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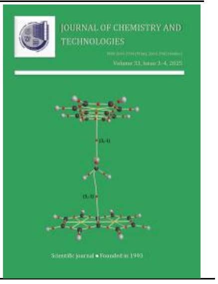

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STUDY OF THE PROPERTIES OF A CATALYST PRODUCED FROM GALVANIC SLUDGE WASTE

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Abstract

The problem of industrial waste disposal is relevant throughout the world. Toxic industrial waste from the technological use of galvanic coatings is a global environmental problem. In this work, a catalyst made from galvanic production sludge waste at the Instrument-Making Plant in Cherkasy (Ukraine) was obtained and studied. The galvanic sludge was analysed using polarographic, complexometric, thermogravimetric and photocolorimetric methods to determine its elemental composition and heavy metal content: iron, copper, nickel, chromium, zinc. A technological process was developed and a catalyst based on waste sludge from electroplating plants was manufactured from a sludge suspension obtained after wastewater treatment in electroplating production using the following technology: dehydration of sludge after fermentation to dry powder, mixing the resulting powder with a Cr(IV) to Cr(III) reducing agent solution and drying the resulting suspension at 150 °C for 4 hours; forming the catalyst by mixing the sludge powder with the carrier suspension and calcining for 4 hours at 700–750 °C. A basic technological scheme of a pilot plant for determining the activity of an iron-chromium (sludge) catalyst has been created, which allows the catalyst to be used effectively to neutralise organic vapours of ethanol, acetone, butanol and toluene by means of catalytic oxidation. It has been established that at a maximum volumetric gas flow rate of 1900 g/h in the catalytic reactor, the degree of catalytic oxidation increases for all classes of organic compounds. Starting at a temperature of 370 °C in the catalysis zone, the conversion of ethanol, acetone and butanol enters the kinetic region, while the nature of the process for toluene remains unchanged. The maximum rate of catalytic oxidation is achieved at a temperature of 400 °C. Under these conditions, the maximum conversion rate is achieved: for ethanol – 97.1 %, for acetone – 99.2 %, for butanol – 90 %, for toluene – 95.7 %.

Keywords: galvanic waste; heavy metals; disposal, catalyst; hydrocarbon compounds; catalytic oxidation; exhaust gas; purification efficiency.

ДОСЛІДЖЕННЯ ВЛАСТИВОСТЕЙ КАТАЛІЗАТОРА, ВИГОТОВЛЕНОГО ІЗ ШЛАМОВИХ ВІДХОДІВ ГАЛЬВАНІЧНИХ ВИРОБНИЦТВ

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Анотація

У роботі отриманий та досліджений каталізатор, виготовлений із відходів шламу гальванічного виробництва на Приладобудівному заводі в м. Черкаси (Україна). Гальванічний шлам проаналізований полярографічним, комплексометричним, термогравіметричним та фотоколориметричним методами на предмет його елементного складу та вмісту важких металів: залізо, мідь, нікель, хром, цинк. Розроблений технологічний процес і практично виготовлений каталізатор на основі відходів шламу гальванічних заводів із суспензії шламу, отриманої після очищення стічних вод гальванічного виробництва за такою технологією: дегідратація шламу після ферментації до сухого порошку, змішування отриманого порошку з розчином відновника Cr(IV) до Cr(III), сушіння отриманої суспензії за температури 150 °C протягом 4 год; формування каталізатора шляхом змішування порошку шламу з суспензією носія і прожарювання протягом 4 год за температури 700–750 °C. Створено принципову технологічну схему пілотної установки для визначення активності залізо-хромового (шламового) каталізатора, що дозволяє ефективно використовувати каталізатор для нейтралізації органічних парів етанолу, ацетону, бутанолу і толуолу, шляхом проведення процесу їх каталітичного окислення. Встановлено, що при максимальній об'ємній швидкості потоку газу 1900 г/год у каталітичному реакторі ступінь каталітичного окислення збільшується для всіх класів органічних сполук. Починаючи з температури в зоні каталізу 370 °C, конверсія етанолу, ацетону та бутанолу переходить у кінетичну область, а характер процесу для толуолу зберігається. Максимальна швидкість каталітичного окислення досягається при температурі 400 °C. За цих умов досягається максимальна швидкість конверсії: для етанолу – 97.1 %, для ацетону – 99.2 %, для бутанолу – 90 %, для толуолу – 95.7 %.

Ключові слова: відходи гальваніки; важкі метали; утилізація; каталізатор; вуглеводневі сполуки; каталітичне окислення відхідний газ, ступінь очищення.

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Introduction

The issue of waste accumulation, which has persisted over extended periods, has now reached a global scale. In the metallurgy and heat and power sectors, up to 40 % of the company's space is used for waste storage. The disposal and storage of industrial and household waste has become particularly critical. Approximately 8 % of Ukraine's total space is used for the accumulation of industrial and household waste in tailing ponds, landfills, heaps, slag collectors, and other repositories [1].

The most acute problem is environmental pollution caused by toxic industrial waste. Galvanic coatings are widely used in the technological cycles of most machine-building, metalworking, instrumentation, and other industries to enhance corrosion resistance, improve wear resistance, and provide decorative finishes to products [2].

Electroplating sludge is classified as hazardous solid waste. Improper disposal and haphazard dumping of ES not only take up a significant amount of land resources, but also pose a serious threat to the environment and human health. Heavy metals in sludge can migrate through weathering and rainwater leaching, leading to environmental contamination through the sludge-soil-crop-human pathway and posing a significant risk to human health [3; 4]. According to the authors of [5], modern electroplating facilities generate large volumes of sludge. Only 30–80 % of metals are effectively used in galvanic processes; the rest enters wastewater, which becomes the main source of environmental contamination. Incomplete wastewater treatment results in the pollution of the entire ecosystem—soil, water bodies, humans, and flora and fauna are all affected. Even fully treated galvanic wastewater does not guarantee environmental safety. During the operation of treatment facilities, solid waste is formed, which is then buried in landfills, placed in dumps, formed into heaps, or stored in sludge and tailing reservoirs. Heavy metal ions can return to the surface soil layer and water bodies via groundwater infiltration.

These processes cause anthropogenic geochemical anomalies in the atmosphere and hydrosphere, weaken the activity of soil bacteria responsible for soil fertility, and adversely affect living organisms. For instance, cadmium accumulates in the liver, kidneys, and spleen of the human body, leading to kidney stones, anemia, and reduced blood oxygen levels. Excess copper deposits in the brain, skin, liver, and pancreas. Chromium and nickel are carcinogenic and cause tumor formation. Other heavy metals accumulate in the human body and cause various diseases, making them particularly hazardous to both the environment and human health. Therefore, the issue of galvanic sludge disposal is becoming increasingly critical due to tightening environmental regulations [6; 7].

The burial of galvanic waste in sludge repositories also results in the loss of valuable raw materials [8]. The concentration of heavy metals in such waste can reach (mg/kg): zinc – up to 5740, nickel – up to 200, chromium – up to 5000, lead – up to 600, copper – up to 5600, cobalt – up to 30, cadmium – up to 54, antimony – up to 200. These metals are mainly present in the form of chemically bound compounds [9].

The secondary environmental harm of electroplating sludge is greater than that of electroplating wastewater. Various organic substances are often added to the electroplating process to improve the quality of electroplating products, such as brighteners, levelling agents, surfactants. Most of them are harmful substances, such as sodium allylsulfonate, alkynol, citric acid, malic acid and acetone [10].

Significant attention in recent years has been given to technologies that allow galvanic sludge waste to be converted into useful products. One established direction involves using these wastes in the production of construction materials.

The use of industrial waste as a partial substitute for raw materials in the construction sector saves precious landfill space and reduces the need to extract traditional raw materials. Steel sludge is attracting researchers' attention as a potential environmentally friendly and sustainable construction material due to its unique chemical composition, physical properties and mechanical characteristics [11]. Sludge is an improved and more environmentally friendly alternative to traditional building materials. It is useful in a variety of applications, such as aggregate in concrete and asphalt mixtures, railway ballast, cement, etc. Historic Roman roads in the Sussex region of England were built using discarded furnace slag. Since the beginning of the eleventh century, slag has been used in the United States to build pavements as a base and in asphalt mixtures, railways and cement [12]. For example, chromium-containing sludge, after drying, can be used as pigments in the manufacturing of decorative glass, producing shades such as green, blue, brown, and black, depending on sludge composition [13]. Sludge can also be incorporated into ceramic tile production, where the addition of heavy metal sludge not only ensures safe immobilization but also improves the mechanical properties of the final product [14; 15].

A review of recent scientific literature over the last five years indicates that researchers are actively exploring the potential for recycling galvanic sludge waste to produce catalysts for gas purification. Several authors have examined the thermal treatment of galvanic sludge to obtain metal oxides that demonstrate high catalytic activity in the oxidation of volatile organic compounds (VOCs) [2]. Others have investigated catalysts derived from galvanic sludge for the reduction of nitrogen oxides (NO_x) in flue gases [5], reporting effective NO_x reduction under appropriate operating conditions.

Additional studies describe the synthesis of oxide-based catalysts from galvanic waste and their application in the removal of VOCs from gas streams, with results confirming high oxidation efficiency [16]. Hydrothermal treatment has also been explored as a means to obtain catalysts with a high specific surface area and favorable catalytic properties [6]. Authors in [17] have evaluated various sludge treatment technologies and their potential for reducing gaseous emissions, including the use of such catalysts in industrial SO_2 absorption processes with positive results. Work in [18] has examined the combination of galvanic waste with other industrial by-products, such as metallurgical slag, to enhance the performance and durability of the resulting catalysts. These hybrid catalysts exhibit better stability and efficiency in toxic gas purification compared to single-source sludge-based catalysts.

A comprehensive environmental solution is proposed in [19], where galvanic sludge is repurposed to produce multifunctional catalysts. These can be used not only in gas purification but also in processes for degrading heavy metals in aqueous solutions-addressing both air and water pollution.

Durability studies of these catalysts in industrial settings are described in [20], showing that some formulations maintain stability over several years, making them promising for long-term industrial use.

Economic analyses in [16] compare the cost of producing and using galvanic sludge-based catalysts with conventional gas treatment methods. Despite higher initial costs, the long-term efficiency and lifespan of such catalysts make them economically viable alternatives.

Based on a review of the literature, it can be asserted that particular attention is currently being paid to technologies that enable the conversion of galvanic sludge waste not only into auxiliary products but also into catalysts for the purification of gaseous and liquid streams. The use of sludge as catalysts is a promising approach that simultaneously addresses waste disposal issues and reduces atmospheric pollution. This could serve as an effective solution for the integrated processing of toxic waste and the simultaneous improvement of environmental quality. The relevance of this problem is reinforced by both increasingly strict environmental requirements for industrial enterprises and the need to reduce waste disposal costs.

The aim of this work is to develop a method for producing iron-chromium catalysts based on galvanic production waste and to evaluate their catalytic activity in technological processes for cleaning gas streams from organic compounds. The work was carried out to reduce the toxicity of exhaust ventilation gases from small mechanized diesel engine repair facilities, which will dramatically increase the productivity of repair work and reduce the time required to restore the existing equipment fleet, as well as preserve the health of repair workers.

To achieve this goal, the following tasks were performed: the composition of electroplating sludge waste was determined; a methodology for producing an iron-chromium catalyst based on electroplating waste was developed; the catalyst was manufactured; and a study was conducted to test the catalytic activity of the catalyst in the technological process of cleaning gas streams from hydrocarbon compounds.

Materials and Methods

The raw material used for the preparation of the catalyst was a sludge suspension obtained after the treatment of wastewater from the galvanic production facility of the Instrumentation Plant in Cherkasy (Ukraine). The catalyst was made from sludge from the treatment with reducing agents. Waste metallic iron can be used (in the form of steel shavings, scrap, etc.), or ferrous (II) sulphate - the ferritic method. In the first case, wastewater acidified to pH = 2 is filtered through a layer of iron filings in the reactor with constant bubbling with air. In the second case, a solution of ferrous (II) sulphate in the form of a 10 % aqueous solution is introduced into the reactor, which receives wastewater after chromium plating. The reduction of Cr (VI) to Cr

(III) by Fe (II) salts occurs at a fairly high rate not only in acidic but also in neutral and alkaline environments. In particular, the following reaction occurs in an acidic environment:

$$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$$

In the case of using ferrous (II) sulfate as a reducing reagent, preliminary acidification of wastewater is not required, and only a slight excess of the reagent (about 5 % of the stoichiometric amount) is required for the complete reduction of Cr (VI) to Cr (III), regardless of the initial concentration of Cr (VI) in wastewater and the pH value [21]. According to the fertilization method, 3.12 mass parts of ferric (III) hydroxide precipitate are additionally formed per 1 mass part of chromium (III) hydroxide precipitate.

The catalyst was made from a sludge precipitate obtained by mixing the suspension with a reducing reagent and drying it in a vacuum drying oven SV-50 at a temperature of 150 °C for 4 hours. To shape the catalyst, the sludge powder was mixed with a suspension of a carrier and calcined for 4 hours in a muffle furnace SNOL 12/1300 I4A at a temperature of 700–750 °C.

The physical properties and elemental composition of the galvanic sludge were determined using gravimetric, thermal, complexometric, and photocolorimetric methods. The quantitative composition of the sludge, specifically the content of heavy metal ions, was determined using the polarographic method. The sludge composition was analyzed using an LP-9 polarographic analyzer. A schematic diagram of the pilot polarographic unit is shown in Figure 1.

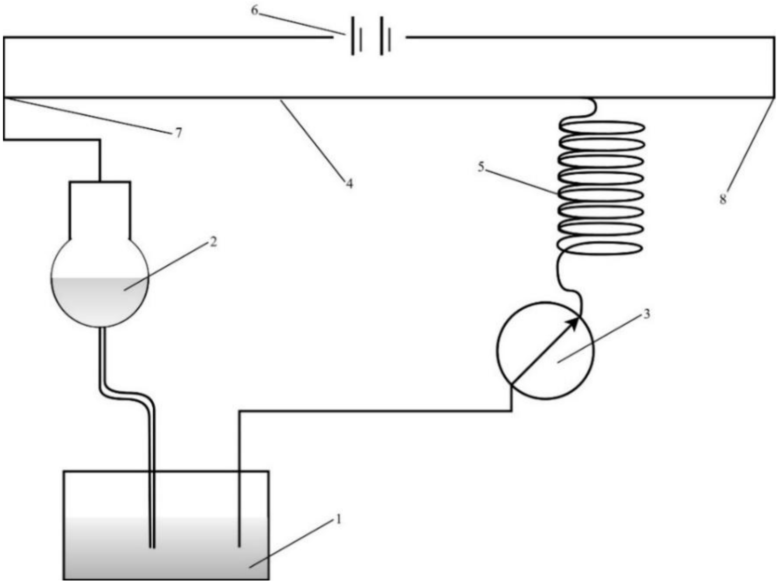

Fig. 1. Schematic diagram of a polarographic setup: 1 – electrolyser; 2 – mercury container; 3 – galvanometer; 4 – resistance wire; 5 – moving contact; 6 – battery; 7, 8 – ends of the resistance wire

The analysis was carried out by the addition method. First, a polarogram of the analyzed solution was taken, then a standard solution containing the ion to be determined was added dropwise to the same electrolyser with a precisely defined concentration so that the wave almost doubled. The polarogram was taken at the same sensitivity of the galvanometer and calculated according to the formula:

$$C_x = \frac{C_{st} \cdot V_{st}}{V_{st} + V_x} \cdot \frac{h_x}{h_{st} - h_x}, \quad (1)$$

where C_x is the concentration of the ion to be determined, mg/cm^3;
C_{st} is the initial concentration of the standard solution, mg/cm^3;
h_x is the wave height of the substance to be determined, mm;
V_{st} is the volume of the standard solution, cm^3;
V_x is the volume of the solution to be analyzed in the electrolyzer, cm^3;
h_{st} is the wave height of the standard solution, mm.

The catalytic activity of the catalyst obtained in this way was tested in the reactor of the laboratory-scale setup by conducting catalytic oxidation of hydrocarbon compounds in model gas mixtures.

Method for preparing model gas mixtures. The model gas mixtures are obtained by passing air through a bubbling vessel that has been pre-filled with ethanol, acetone, butanol or toluene. The concentrations of hydrocarbon compounds in the model mixtures ranged from 22 to 270 g/m^3.

Study of the kinetics of the catalytic oxidation of hydrocarbon compounds: The research was carried out using a laboratory-scale setup consisting of three main units:

- ✓ a unit for supplying air to the catalytic reactor,
- ✓ a unit for saturating the air with vapors of hydrocarbons (ethanol, acetone, butanol, toluene),
- ✓ and a unit for cleaning the exhaust gases.

The setup also included devices for sampling gas at the inlet and outlet of the catalytic reactor, as well as instruments for controlling the flow rate and temperature of the gas stream, and temperature within the reactor.

In the course of the study, in addition to the concentration of hydrocarbons in the model gas mixtures, the volumetric flow rate was varied within the range of 20–53 cm^3/s, and the temperature in the catalytic reactor was set to 350 °C, 370 °C, and 400 °C.

The degree of conversion of the hydrocarbon compounds over the catalyst was calculated using the formula:

$$X = \frac{C_{initial} - C_{final}}{C_{initial}} \times 100\%, \qquad (2)$$

where C_{int}, C_{final} are the initial and final concentrations of hydrocarbon compounds in the model gas mixtures, in g/m^3.

The experimental data were processed using applied software packages, including Microsoft Excel and CurveExpert 1.3.

Results and Discussion

The composition of the sludge waste was determined by polarographic analysis using a specific method. Firstly, the sludge is dried to a constant mass at t = 105–110 °C. A 1 g weight of dry sludge is dissolved in concentrated hydrochloric acid, the resulting solution is filtered and the filtrate is brought to a volume of 100 cm^3 with distilled water. The resulting solution is the stock solution, on the basis of which three model solutions are prepared and tested.

To prepare solution I, take 10 cm^3 of the initial solution, add 5 cm^3 of ammonia-buffered solution (pH = 10.0), filter and bring the filtrate to 25 cm^3 in a measuring flask with the same buffered solution.

To prepare solution II, take 1.0 cm^3 of the stock solution and add tartrate buffer solution (pH 7.0) to 25 cm^3 in a volumetric flask.

To prepare solution III, 0.1 cm^3 of the initial solution is required and made up to 25 cm^3 in a measuring flask with tartrate buffer solution (pH 7.0).

For polarography, 5.0 cm^3 of each solution is taken. The following 0.1 M solutions were used as standard solutions:

for the determination of Cu ions, $CuSO_4 \cdot 5H_2O$, $C_{st} = 6.4\ g/m^3$;

for the determination of Nickel ions, $NiCl_2$, $C_{st} = 5.8\ g/m^3$;

for the determination of Zinc ions, $ZnSO_4 \cdot 7H_2O$, $C_{st} = 6.5\ g/m^3$;

$Cr(NO_3)_3 \cdot 3H_2O$, $C_{st} = 5.2\ g/m^3$ was used for the determination of Chromium ions;

$FeCl_3$, $C_{st} = 5.6\ g/m^3$ was used for the determination of Ferric (III) ions.

The mass fraction of each component was calculated by the formula:

$$W(Me) = \frac{C_{st} \cdot V_{st}}{V_{st} + V_x} \cdot \frac{h_x}{h_{st} - h_x} \cdot \frac{S \cdot 25}{10}, \% \qquad (3)$$

where $S = \frac{V_{in}}{V_{al}}\ sm^3$

Two samples of sludge were subjected to the study. The results of the analysis and calculations for sludge sample 1 are shown in Tables 1 and 2.

Table 1

Results of the sludge study 1

Name of metal	Solution I			Solution II	Solution III
	Cu	Ni	Zn	Cr	Fe
Mass fraction (W), %	0.031	0.013	0.042	21.24	37.86
Sweep speed, Vp, MW/s	5	5	5	5	5
Differential pulse amplitude A, mV	50	50	50	50	50
Mercury column height h, cm	30	30	30	30	30
Input R, mV/cm	2	2	2	2	2

Table 2

Results of sludge 1 after addition of additives

General background	Ammonia buffer solution, pH=10.0			Tartrate buffer solution, pH=7.0	
Additive, cm^3	$CuSO_4 \cdot 5H_2O$ (0.1M); 0.02	$NiCl_2$ (0.1M); 0.02	$ZnSO_4 \cdot 7H_2O$ (0.1M); 0.05	$Cr(NO_3)_3 \cdot 9H_2O$ (0.1M); 0.1	$FeCl_3$ (0.1M); 0.01
Peak height h, mm	h_1= 19 $h_1/$ = 58	h_2 = 14.5 $h_2/$ =79	h_3 = 47.5 $h_3/$= 230	h_4 = 2.5 $h_{4\cdot}/$= 5.5	h_5 = 21 h_5 /= 36.5

The results of the analysis and calculations for sludge sample 2 are presented in Tables 3 and 4.

Table 3

Results of the sludge study 2

Name of metal	Solution I	Solution II	Solution III
	Zn	Cr	Fe
Mass fraction (W), %	1.1	6.06	87.13
Sweep speed, Vp, MW/s	5	5	5
Differential pulse amplitude A, mV	50	50	50
Mercury column height h, cm	30	30	30
Input R, mV/cm	2	2	2

Table 4

Results of sludge 2 after addition of additives

General background	Ammonia buffer solution, pH=10.0	Tartrate buffer solution, pH=7.0	
Additive, cm^3	$ZnSO_4 \cdot 7H_2O$ (0.1M); 0.01	$Cr(NO_3)_3 \cdot 9H_2O$ (0.1M); 0.5	$FeCl_3$ (0.1M); 0.01
Peak height h, mm	$h_1=10$ $h_1/=156$	$h_2=4$ $h_2/=82$	$h_3=44$ $h_3/=114$

The prepared sludge was studied experimentally for the possibility of catalytic mass formation. The sludge was washed with distilled water and dried to a constant mass at t°=105 °C (after the precipitation stage with a 20 % KOH solution) was analyzed using an LP-9 polarographic analyzer by the addition method.

For the analysis, 250 cm^3 of dry sludge precipitate is used, dissolved by heating in 2 cm^3 of hydrochloric acid and brought to 50 cm^3 in a measuring flask with distilled water. The resulting solution is the initial solution.

To prepare solution I, take 2 cm^3 of the initial solution, transfer to a 25 cm^3 volumetric flask and make up to the required volume with ammonia-buffered solution (pH = 10.0).

To prepare solution II, take 0.2 cm^3 of the initial solution, transfer to a 25 cm^3 volumetric flask and make up to the required volume with tartrate buffer solution (pH 7.0).

Each of these solutions is analyzed on an LP-9 polarographic analyzer. The results of the precipitate analysis are summarized in Tables 5 and 6 (precipitation pH = 8.0) and Tables 7 and 8 (precipitation pH = 10.0).

The qualitative composition of the precipitate calcined at t° = 450 °C was studied using the DRON-2.0 unit. The lines were interpreted according to the general method of interpreting powder radiographs.

The samples were radiography with CrK_2 radiation at λ=2.29092 Å using a vanadium β-filter. Radiography diffraction conditions: anode current I_a = 30 mA; anode voltage U_a = 30 mV; slits: vertical – 6 mm, Soller – 2.5 mm, horizontal – 2 mm; horizontal input – 0.5 mm, Soller input – 2.5 mm, analytical – 10 mm.

Table 5

Results of the sludge sludge study (sludge pH = 8.0)

Name of metal	Solution I			Solution II	
	Cu	Ni	Zn	Cr	Fe
Mass fraction (W), %	0.016	0.09	0.20	14.13	69.67
Sweep speed, Vp, MW/s	5	5	5	5	5
Differential pulse amplitude A, mV	50	50	50	50	50
Mercury column height h, cm	30	30	30	30	30
Input R, mV/cm	2	2	2	2	2

Table 6

Results of the sludge sludge study (sludge pH = 8.0) after adding additives

General background	Ammonia buffer solution, pH=10.0			Tartrate buffer solution, pH=7.0	
Additive, cm^3	$CuSO_4 \cdot 5H_2O$ (0.01M); 0.02	$NiCl_2$ (0.01M); 0.03	$ZnSO_4 \cdot 7H_2O$ (0.01M); 0.01	$Cr(NO_3)_3 \cdot 9H_2O$ (0.1M); 0.06	$FeCl_3$ (0.1M); 0.01
Peak height h, mm	$h_1=11$ $h_1/=54$	$h_2=4$ $h_2/=42$	$h_3=65$ $h_3/=173$	$h_4=11$ $h_4/=23$	$h_5=57$ $h_5/=80$

Table 7

Results of the sludge sludge study (sludge pH = 10.0)

Name of metal	Solution I			Solution II	
	Cu	Ni	Zn	Cr	Fe
Mass fraction (W), %	0.22	0.07	0.14	11.93	67.07
Sweep speed, Vp, MW/s	5	5	5	5	5
Differential pulse amplitude A, mV	50	50	50	50	50
Mercury column height h, cm	30	30	30	30	30
Input R, mV/cm	2	2	2	2	2

Table 8

Results of the sludge sludge study (sludge pH = 10.0) after adding additives

General background	Ammonia buffer solution, pH=10.0			Tartrate buffer solution, pH=7.0	
Additive, cm^3	$CuSO_4 \cdot 5H_2O$ (0.1M); 0.01	$NiCl_2$ (0.1M); 0.01	$ZnSO_4 \cdot 7H_2O$ (0.1M); 0.01	$Cr(NO_3)_3 \cdot 9H_2O$ (0.01M); 0.05	$FeCl_3$ (0.1M); 0.01
Peak height h, mm	$h_1=18$ $h_1/=285$	$h_2=6$ $h_2/=240$	$h_3=26$ $h_3/=640$	$h_4=25$ $h_4/=52$	$h_5=72$ $h_5/=102$

The analysis of the sludge for metal content showed that its composition corresponds to the presence of metals in the iron-chromium catalyst STK-1, taken as a reference, intended for the purification of waste gases from thermal power plants, non-ferrous and ferrous metallurgy enterprises, sulfuric acid plants and pulp sulfate production from sulfur-containing compounds by oxidation. In terms of mass metal content, the sludge obtained at a pH of 8.0 is closer to the industrial STK-1. Table 9 shows a comparative technical characteristic of the properties of the STK-1 catalyst and the studied (sludge) catalyst (at pH = 8).

Table 9

Comparative technical characteristics of the studied catalysts

Indicator	Catalyst STK-1 [22]	The resulting (sludge) catalyst (at pH=8)
Mechanical strength, MPa,	1.5	2.0
Bulk density, kg/м^3	1.7	1.1
Specific surface area, m^2/m^3	25-30	28
Porosity, %	45-50	42

The resulting catalyst was subjected to pressing and tableting after drying the slurry. These processes took place on stationary laboratory presses under a pressure of up to 30 MPa. Depending on the shape of the press matrix, catalyst granules were obtained in the form of cylinders or tablets.

Figure 2 shows the appearance of the resulting slurry powder after calcination before the micro-press tableting step.

Fig. 2. The resulting iron-chromium catalyst before the grinding and tableting stage

In order to test the activity of an iron-chromium catalyst obtained from electroplating waste, a pilot plant was set up (Fig. 3) and a number of studies were conducted.

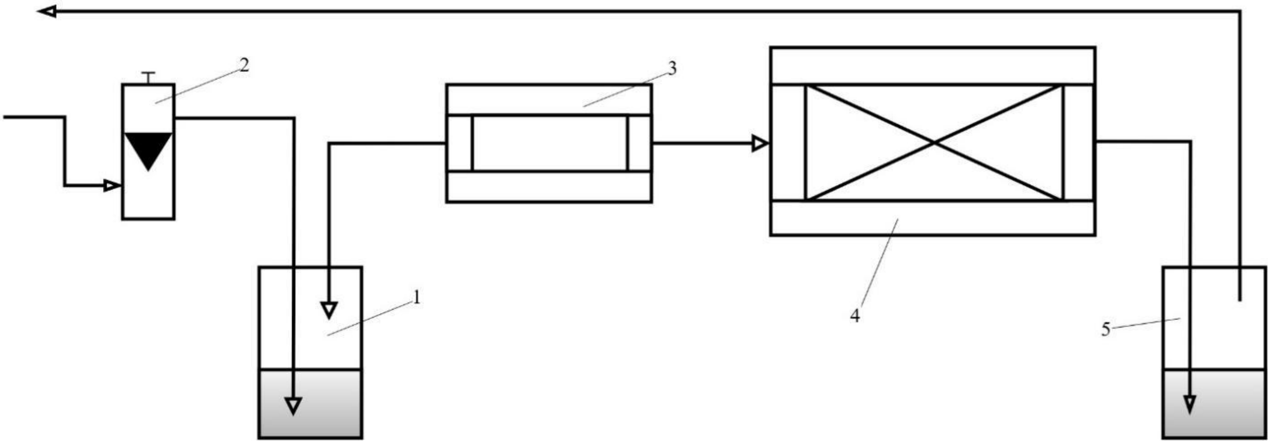

Fig. 3. Schematic diagram of a pilot plant for determining the activity of an iron-chromium (sludge) catalyst: 1 - rotameter; 2 - container for obtaining a gas-air mixture; 3 - tubular heater; 4 - catalytic reactor; 5 - drexel

The scheme includes a system of shut-off valves and pipelines connecting the flow meter, bubbling tank, tube heater, catalytic reactor, and drexel. The principle of operation of the pilot plant is as follows. Compressed air is supplied through the pipeline to the rotameter RM-4 of the GUS (1), from where, after setting the required carrier (air) flow rate, it enters the bubbling tank (2), which contains a mixture of solvents (ethanol, acetone, butanol, toluene) in the amount of 150–200 cm^3. The air passing through the organic solvents is saturated with their vapours.

At the outlet of the tank (2), samples are taken to determine the initial concentration of organic solvent vapours. The vapours are fed into a tube heater (3), which is a tubular furnace with a glass tube filled with ceramics for better heat exchange between the surface to be heated and the vapour-air mixture. The steam-air mixture passes through the tube heater and is heated to 300–350 °C. The heating temperature of the tube furnace is regulated by a 10A 50Hz regulated transformer LATR 220-127. The temperature of the steam-air mixture is monitored at the outlet of the tube furnace using a mercury thermometer with a maximum measuring temperature of 800 °C. The steam-air mixture heated in this way enters the catalytic reactor (4) filled with a tableted iron-chromium catalyst. The catalytic reactor is a tubular furnace into which a quartz tube with a catalyst is inserted. A quartz pocket is soldered into the quartz tube, in which a thermocouple is placed to measure the contact temperature. The catalyst is heated to its ignition temperature (up to 250–300 °C). Due to the exothermic nature of the catalytic oxidation reaction, the temperature in the reaction zone rises to 400–450 °C. Temperature control is carried out by switching on (off) the heater SUOL-0.25.1/12-M1 heater according to the established mode and an alumina thermocouple located in a quartz pocket in the catalysis zone. The temperature is controlled by a mercury thermometer with a maximum measurement temperature of 800 °C. At the outlet of the catalytic reactor, samples are taken to determine the concentration of organic solvent vapour after purification. The purified gas passes through a drexel (5) and is discharged into the atmosphere. To set the flow rate, a drum gas meter with a liquid shutter (type GSB-400 class 1) was used.

The studies involved varying two main parameters: the temperature in the catalysis zone (350 °C, 370 °C, and 400 °C), and the volumetric flow rate of the vapor-gas mixture in the catalytic reactor (720 h^{-1}, 1300 h^{-1}, and 1900 h^{-1}). The degree of conversion was calculated based on the measured concentrations of hydrocarbons in the gas mixture before and after passing through the catalytic reactor.

Guided by the physicochemical foundations of the kinetic laws of heterogeneous catalysis reactions and the practical results of the studied industrial catalyst brands [23–28], the kinetic laws of the catalytic conversion of hydrocarbon compounds were obtained in the present work, which are presented in the form of graphical dependencies for each model of the gas mixture; the results obtained were analyzed.

Figures 4 and 5 show the kinetics of ethanol catalytic oxidation.

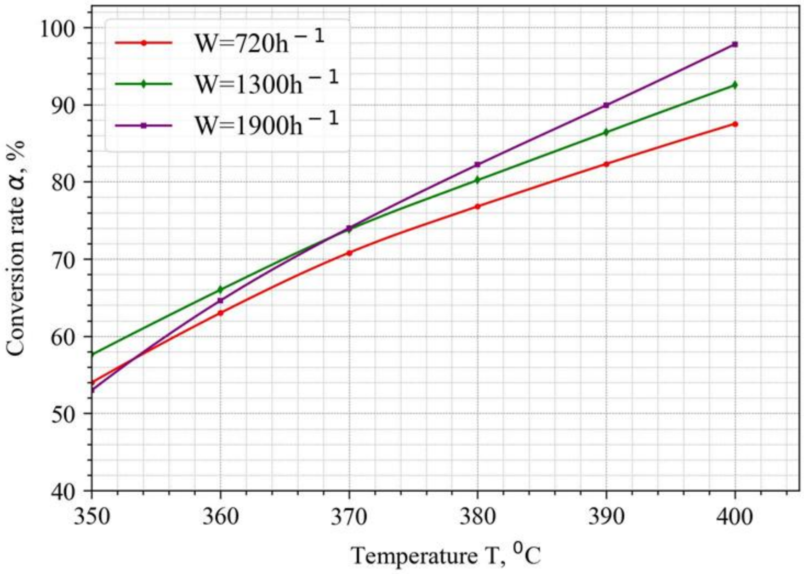

Fig. 4. The duration of changing the ethanol conversion stage due to changing the temperature in the catalysis zone and the volumetric fluidity of the gas flow w

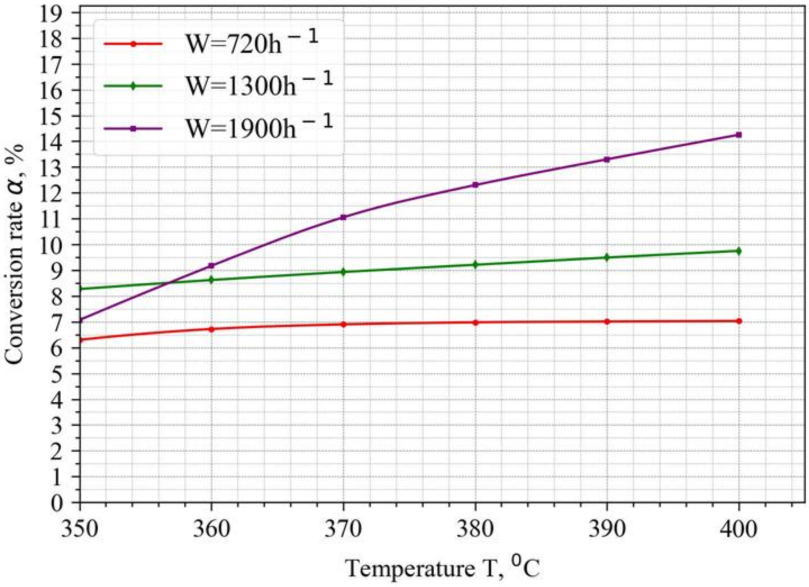

Fig. 5. The importance of changing the fluidity of the reaction of catalytic oxidation of ethanol due to changes in temperature in the catalysis zone and volumetric fluidity of the gas flow w

The nature of the curves in the graphs suggests that the degree of ethanol conversion increases steadily with rising catalytic temperature. At a temperature of 350 °C and a gas flow rate of 720 h^{-1}, the conversion degree was 53.8 %, while at 370 °C and 400 °C, it reached 70.5 % and 86.7 %, respectively. This indicates that the catalytic conversion of ethanol over the catalyst derived from galvanic production sludge generally follows the typical principles of hydrocarbon catalysis.

At lower temperatures (350 °C), the reaction rate is significantly lower than the rate of ethanol diffusion to the catalyst surface, resulting in no substantial concentration gradient of reactants and products within the catalyst granules or in the gas stream. This also demonstrates that diffusion processes under these conditions do not significantly affect the rate of chemical transformations. Under such conditions, the activation energy remains constant, and the catalytic process occurs in the kinetic region, which is reflected in the nearly linear shape of the reaction rate curves.

The same trend is observed for curves 6 and 7, corresponding to gas flow rates of 1300 h^{-1} and 1900 h^{-1}, respectively. A further increase in temperature from 350 °C to 370 °C and 400 °C introduces changes in the reaction process.

As the temperature increases, the reaction rate grows, but the diffusion rate increases at a slower pace. This leads to a situation where diffusion is no longer sufficient to maintain a uniform composition of the reaction mixture across the catalyst grain depth, and as a result, the process transitions into the internal diffusion regime. In this regime, the apparent activation energy decreases compared to that in the kinetic region. This transition is clearly seen in the deviation of the curve shapes from a linear trajectory.

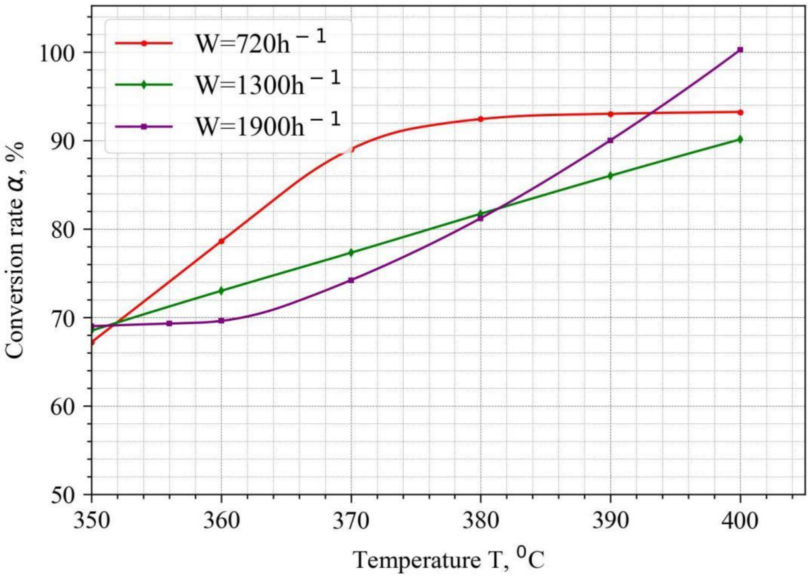

Fig. 6. Dependence of the change in the degree of acetone conversion under conditions of temperature change in the catalysis zone and the volume velocity of the gas flow w

The kinetics of acetone catalytic oxidation is presented in Figures 8 and 9. The character of the curves in Figure 6 demonstrates that the molecular structure of the hydrocarbon compound can significantly influence the catalytic process. A sharp increase in the degree of acetone conversion with rising temperature from 350 °C to 370 °C can be explained by the adsorption of acetone molecules on the catalyst surface, followed by dehydrogenation of the hydrocarbon and bond weakening due to molecular polarization, occurring at 350 °C and low gas flow rates.

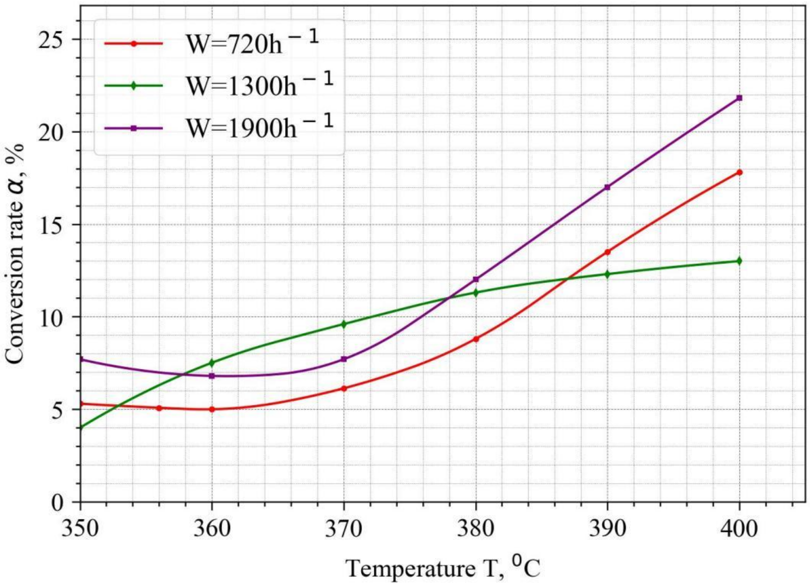

Fig. 7. Dependence of the change in the rate of the catalytic oxidation reaction of acetone under conditions of temperature change in the catalysis zone and the volumetric velocity of the gas flow w

This preparatory stage, intensified by the temperature increase, leads to a sharp rise in the rate of chemical reactions. With a further temperature increase to 400 °C, the conversion of acetone stabilizes due to the reduced concentration of reactants in the catalysis zone and gradually reaches a maximum degree of 90.3 %, despite the fact that the reaction rate continues to increase and reaches its peak at this temperature.

At a higher volumetric flow rate of 1300 h^{-1}, the influence of acetone molecule adsorption and subsequent dehydrogenation on the catalyst surface becomes less significant. Under such conditions, the activation energy remains constant, and the catalytic process proceeds within the kinetic region. This is reflected in the nearly linear shape of the curve for the gas flow rate of 1300 h^{-1} shown in Figure 6.

The adsorption of acetone molecules, dehydrogenation of hydrocarbons, and bond weakening due to molecular polarization is also observed at 350 °C when the volumetric gas flow rate is increased to 1900 h^{-1}. This preparatory stage, enhanced by temperature elevation, again leads to a sharp increase in reaction rate, similar to the behavior observed at 720 h^{-1}. However, at this higher flow rate, gas turbulence begins to occur, which significantly intensifies diffusion processes. As a result, under these conditions, the acetone conversion reaches 99.2 %. This conclusion is also supported by the achievement of the maximum reaction rate at a temperature of 400 °C and a volumetric gas flow rate of 1900 h^{-1}.

Figures 8 and 9 illustrate the kinetics of butanol oxidation on the catalyst produced from galvanic sludge.

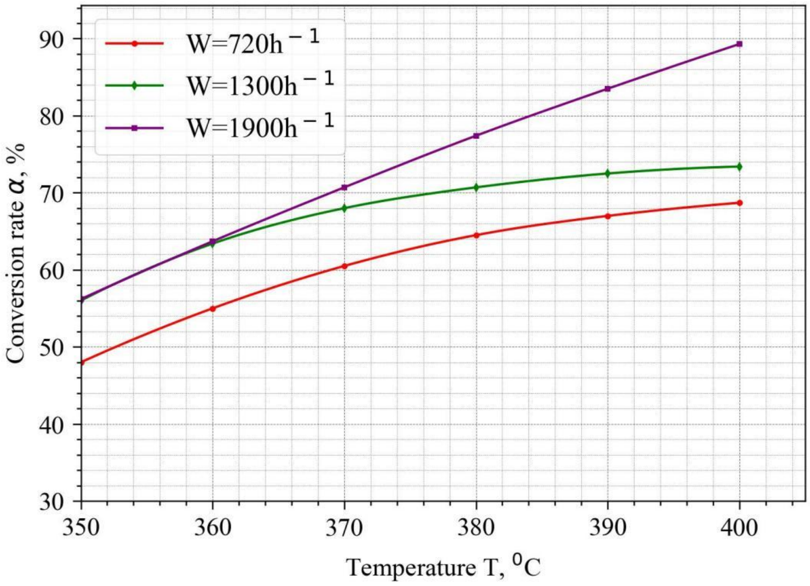

Fig. 8. Dependence of the change in the degree of butanol conversion under conditions of temperature variation in the catalysis zone and volumetric gas flow rate w

Given that butanol belongs to the same class of organic compounds as ethanol (alcohols), the character of chemical processes on the catalyst is similar. The optimal conditions for the catalytic conversion of butanol on the iron-chromium catalyst produced from galvanic sludge waste were found to be a temperature of 400 °C and a volumetric gas flow rate of 1900 h^{-1}, under which the maximum conversion degree of 90 % was achieved.

The slightly lower maximum conversion degree of butanol on this catalyst compared to ethanol can be explained by the fact that, unlike ethanol, butanol can exist in several isomeric forms: n-butanol, sec-butanol, isobutanol, and tert-butanol. Each isomer has its own structural formula, and the mechanism of their decomposition on the catalyst surface differs. All of this requires greater energy input for the reaction to proceed effectively.

Figures 10 and 11 present the results of studies on the catalytic purification of gas from toluene.

Toluene belongs to a class of organic compounds known as arenes (aromatic hydrocarbons). It is characterized by electrophilic substitution reactions in the aromatic ring and radical substitution in the methyl group. These properties of toluene introduce specific features into the course of chemical processes occurring in the catalysis zone.

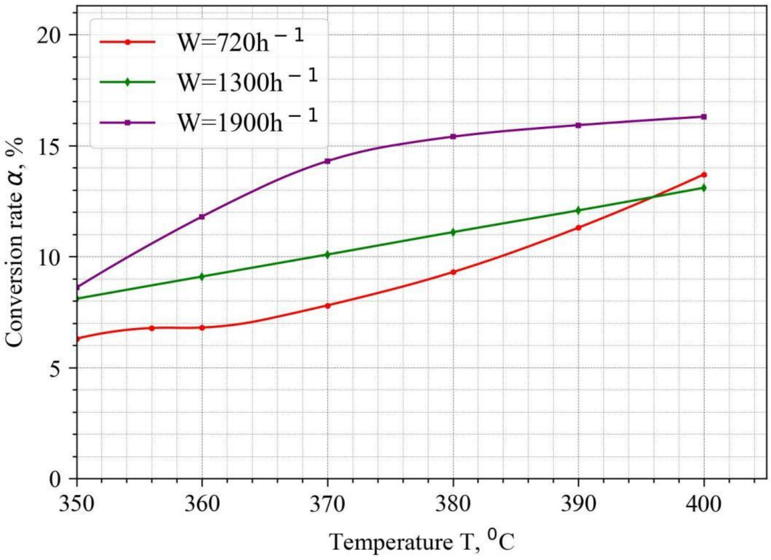

Fig. 9. Dependence of the change in the rate of the catalytic oxidation of butanol reaction under conditions of temperature change in the catalysis zone and the volumetric velocity of the gas flow w

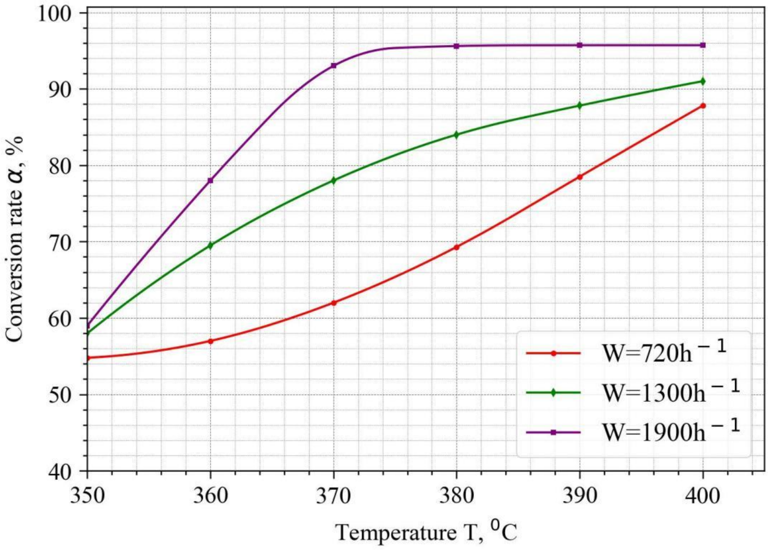

Fig. 10. Dependence of the change in the degree of conversion of toluene under conditions of temperature change in the catalysis zone and the volumetric velocity of the gas flow w

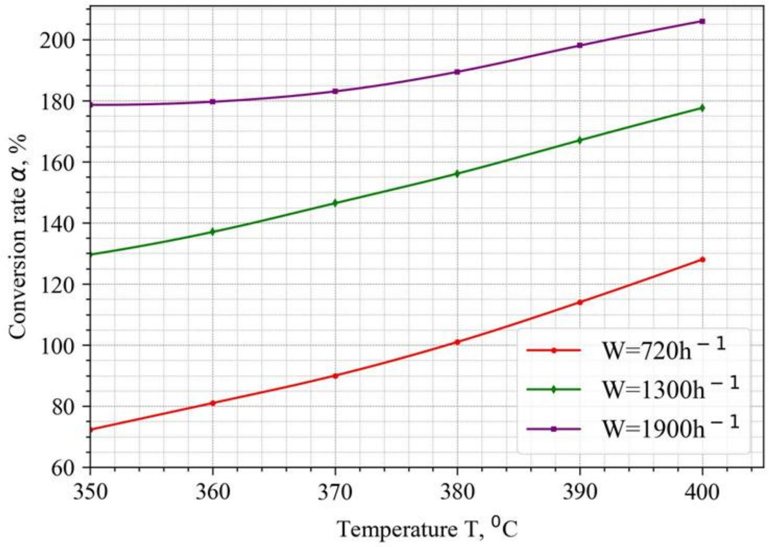

Fig. 11. Dependence of the change in the rate of the catalytic oxidation of toluene reaction under conditions of temperature change in the catalysis zone and the volumetric velocity of the gas flow w

Similar processes have been studied by other researchers. According to the authors of [28], at temperatures above 300 °C, the oxidation of unsaturated hydrocarbons on catalysts is limited by the increase in π-electron density at the reactive bond. They also note that an essential feature of the coupled oxidation mechanism is that the presence of oxygen in the reaction mixture can both increase the rate of oxidative decomposition of carbonate structures and significantly reduce their thermal stability, shifting the reaction toward lower temperature regions.

It has also been demonstrated that in the presence of oxygen, oxidation reactions proceed via a coupled electron transfer mechanism, involving the cleavage of bonds in the surface complex with the catalyst, which contributes to a reduction in hydrocarbon concentration. This facilitates the activation of hydrocarbons due to their greater tendency for electron-acceptor interactions compared to oxides. The electronic nature of the initial interaction between hydrocarbons and the catalyst surface determines the high reaction rates, reduced activation energy, and lower temperature thresholds of the process.

This oxidation mechanism can indeed be taken as a basis when interpreting the experimental data on the catalytic oxidation of toluene. The graphical dependencies shown in Figure 10 support the authors' [28], conclusions, indicating that the conversion degree of toluene increases with rising temperature in the catalysis zone. This confirms that the process is facilitated by the enhanced dissociation of the hydrocarbon–catalyst surface complex, resulting in a decrease in hydrocarbon concentration.

The graphical dependencies presented in Figure 11 also clearly demonstrate a consistent increase in the reaction rate of toluene oxidation in the catalysis zone as both temperature and volumetric gas flow rate increase.

When comparing the experimental data on the degree of oxidation of organic compounds in the obtained sludge catalyst and the comparison catalyst STK-1, it can be noted that at the same temperatures and volumetric rates, the performance of the experimental catalyst is 1.5–2.5 % higher. This trend is observed for all organic compounds. This fact can be explained by the fact that the composition of the sludge catalyst during precipitation from wastewater included cations of Copper, Nickel, Zinc in the form of oxides and hydroxides, which play the role of promoting additives.

Conclusions

As a result of the conducted research, a method for producing an iron-chromium catalyst from galvanic sludge of the Instrumentation Plant in Cherkasy (Ukraine) was developed for the first time, and the catalyst was successfully fabricated.

The results of the polarographic analysis showed that the proposed method of sludge processing results in almost complete utilization of galvanic waste.

A basic technological scheme of a pilot plant for determining the activity of an iron-chromium (sludge) catalyst was created, which makes it possible to effectively use a catalyst with such properties for the neutralization of organic vapours.

The activity of the catalyst in the oxidation of such hydrocarbon compounds as ethanol, acetone, butanol and toluene was tested in a laboratory pilot plant.

The catalytic activity of the obtained material was tested on a laboratory-scale experimental setup for the oxidation of hydrocarbon compounds such as ethanol, acetone, butanol, and toluene.

Experimental results demonstrated that the catalytic oxidation mechanism of these hydrocarbons is comparable to that observed in previous studies conducted by other authors using commercial catalyst grades.

The optimal process conditions for the catalytic oxidation of ethanol, acetone, butanol, and toluene over the catalyst derived from galvanic sludge were determined experimentally:

- ✓ temperature in the catalysis zone: 400 °C,
- ✓ volumetric gas flow rate: 1900 h^{-1}.

The achieved conversion degrees were:

- ✓ ethanol – 97.1 %;
- ✓ acetone – 99.2 %;
- ✓ butanol – 90 %;
- ✓ toluene – 95.7 %.

Following successful industrial trials, the synthesized catalyst can be recommended for use in gas purification units aimed at removing organic compounds from industrial emissions.

The developed method of sludge processing can be recommended for implementation in enterprises that have a similar composition of sludge after treatment of wastewater from electroplating shops.

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