gas. During desorption, the substance in the gas phase passes through the cell of the katharometer, the obtained signal is recorded on the diagram sheet of the potentiometer. A sample (0.5 g) was weighed into a quartz reactor and calcined in a carrier gas current (He) for 1 hour at a temperature of 600°C. Carrier gas velocity – 0.7 mL/s. The degree of preparation of the sample for experience was monitored by the location of the potentiometer pen, which should reach the "zero" line. After "training," the reactor was cooled to 100°C, and ammonia adsorption was carried out until the sample was fully saturated. Then, to remove the weakly bound ammonia (physical adsorption), the sample was purged with helium at this temperature until the potentiometer pen returned to the zero line. The reactor with the test sample was cooled to room temperature (20–21°C) and included programmed heating of the furnace at a rate of 10 deg/min to 600°C, a rate of helium of 0.7 ml/s. The concentration of acid sites in the test samples was determined by the amount of ammonia desorbed at the time of fixing the desorption peaks and expressed in micromoles per 1 gram of catalyst. The accuracy of determination of the amount of desorbed ammonia by gas chromatography method is ±5%. Table 1 shows the acid characteristic of the microsilicate. Prepared catalyst samples containing microsilicate with supported metals (nickel, cobalt, and iron) showed zero concentration of acidity, and microsilicate at a maximum temperature of 140 ° C showed a concentration of acid centers of 64 μmol

The appearance of zero acidity and acid centers in the impregnated sample can be explained by the deposition of metals (nickel, cobalt and iron) on the microsilicate substrate. These metals could block or adsorb acidic regions, thereby significantly reducing the acidity concentration.

This characteristic could have a significant impact on the catalytic pyrolysis of oil sludge. Acid centers play a critical role in the cracking and conversion of heavy oil fractions during pyrolysis. The absence of acid centers can prevent the cracking of long-chain hydrocarbons to form lighter and more valuable products, resulting in a low liquid oil and gas yield. Moreover, it can also lead to the formation of undesirable by-products such as coke and charred coal, which can lead to the deactivation of the catalyst and contamination of the reactor surfaces.

Therefore, it is critical to optimize the deposition of metals on the microsilicate support to achieve a balance between acidity and metal content, which can increase the catalyst efficiency in pyrolysis of oil sludge.

X-ray phase analysis of the original microsilicate and the prepared samples was taken on a Drone-4-07 X-ray diffractometer. Under the following conditions: tube with cobalt anode, shooting mode: – scanning speed 4 degrees/min; – tube operating parameters: 30 kV, 20 mA. Figure 2 shows the diffractogram of the original microsilicate and the nickel-supported microsilicate.

RESULTS AND DISCUSSION

Previously, we used an integral method to determine thermogravimetric parameters and a method by the inflection point on the thermogravimetric curve[20]. However, the above methods in our work[20] did not allow to study the process of thermal destruction of a mixture of primary coal tar resin with different catalytic additives at different heating rates.

Curve dependences of loss of mass of samples on temperature are presented in Figure 3 at a heating speed β – 10ºC/mines, β – 20ºC/mines, β – 30ºC/mines at an interval from 140–480ºC with use of a method of the Ozawa-Flynn-Wells (OFW). The reactivity of the substance can be characterized by the magnitude of the activation energy. The determination of the activation energy value was based on the generalized expression (1) of the solid phase reaction rate under non-isothermal conditions:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{\left(\frac{-E_a}{RT}\right)} f(\alpha) \quad (1)$$

Where – α is the degree of conversion of the feedstock; β – linear rate of sample heating, ºC/min; A – is a pre-exponential factor, c^{-1}; T – absolute temperature, K; E – activation energy, kJ/mol; *R* is the universal gas constant, J/mol K, *f(α)* is a mathematical model of a di-

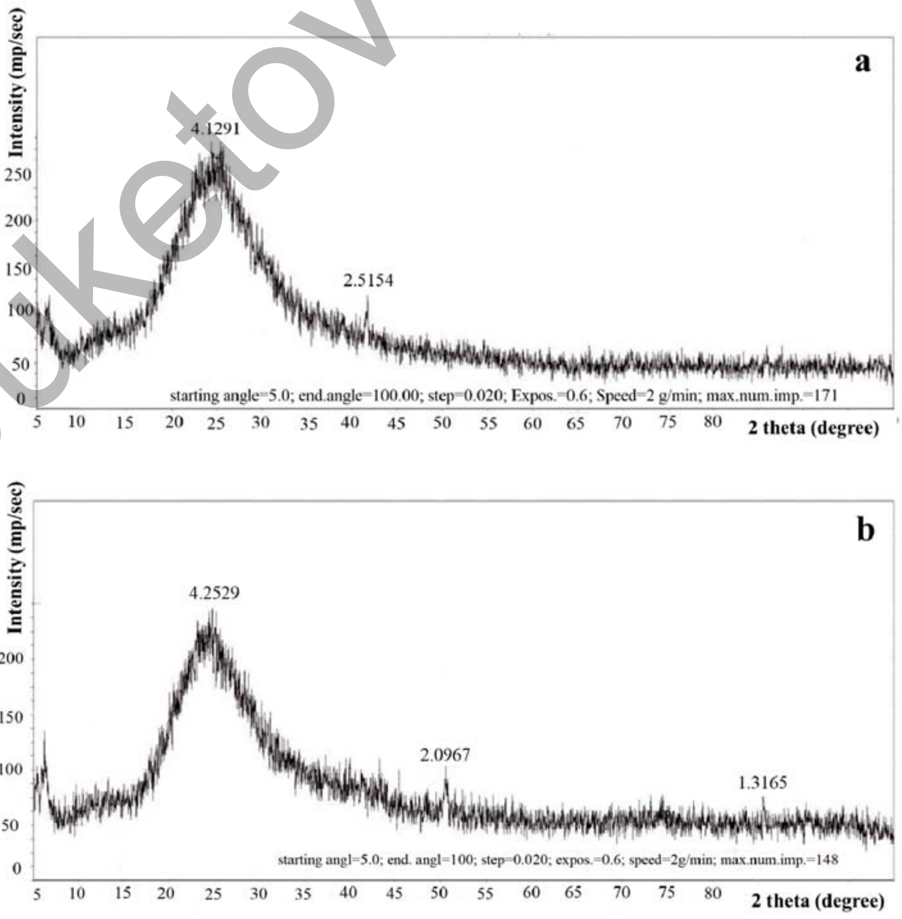

Figure 2. Diffractogram of starting microsilicate (a) and nickel-supported microsilicate (b) (phase composition)

mensionless kinetic function, depending on the type and mechanism of reaction. The α value in equation (1) is the relative degree of conversion of oil sludge, defined as как $\alpha = \frac{m_s - m}{m_s - m_f}$ where m_s and m_f are the initial and final mass of the substance, m is the mass of the substance at the measurement point[12].

Ozawa-Flynn-Wells method. According to the Ozawa-Flynn-Wells method of non-isothermal kinetics, when integrating and then logarithmizing equation (1), we obtain the expressions (2)

$$\ln G(\alpha) = \ln\left(\frac{AE}{R}\right) - \ln\beta + \ln p(z) \tag{2}$$

$G(\alpha)$ for the first order reaction is

$$\int_0^a \frac{d\alpha}{f\alpha} = \int_0^a \frac{da}{1- a} = -\ln(1-a);$$

$$p(z) = \frac{e^{-z}}{z} - \int_{-\infty}^{z} \frac{e^{-z}}{z} dz; z = \frac{E}{RT}$$

Using the Doyle approximation[21], we obtain equation (3) for substitution into expression (2):

$$\ln p(z) = -5.3305 - 1.052z \tag{3}$$

The OFW method is based on the assumption that the reaction rate at a constant α value depends only on temperature. The following equation is used in the analysis of non-isothermal kinetics:

$$\ln\beta_i = \ln\left[\frac{A_\alpha E_a}{Rg(\alpha)}\right] - 5.331 - 1.052\frac{E_a}{RT_{\alpha,i}} \tag{4}$$

substitution (2) and (3) gives the equation of OFW (4) for calculating the dependence of the rate of thermal decomposition of mixtures of catalyst with oil sludge. From the inverse temperature, the activation energy and the pre-exponential factor were calculated[12].

Thermogravimetric (TG) curves (Fig. 3) were constructed to assess the impact of supported metal microsilicate catalysts (iron, nickel, cobalt) on the rate of oil sludge thermal degradation. Based on the thermogravimetry data of oil sludge and catalyst, TG curves were calculated for their mixtures of known composition, which describe the process of thermolysis of the mixture of oil sludge and catalyst (Fig. 3).

The mass loss curve of the initial oil sludge (Sample 1) shows that at a temperature of 668 K, a maximum thermal decomposition of 45.1% is achieved, and at a heating rate of β – 10°C/min. When a catalyst (Sample 3) is

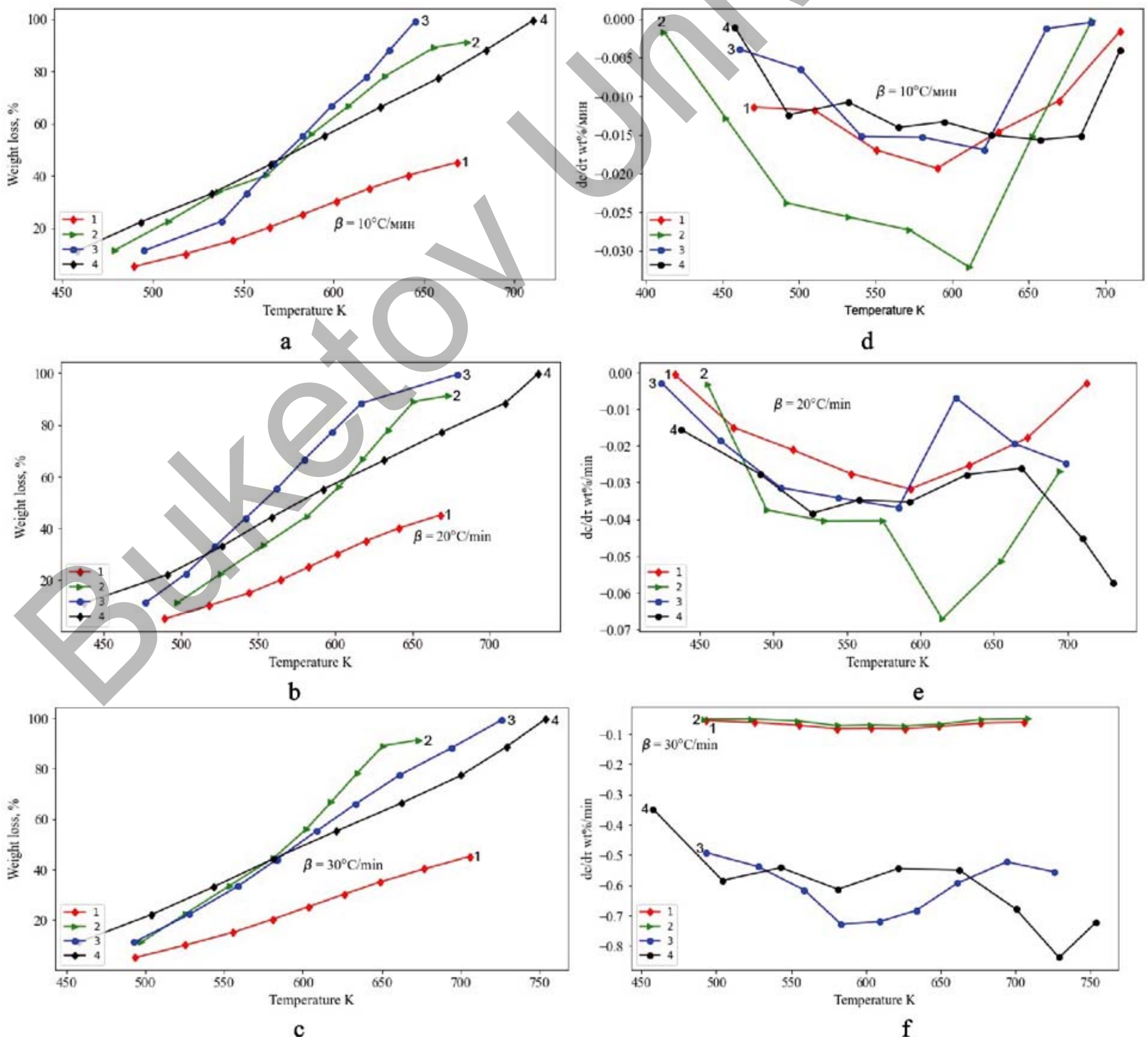

Figure 3. Thermogravimetric curves of mass loss (a), (b), (c) and mass loss rate (g), (e), (e) of the studied samples of oil sludge in the presence of microsilicate with catalyst applied: 1 – initial oil sludge, 2 – oil sludge with nickel applied, 3 – oil sludge with cobalt applied, 4 – oil sludge with iron applied

added to the oil sludge, the maximum thermal decomposition of 99% is achieved at a temperature of 645 K (Fig. 3 a), which indicates the active influence of cobalt on the thermal destruction of oil sludge. Figure 3 (b) shows that the addition of cobalt oxide to the oil sludge (Sample 3) achieves a maximum thermal decomposition of 99.12% at temperature of 679 K and a heating rate of β of 20°C/min. Figure 3 (c) shows that the addition of nickel oxide to the oil sludge (Sample 2) achieves a maximum thermal decomposition of 91% at temperature of 673 K and a heating rate of β of 30°C/min. At different heating rates β: 10°C/min, 20°C/min, 30°C/min, maximum decomposition of oil sludge does not exceed 45.1%.

On the mass loss rate curves at three heating rates β: 10°C/min, 20°C/min, 30°C/min one minimum is observed (Fig. 3 g, e, e), which is associated with the decomposition of the organic mass of oil sludge with the formation of volatile substances. It was found that when nickel is applied to the microsilicate (Fig. 3 g, e), a high rate of destruction of the organic mass of oil sludge is achieved at heating rates of β: 10°C/min, 20°C/min, and at β rates – 30°C/min the rate of destruction is minimal.

It follows from equation 4 that for a number of measurements of the temperature of thermal decomposition of mixtures of catalyst with oil sludge (Atasu – Alashankou) obtained at different β heating rates of samples and fixed values of their degree of α conversion, the graph of lnβ= *f*(1/*T*) function gives straight lines (isoconversion lines), the tangent of the slope of which is 1.052E/R directly proportional to the activation energy[12] (Fig. 4).

In the mathematical processing of thermogravimetric data, the Doyle approximation was used. The data points adequately lie on straight lines over the whole range of conversions[20] The calculated values show a high correlation coefficient ($R^2 \geq 0.997$) in Table 3. From the tangents of the inclination angles of the isoconversion lines (Fig. 4), the values of the activation energy *E* of the thermal degradation process of samples are calculated, which depends on the degree of loss of their mass.

Table 3 shows the dependence of the change in the activation energy value on the α degree of thermal decomposition of samples of oil sludge and a mixture of oil sludge with a catalyst. By analyzing Sample 1, the activation energy with increasing conversion increases from 67.1 kJ/mol to 131.4 kJ/mol. When the α conversion increases from 0.4 to 0.9, the curve has an extremum. Samples 2, 3, 4, and 5 showed an effect on the reduction of activation energy with an increase in the α degree of conversion from 0.1 to 0.9. A significant decrease in activation energy from 101.88 kJ/mol to 51.9 kJ/mol is typical for sample 3, which is consistent with the results of the maximum degradation rate of the mixture of oil sludge and cobalt (Fig. 3 e).

Figure 5 shows the dependence of activation energy on the degree of conversion of α samples 1–5. The dependence of the activation energy on the degree of conversion of the α mixture of oil sludge samples with catalysts shows the complexity of the process of thermal decomposition of the mixture of oil sludge with the catalyst. Changes in the calculated activation energy values appear to be due to the cleavage of weak covalent bonds and the destruction of stronger C-C bonds that occur at elevated temperatures with higher activation energy values and the involvement of thermal more stable molecular fragments of oil sludge.

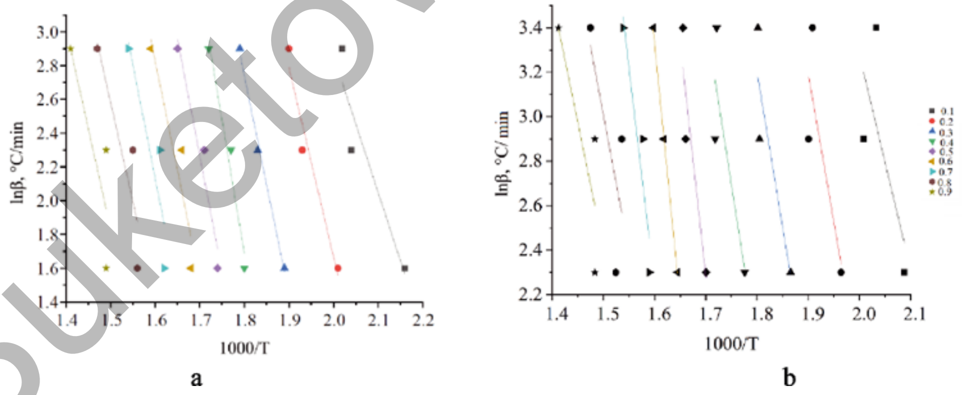

Figure 4. Dependence of heating rate constants β – 10 °C/min, β – 20 °C/min, β – 30 °C/min sample 1 (a), mixture samples (b – sample 2) on reverse temperature, K

Table 3. Thermal activation energy of the initial oil sludge and mixture of oil sludge (Atasu-Alashankou) and microsilicate with supported catalysts

Relative conversion rate, *α*	Sample 1		Sample 2		Sample 3		Sample 4		Sample 5	
	E_a, kJ/mol	$lnAc^{-1}$	E_a, kJ/mol	$lnAc^{-1}$	E_a, kJ/mol	$lnAc^{-1}$	E_a, kJ/mol	$lnAc^{-1}$	E_a, kJ/mol	$lnAc^{-1}$
0.1	67.1	19.02	80.06	22.54	101.88	27.96	67.35	20.8381	29.11	10.33
0.2	93	24.04	110.4	28.45	67.047	18.29	147.39	38.6132	25.4444	9.33
0.3	107.2	25.95	115.8	28.29	64.6419	17.16	154.99	37.7841	27.6511	9.25
0.4	131.4	30.15	121.88	28.36	68.2321	17.42	125.169	29.3639	42.9380	12.35
0.5	115	25.74	174.42	37.95	66.3654	16.53	83.7157	19.5639	71.9185	18.18
0.6	107.3	23.48	193.05	40.49	60.4824	14.92	87.7961	19.3685	110.7527	25.74
0.7	112	23.60	161.20	33.28	54.035	13.26	90.2490	18.936	167.4285	36.47
0.8	98	20.25	102.42	21.50	43.9957	11.05	100.2718	19.913	169.8460	35.58
0.9	99	19.64	93.28	19.25	51.9026	12.01	111.3388	21.1723	173.7741	34.92
$R^2 \geq$	0.68		0.99		0.81		0.70		0.92	

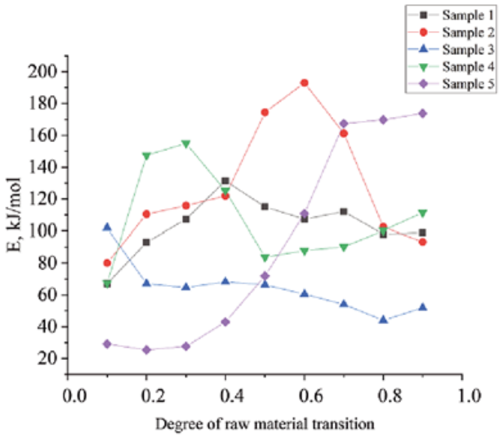

Figure 5. Dependence of activation energy E on the degree of conversion of α samples (Ozawa-Flynn-Wells analysis)

The complex dependence of the calculated activation energy value on the conversion degree of α samples 1–5 (Fig. 5) is due to the fact that during thermal degradation there are many parallel reactions with different activation energy values. The decrease in activation energy is due to the activity of the prepared nanocatalysts containing nickel, cobalt, iron, and microsilicate. The highest activity in the process of thermal degradation of oil sludge was shown by a cobalt-containing nanocatalyst. The cobalt-containing nanocatalyst had a high effect on the reaction rate of thermal destruction of oil sludge and a reduction in activation energy of 60.5 kJ/mol (α = 0.6). Based on the obtained data (Fig. 5), a number of activities of nanocatalysts containing metal oxides were built: cobalt > iron > mikrosilikat > nickel at α = 0.4–0.6.

The kinetic study of the process of thermolysis of oil sludge in the presence of nickel, cobalt and iron-based microsilicate has provided an important idea of the main mechanisms and reaction routes involved in this process. From the results obtained, it is clear that the presence of these metal catalysts plays a crucial role in accelerating the decomposition of oil sludge, which leads to an increase in the yield of valuable products such as hydrocarbons and coke.

Moreover, the data obtained from this study can be useful in developing more efficient and sustainable methods for the treatment and disposal of oil sludge waste. By understanding the complex reaction kinetics and the role of metal catalysts in this process, it is possible to develop optimized reaction conditions and catalyst compositions that can lead to higher yields of valuable products and less environmental impact.

Overall, the results of this study highlight the potential benefits of using metal-based microsilicate catalysts in processing oil sludge waste and pave the way for further research in this direction. Clearly, further work is needed to fully understand the mechanisms underlying this process and to develop optimized catalyst formulations that can provide maximum benefit with minimal environmental impact.

CONCLUSIONS

1. For the first time, using the BET, TPD, PPA method, the following values were determined: the specific surface area of the microsilicate is 18.3 m^2/g, the nickel-supported microsilicate is 20.9 m^2/g; the acidity of the prepared microsilicate was – 64 μmol/g; X-ray phase analysis of the original microsilicate showed the presence of silicon oxide and nickel oxide. Based on the content of silicon oxide, aluminum oxide and the established acidity of the microsilicate (64 μmol/g), it can be attributed to a zeolite catalyst.

2. Dynamic thermogravimetry at different heating rates studied the dynamics of oil sludge decomposition in the presence of prepared nanoocatalysts containing active metals of group VIII of the periodic system.

3. Based on thermogravimetric analysis, the main kinetic parameter of the oil sludge thermal degradation reaction was evaluated for the observed activation energy using the Ozawa-Flynn-Wells (OFW) model-free kinetics method. When thermally disassembling a mixture of oil sludge and nickel with its conversion α = 0.9 energy, the activation is 93.28 kJ/mol, a mixture of oil sludge and cobalt at its conversion degree α = 0.8 energy activation – 43.9 kJ/mol, mixture of oil sludge and iron (sample 4) at its conversion degree α = 0.1 energy activation – 67.3 kJ/mol, mixture of oil sludge with microsilicate at a conversion degree of its α = 0.2 energy activation – 25.4 kJ/mol. According to the calculated values of the activation energy and taking into account the high degree of conversion of the organic mass of oil sludge, it can be concluded that the dominant influence of the heterogenic nanocatalyst contains active cobalt or nickel nanoparticles.

4. The use of non-isothermal kinetics made it possible not to divide the process of thermal decomposition of oil sludge into periods of destruction and polycondensation. These degradations and polycondensation reactions are characterized by the yields of volatile substances and their components (oils, asphaltenes, resins and gas) expressed by the degree of decomposition of the organic mass of oil sludge. It was found that when the rate of heating of oil sludge increases from 20 to 30 degrees min^{-1} in the presence of nickel and cobalt, the decay process proceeds more deeply and completely, and the synthesis processes occur earlier and are more developed.

5. The developed method relates to methods of solving the problem of obtaining high-quality, environmentally friendly materials as a result of the technological processing of technogenic wastes of silicon and oil sludge production.

In the future, it is planned to develop a model method for assessing the thermal degradation kinetics of oil sludge in the presence of prepared nanocatalysts.

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