Експериментально досліджено технічні характеристики каталізатора, що містить оксиди Al, Mg, Cr, Ni, нанесені на алюмосилікатний волокневий матеріал, та кінетика повного окиснення метану на ньому. За визначеними значеннями питомої поверхні, вологоємності, порозності, гідродинамічного опору, температур початку реакції та повного окиснення, досліджуваний каталізатор не поступається відомим аналогам

Ключові слова: каталізатор, шпінель, оксидні метали, мінеральне волокно, окиснення метану, питома поверхня

Приведены результаты исследований технических характеристик разработанного катализатора на основе оксидов Al, Mg, Cr, Ni, нанесенных на алюмосиликатный волокнистый материал, и кинетика полного окисления метана на нем. По определенным значениям удельной поверхности, влагоемкости, порозности, гидродинамического сопротивления, температур начала реакции и полного окисления, исследуемый катализатор не уступает известным аналогам

Ключевые слова: катализатор, оксиды металлов, минеральное волокно, окисление метана, удельная поверхность

RESEARCH INTO METHANE OXIDATION ON OXIDE CATALYST OF THE APPLIED TYPE

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1. Introduction

The 21st century is characterized by diametrically opposed attitude of scientists and manufacturers to the use of natural resources in comparison with the early 20th century. A constant decrease in the raw materials reserves and strict environmental regulations, adopted at the Paris Climate Conference, stimulate development and implementation of the latest environmentally friendly technologies of obtaining synthetic compounds and energy. One example of such technologies is the technology of catalytic (catalytically stabilized) oxidation of various types of hydrocarbon fuels [1, 2]. The main advantages of catalytically stabilized oxidation include:

– minimal concentration of harmful substances in exhaust gases (CO content is 15 mg/m³ and NO_x content is 2–8 mg/m³) [3];

– high efficiency;

– low temperature of fuel combustion in a chamber (t=660–1000 °C);

– high performance of a catalytically stabilized burner;

– stable operation of catalyst on depleted mixtures [2];

– low temperature of exhaust gases (t=55 °C).

Given this, development of new catalytic systems and catalytic burner devices is a relevant task.

2. Literature review and problem statement

Catalytic methane oxidation is one of the rational directions to improve the environmental situation. The most active catalysts for methane oxidation are catalysts of Pt–Pd group, the main shortcoming of which is high cost of the active component, deactivation because of presence of water and carbon. The main advantages and disadvantages of existing catalysts are discussed below.

In paper [4], the authors proved effectiveness of palladium catalyst in the reaction of methane oxidation. Catalyst with highest activity consisted of 11.3 % by weight of PdO 20 % by weight of $Ce_{0,64}Zr_{0,16}Ni_{0,2}O_{1,9}$, the rest was γ-Al_2O_3. Such a complex composition is required for the intensification of oxidation due to the presence of oxygen in the structure of a catalyst. Nickel oxide NiO was used as a promoter. On this catalyst, effective oxidation took place at temperatures of up to 300 °C. Effectiveness of palladium catalyst, applied on silicon nitride, was proved in article [5]. In this work, the authors found agglomeration of platinum crystals to 30–70 μm, resulting in the deactivation of platinum catalysts and partial destruction. To decrease the cost of catalyst blocks, platinum and palladium are used as promoters to the main oxicobalt catalyst [6]. As a result of the introduction of promoters, activity of a catalyst in three-component transformations with $CO/NO/C_nH_m$ increased; according to the authors, the increased activity was caused by a decrease in bonds of strength between oxygen and a catalyst.

The negative effect of water on activity and deactivation of palladium catalysts, used for oxidation of uncombusted methane that exists in vehicle exhausts, was proved by the author in research [7]. Water initiates sintering of catalysts, reduces the activity of a catalyst. To reduce the negative impact of water, the author recommends conducting a process at temperatures

of above 500 °C and introduction of rhodium or platinum catalyst to composition to increase activity of oxygen.

A decrease in the activity of a palladium catalyst because of existence of water and catalytic poisons was proved in paper [8]. Thus, after aging, a catalyst cannot ignite methane gas at temperature of 400 °C, while a fresh catalyst provided 80 % conversion of methane at the same temperature. A decrease in activity is explained by formation of unbreakable compound $PdSO_4$.

An alternative to platinum and palladium catalysts is the catalysts containing spinel compounds of transition metals. In numerous works, high activity of transition metal-based catalysts, such as Co, Ni, Cu, Fe, Mo, was proved. For example, article [9] proves activity of NiO/ZrO_2 and NiO/YSZ catalyst, prepared by co-precipitation method. The temperature of 50 % methane transformation amounted to 470 and 500 °C.

It was found that for low-temperature methane oxidation, it is more rational to use oxides of elements, rather than individual elements, if it is necessary to carry out oxidation process at temperatures of above 1000 °C, catalysts with structures of fluorite $CeO_2–La_2O_3$, $CeO_2–ThO_2$ and pyrochlore $La_2Ce_2O_7$ are used [10]. The authors also proved positive influence of existence of a catalyst in catalytic oxide composition of silver oxide on a decrease in temperature and an increase in environmental parameters of a catalyst.

The author of paper [11] proposes to use a protective film from perovskite $La_{0,6}Sr_{0,4}Co_{0,2}Fe_{0,8}O_3$ to improve performance of a nickel catalyst in fuel elements. The use of a protective film provided for a decrease in carbon deposits and destruction of fuel element. Resistance of perovskite structure at temperature of above 700 °C was proved experimentally.

In research [12], the authors suggest using nickel and vanadium oxides as catalytically active components. The use of these components provides for sufficient activity and effectiveness. They established a row of catalytic activity of metal oxides: Co_3O_4, $PdO>Cr_2O_3>Mn_2O_3>CuO>$ $>CeO_2>Fe_2O_3>V_2O_5>NiO>MoO_3$, TiO_2. This research also indicated a positive impact of presence of oxygen in the structure of a catalyst on quality and rate of methane oxidation, and the fact that existence of strontium in a catalytic composition leads to a decrease in its activity.

An important factor in the process of creation of an effective catalyst of deep methane oxidation is selection of heat-resistant base. Selection of a carrier depends on conditions of using a catalyst and production technology. Thus, in paper [13], the author proposes carriers from fiberglass and basalt fibre.as an alternative replacement of known carriers. Unlike ceramic, metal carriers, the proposed carriers possess enhanced thermophysical, strength and gas-dynamic characteristics, which makes it possible to increase the service life of a catalyst and to extend the temperature range of operation.

Therefore, the problem that remains promising is creating a catalyst capable of withstanding high volumetric load, lengthy exposure to high temperatures, local temperature rises, temperature acceleration, and the influence of catalytic poisons.

In view of the above, it was decided to explore the possibility of using aluminosilicate fiber material "AlsiFlex-KT1600" as a catalyst carrier that is resistant to influence of high temperatures and voluminous loads. Oxides of Cr, Ni, Mg and Al, applied on fibers by impregnation method, were used as catalyt-

ically active components. Selection of catalytic components was conditioned not only by possibility of establishing contact with sufficient activity in oxidation reaction, but also by ability to withstand lengthy exposure to high temperatures.

3. The aim and objectives of the study

The goal of present research is to study technical characteristics of the synthesized catalyst based on oxides of Cr, Ni, Mg and Al, applied on aluminosilicate fibre material, and the kinetics of methane oxidation by air oxygen on it.

To accomplish the set goal, the following tasks had to be solved:

– to determine technical characteristics of material for its subsequent use as both a catalyst carrier and a finished catalyst;

– to establish activity of the developed catalyst.

4. Materials and methods for studying technical characteristics and activity of oxide catalyst

4. 1. Examined materials and equipment used in the experiment

As an experimental sample, we used a spinel catalyst, applied on fibers of aluminosilicate material of "Alsi-Flex-KT1600" make. It is a fireproof ceramic material, composed of 47 % of aluminium oxide Al_2O_3 and 53 % of silicon oxide. Outwardly, this is polycrystalline fibers with a fiber diameter of up to 3 μm. It is widely used in industry as a lightweight and durable insulating material, resistant to lengthy exposure to high temperatures and chemical compounds.

The catalyst was obtained by method of sequential impregnation with aqueous solutions of aluminium nitrate $Al(NO_3)_3 \cdot 9H_2O$, nickel nitrate $Ni(NO_3)_2 \cdot 6H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$, CrO_3 of "R" qualification. Then it was dried and calcined in a muffle furnace at temperature of 750 ± 8 °C. Composition of the resulting spinel (% by weight): Al_2O_3 – 10; MgO – 3; (Cr_2O_3+NiO) – 0,4. The value of porosity indicator of 90.4 % was provided by punching of longitudinal channels. Physical appearance of the catalyst sample is shown in Fig. 1.
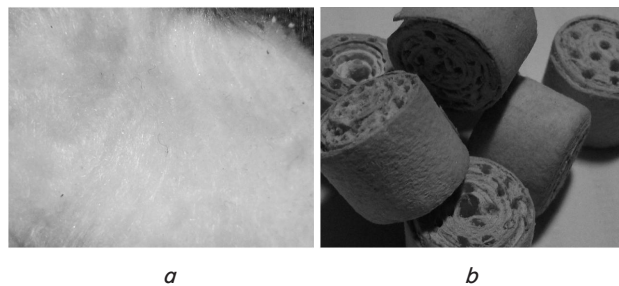

a   *b*

Fig. 1. Experimental sample: *a* — physical appearance of the original fiber; *b* — synthesized catalyst

After all stages of preparation of a catalyst, averaged technical characteristics of its granules made up: specific weight $\rho=0.3$ g/cm³, volume $V=4.6$ cm³, cross-sectional diameter $d=1.4$ cm, height $h=3$ cm. Changes in the structure of the sample during successive impregnation, drying and calcining are shown in Fig. 2.
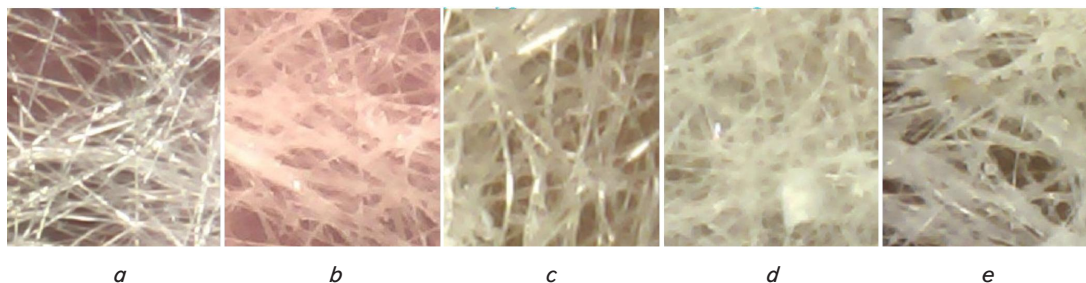
Fig. 2. Change in the structure of sample: *a* — pure fiber; *b* — after application of aluminum oxide; *c* — after application of magnesium oxide; *d* — after application of nickel oxide; *e* — after application of chromium oxide

Changes in the structure of a carrier after impregnation were examined using the microscope MIM 7, manufactured in the Soviet Union. Sample weight gain was controlled using the analytical balance BRL 200, manufactured in the Soviet Union.

Schematic of laboratory plant for the exploration of kinetic characteristics of a catalyst in the reaction of catalytic oxidation of methane is represented in Fig. 3.
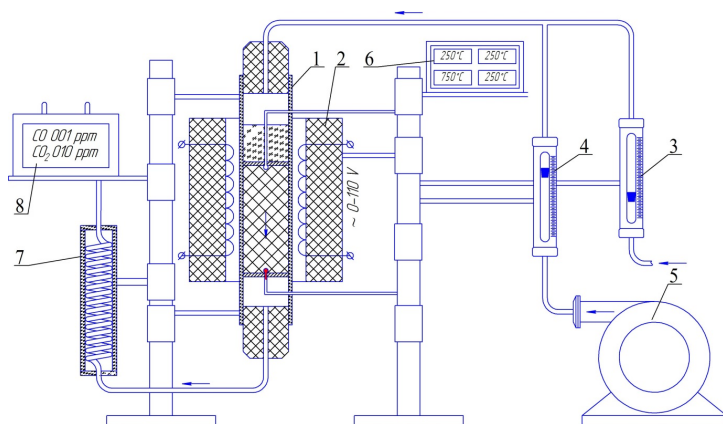

Fig. 3. Laboratory plant for carrying out kinetic studies: 1 — quartz reactor; 2 — laboratory tunnel furnace; 3 — rotameter to measure natural gas consumption; 4 — rotameter for measurement of air consumption; 5 — fan; 6 — thermocouples; 7 — refrigerator; 8 — gas analyzer "Dozor CM-5M"

The studies were performed in the reactor of ideal displacement of 1 s by a fixed bed catalyst. The reactor is a quartz tube with an inner diameter of 14 mm and height of 300 mm. To provide adequate mixing and heating, a layer of the catalyst is covered with ceramic powder. To minimize the impact of heat, which is released at methane oxidation, on the rate of reaction, catalyst loading made up $m=1.5$ g. methane concentration in the mixture ranged from 1.75–2 % by volume, volume velocity of gas mixture was $Q=107000$ h^{-1} (contact time $\tau=0.03$ s). Such parameters provided the temperature fluctuations in a layer of the catalyst, admissible for isothermal conditions.

For initial heating of gas mixture up to temperature of 300 °C, we used a tunnel furnace 2. Measurement of temperature of heating of methane-air mixture and a catalyst in the reactor was carried out using thermocouple 6. Natural gas was supplied from the network with consumption of 0.0086–0.009 m³/h and regulated by the rotameter 3. With the help of the fan 5, the air was fed to the reactor in the volume, which provides consumption of mixture of 0.49–0.51 m³/h, and regulated by the rotameter 4. Measure-

ment of concentrations of components, cooled in the refrigerater 7, was carried out using gas analyzer "Dozor SM-5M", manufactured by "Orion" company, Kharkiv, Ukraine. The device is equipped with anti-explosion thermocatalytic sensitive elements: TCM-2.8-1 (sensor of combustible gases); three-electrode electrochemical cell (CO sensor), dielectrode electrochemical cell (O$_2$ sensor). The limit of admissible basic error is ±25 %.

4. 2. Procedure for determining technical characteristics and catalyst activity

For designing experimental samples of catalysts, we used the method of subsequent impregnation of the carrier with solutions of salts with the assigned concentration. After impregnation, the samples were dried and calcined. The carrier with the form, prepared beforehand, was dried at temperature of 110 °C.

The time of keeping the carrier in solutions of salts was 30 minutes. For thermal decomposition of aluminium, magnesium and sodium nitrates, the samples were calcined in a muffle furnace at temperature of 760 °C, the duration of each calcination stage was 30 minutes. After calcination, the weight gain of the catalyst sample was determined.

Changing in the structure of the sample was determined by microscopic examination on the MIM7 microscope, fitted with a camera.

Anisotropy was determined by hydrodynamic resistance, generated by the sample, specific surface area was determined by the Gelperin-Kagan method. Activity of the catalyst was determined experimentally, by changing in methane concentration after the process of reaction. Changes in concentration of methane, carbon dioxide and monoxide were determined by the gas analyzer "Dozor CM-5M" (Ukraine).

According to changes in methane concentration at the inlet and outlet of the reactor, a degree of reaction of methane transformation was determined. Constant of methane oxidation rate on the catalyst was determined by the integral method in accordance with dependence of $\ln(C_0/C_i)$ on the time of the contact.

The value of the rate of impregnation of the carrier was established experimentally: we submerged the samples at 2 millimeters in the solution and measured time and height of the layer, impregnated due to the capillary effect.

5. Results of research into technical characteristics and activity of the catalyst

In the study, we used three samples of the catalyst, prepared under identical conditions, but different from each

other by arrangement of fibres: "X" – the direction of fibers coincides with the direction of gas mixture flow through the sample, "Y" – the direction of fibers provides for lengthwise washing of fibers with the mixture, and "Z" – the direction of fibres is perpendicular to the direction of mixture flow, Fig. 4.

As a result of the studies, we obtained experimental data: the rate of solution absorption, porosity, specific density, and weight gain. Experimental data on weight gain of samples after consecutive impregnation, drying and calcination are presented in Table 1.

Table 1

Experimental data on the impregnation and calcination of samples from basalt fiber in solutions containing catalytic elements

No.	Direc-tion of fibers	Weight gain after impregnation, drying and calcination, g				Poros-ity, ρ, g/cm³	Poros-ity, %
		$Al(NO_3)_3$	$Mg(NO_3)_2$	$Ni(NO_3)_2$	Cr_2O_3		
1	"X"	0.15	0.045	0.003	0.003	0.3	90.4
2	"Y"	0.14	0.044	0.0029	0.0028	0.29	89.2
3	"Z"	0.15	0.042	0.0031	0.0029	0.29	88.5

As a result of conducted hydrodynamic testing, we established anisotropy of properties of aluminosilicate fiber, affecting not only impregnation rate, but also rate of propagation of heat around the skeleton. Fundamental arrangement of fibres was established, Fig. 4.
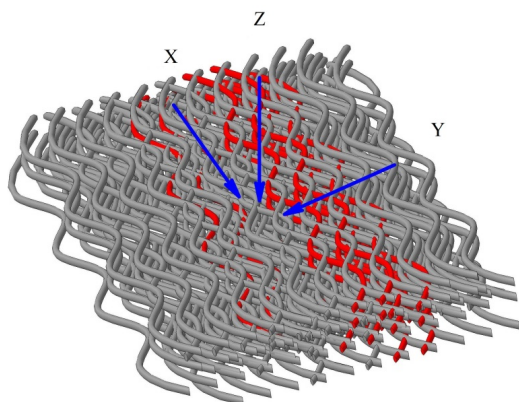

Fig. 4. Schematic arrangement of threads of the aluminosilicate fiber ALSIFLEX®-1260

Thus, for the experimental sample, dependences of impregnation rate on direction of intertwining layers of fibers were established.

Multiple exceeding of impregnation rate for the sample with "X" and "Y" fibers arrangements over the sampe with "Z" fiber arrangement was established. Thus, impregnation rate at the same cross-sectional area for sample with "X" direction amounted to 2 mm/s, and for the sample with "Z" direction it made up 7–8 mm/s. In addition, samples with "X" fibers arrangement were better heated through along the height of the layer than "Z" samples. This fact is explained by different coefficients of thermal conductivity, thus, for samples with "X" direction – λ=0.15 W/m·K, with "Y" direction – λ=0.11 W/m·K, and for samples with "Z" fiber direction – λ=0.09 W/m·K.

Fig. 5 shows dependence of changes in the hydrodynamic resistance of fiber on direction of fibres
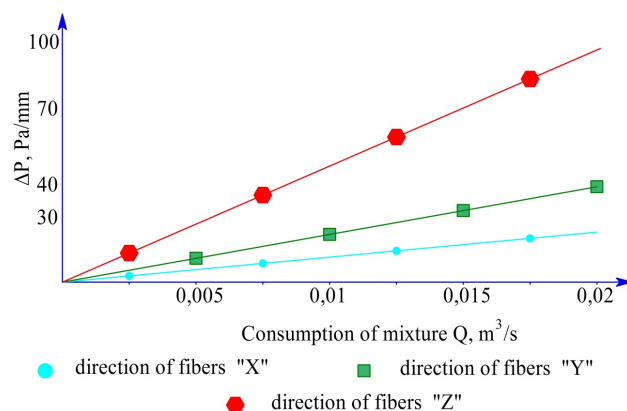

Fig. 5. Dependence of changes in the hydrodynamic fiber on direction of fibres

The study of experimental data showed that the lowest value of hydrodynamic resistance at different consumption is characteristic for the sample with "X" arrangement of fibres, i. e. in direction of fibre by-passing.

According to the requirements applicable to catalysts of methane oxidation, and the obtained data for further research into activity, it was accepted to use a sample with "X" arrangement of fibres.

The value of specific surface area was determined by the Gelperin-Kagan equation [14].

$$S_{ss} = \left(324 \cdot 10^{-6} \cdot \frac{W_o^2}{\upsilon_{gas}^2} + \frac{0,04 \cdot \varepsilon^2 \cdot \Delta P}{\upsilon_{gas} \cdot H \cdot \rho_{gas} \cdot W_o} \right)^{0,5} + 18 \cdot 10^{-3} \cdot \frac{W_o}{\upsilon_{gas}}, \quad (1)$$

where W_0 is the gas flow velocity calculated for full cross-section of the empty machine, m/s; υ_{gas} is the coefficient of kinematic viscosity of gas m²/s; ΔP is the hydraulic resistance of the sample layer, kg/m²; H is the height of packed layer, m; ρ_{gas} is the gas density, kg·s²/m⁴.

Measurements of hydrodynamic resistance, generated by the sample, were made at the average velocity of gas flow of 0.3–0.7 m/s. Such velocity mode provides for laminar air flow with dominating viscosity forces in the reactor with a nozzle. This is the main condition for correct determining of the magnitude of specific surface depending on magnitude of hydrodynamic resistance, because the measured resistance should be determined only by friction of a sample on the surface [14].

Thus, as a result of the experiment, it was found that the magnitude of hydrodynamic resistance, created by a layer of material, makes up 250–350 kg/m². Calculation value of specific surface amounted to 20000–25000 m²/m³ (1).

As a result of kinetic studies, we obtained data on changing the temperature of gas mixture as a result of the process of reaction, changing in concentrations of original reagents and reaction products, and established procedure for reaction by CH_4, determined the constant of rate of chemical reaction and the rate of CO_2 formation.

As it is seen in Fig. 6, the temperature of the beginning of reaction on the experimental sample amounted to 280 °C and even at temperature of 308 °C, the degree of methane conversion was 1.34 %. To compare, the temperature of beginning oxidation on the oxide catalyst, containing lanthanum, ceri-

um and cobalt, was 250 °C [15], and on the platinum catalyst, it was 200 °C [16]. In turn, 100 % conversion of methane on the experimental catalyst was carried out at temperature of 750 °C, which is by 150–300 °C higher than on the catalysts, presented in Fig. 6. The experimental catalyst also demonstrated smoother acceleration of degree of conversion, which is explained by a large specific surface.
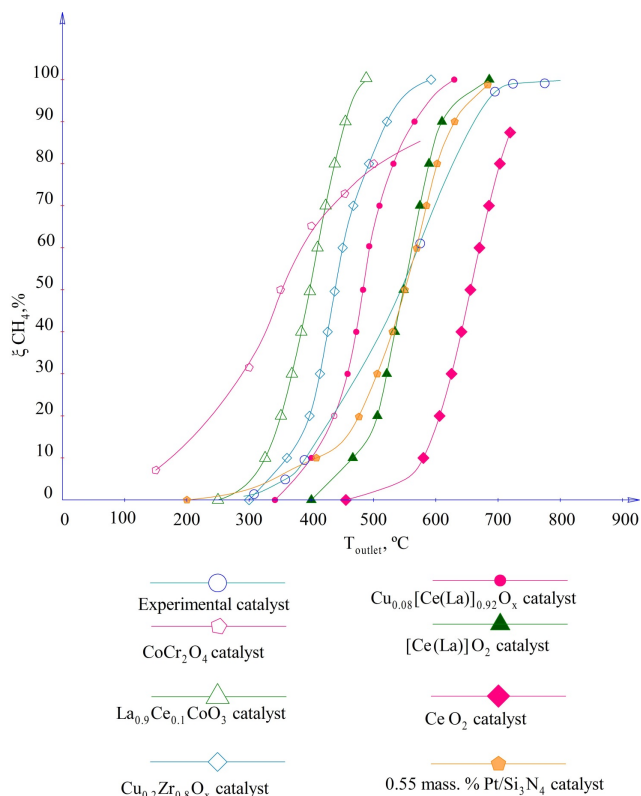

Fig. 6. Comparative data on the activity of catalysts in methane oxidation reactions

To determine the order of the reaction, activation energy and to develop equation of reaction rate, the research into activity of the catalyst at different methane content in the mixture was carried out. Data on the research are given in Table 2.

Using integral methods for determining of constant of reaction rate [17], we established the order of methane oxidation on fibrous catalyst $n=1$, activation energy $E_a=86.241$ kJ/kmol and pre-exponential multiplier $A=3.05 \cdot 10^7$.

Table 2

Results of research into the rate of CO_2 formation depending on the CH_4 content in mixture

No. by order	Temperature of mixture at the inlet of reactor, T, °C	Temperature of mixture at the outlet of reactor, T, °C	Concentration of $CH_{4\,incoming}$ C, $kmol/(m^3 \cdot s)$	Rate of CO_2 formation, r, $kmol/(nm^3 \cdot s)$	Degre of CH_4 conversion, ξ, %
1	300	305	$11.16 \cdot 10^{-5}$	$4.27 \cdot 10^{-5}$	1.29
2	300	306	$16.74 \cdot 10^{-5}$	$6.41 \cdot 10^{-5}$	1.29
3	300	306	$22.32 \cdot 10^{-5}$	$8.61 \cdot 10^{-5}$	1.3
4	300	306	$33.48 \cdot 10^{-5}$	$1.3 \cdot 10^{-4}$	1.32
5	300	308	$78.12 \cdot 10^{-5}$	$3.1 \cdot 10^{-4}$	1.34

To compare obtained activation energy, Table 3 gives the values of activation energy of methane oxidation reaction in various catalytic contacts [18].

Table 3

Activation energy of methane oxidation reaction on various catalytic contacts

Catalyst	Pt	Pd	Cr_2O_3	$NiCo_2O_4$	$MgCo_2O_4$	$CuCr_2O_4$
E, $\cdot 10^3$, J/mol	100.5	92.1	113.0	92.1	113.03	96.3

The developed catalyst has the value of activation energy that is close to that of the known catalysts, which proves its capacity and the fact that its usage is promising.

6. Discussion of results of research into technical characteristics and activity of the synthesized catalyst

Based on results of the study of technical characteristics for designing of the catalyst, applied for complete methane oxidation, it is best to use a carrier, in which fibers of material have the same direction as the mixture flow.

The use of fiber with "X" direction provides:
– a decrease in the wall thickness of up to 0.04 mm;
– an increase in the share of free cross-section of up to 90–95 %;
– minimal hydrodynamic resistance.

The developed outer surface and high porosity are an advantage of mineral-fibrous material, used for making the carrier.

Thus, at the same volumes of catalytic units, the synthesized catalyst will by 3–4 times lighter, which will have a positive effect on reducing heat losses to environment, heating up dynamics and skeleton cooling. Due to high porosity (>90 %), the synthesized catalyst has hydrodynamic resistance, comparable to resistance, created the catalyst on ceramic or metal honeycomb catalyst. This fact will allow us to replace smoothly the existing catalytic units with the developed units, without changing compressor equipment.

The conducted research found that samples from mineral fibers have much larger specific surface area in comparison with the known ceramic (800–1000 m²/m³) and metal carriers (1400–1600 m²/m³).

The resulting spinel catalyst is characterized by activity, comparable with that of the known catalysts, complete conversion is achieved at temperatures close to 800 °C and 50 % conversion was observed at temperature of 550 °C. Due to the large specific surface area, catalyst warms up smoothly and cools down quickly. Catalysts, based on ceramic and metal carriers, do not have this ability.

Macrokinetic equation of rate of complete methane oxidation on the developed catalyst under the studied conditions takes the form:

$$r = A \cdot e^{\frac{-Ea}{RT}} \cdot C_{CH_4} = 3,05 \cdot 10^7 \cdot e^{\frac{-86241}{RT}} \cdot C_{CH_4\,gas}. \quad (2)$$

This equation holds in the region close to kinetic mode (to the point of inflection, S – shaped curve, Fig. 6) in the temperature range

of 290–570 °C. For diffusive mode, it is incorrect to use the obtained kinetic equation, because temperature and methane concentration on the surface of the catalyst are not taken into account.

7. Conclusions

1. Technical characteristics of the developed catalyst based on Cr, Ni, Mg and Al oxides, applied on aluminosilica fibers "ALSIFLEX-KT1600", were determined. Density of the catalyst was 0.3 g/cm³; porosity made up 90.4 %; specific hydrodynamic resistance was 22 Pa/mm; specific surface area was 20000–25000 m²/m³. Optimal arrangement of fibres is longitudinal.

2. By using the integral methods, activation energy (E_a=86.241 kJ/kmol) and temperature of reaction beginning (T_b=280 ºC) were determined.

The developed catalyst is not inferior to the best existing analogues based on platinum, palladium and complex oxide compositions, applied on ceramic or metal carriers. Ability of the carrier to withstand the influence of high volumetric loadings (τ=0.03–0.05 s) was proved.

Conducted studies proved effectiveness of the developed catalyst based on oxides of transition metals (Ni, Mg, Al, Cr), applied on synthetic aluminosilica fibers.

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