

COMPOSITION AND ACTIVITY OF COPPER-PALLADIUM CATALYST ON CARBON FIBER MATERIAL FOR AIR PURIFICATION FROM CARBON MONOXIDE

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Abstract. A set of research methods (X-ray phase, desorption, kinetic) was used to determine the state of the basic components K_2PdCl_4 and $Cu(NO_3)_2$ in the catalyst for the oxidation of carbon monoxide by oxygen. It was found that the palladium (II) and copper (II) initial compounds under the action of carbon fiber carrier change their state. Palladium is reduced to X-ray amorphous Pd^0 , and copper (II) is in the form of a crystalline phase $Cu_2(OH)_3Cl$. It was found that the catalyst exhibits protective properties within the initial concentrations of carbon monoxide $\leq 300 \text{ mg/m}^3$ and an effective contact time of 0.45 s and can be used in human respiratory protection.

Keywords: carbon monoxide, carbon fiber materials, catalysts, oxidation, respiratory devices.

1. Introduction

Carbon monoxide (CO) is a colorless and odorless gas, so it is often called the “invisible killer”. According to sanitary norms, the maximum permissible concentration of carbon monoxide (MPC_{CO}) in the air of the working area is 20 mg/m^3 (Ukraine), or 35 mg/m^3 (USA). As there are industrial sources of air pollution, there is a need for employees to use personal respiratory protective equipment (RPE) against CO and other related toxic gases. In such devices, as a rule, a multi-stage scheme of air purification is carried out at the final stage, which is the carbon monoxide catalytic oxidation by air oxygen.^{1,2}

Despite the fact that in recent years a large number of scientific publications have appeared in the field of the

catalysts development for CO low-temperature oxidation, the analysis of which is presented in our works,³⁻⁵ only some catalysts and RPE have practical applications.⁶⁻⁸ Among them, a catalyst of the hopcalite type, which consists of Mn(IV) and Cu(II) oxides, and new generation catalysts with a high content of platinum or palladium Pt(Pd)/ SnO_2 , and gold-containing catalysts 1 % Au/ TiO_2 , 0.57 % Au/ TiO_2/AC . Despite the significant disadvantages, the hopcalite catalyst is mainly used for RPE equipment due to its low price and relatively simple technology. There is no doubt that among known catalysts, nanocatalysts containing Au and Pt show the greatest activity. At low values of the effective contact time (0.04-0.156 s), these catalysts provide a 100 % degree of CO conversion.⁷ It should be noted that nanocatalysts are obtained using complex technologies and they may lose their activity as a result of the agglomeration of the nanoparticles. The third group includes Wacker-type CO oxidation catalysts, which contain palladium(II) and copper(II) salts in their composition, deposited on various carriers (Al_2O_3 , SiO_2 , AC, zeolites, bentonites, palygorskite, *etc.*).^{1,5} The activity of these catalysts is regulated by changing the precursors of palladium and copper, additives of other salts, the nature of the carrier, and the method of the catalyst preparation. Despite a large number of Wacker-type catalysts, only LT-CAT, which is a composition of $PdCl_2-CuCl_2(NiCl_2)/Al_2O_3$, is recommended by MST (USA) as a commercial product for equipping portable small-sized units.⁶ The LT-CAT catalyst is characterized by multifunctionality and provides air purification not only from CO, but also from O_3 , H_2S , SO_2 , and NO_2 . Unfortunately, in the cited work, the LT-CAT catalyst was tested only at $C_{CO} = 12 \text{ mg/m}^3$ and compared to other catalysts, it is characterized by the lowest activity: LT-CAT < Carulite Dräger < STC < NOVAX. It follows from the patent sources that the catalyst, which is a Pd(II) salt, Ni(II), Cu(II) halides, and copper(II) sulfate, deposited on Al_2O_3 , at $C_{CO} = 130 \text{ mg/m}^3$ and a contact time of 0.10-0.43 s provides CO conversion degree of 54-93 %. Another catalyst¹ containing 0.8 % $PdCl_2$ (converted to palladium), 10 % $CuCl_2$ and Al_2O_3 carrier at $C_{CO} = 6250 \text{ mg/m}^3$ and

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$\tau_{ef} = 1.2$ s and provides 100 % air purification from carbon monoxide. For the last 10-15 years our studies⁹⁻¹¹ were devoted to the kinetics of CO oxidation by oxygen in the presence of catalysts $K_2PdCl_4-Cu(NO_3)_2-KBr/\mathbb{S}$, where \mathbb{S} are the original and modified in various ways natural materials (clinoptilolite (Cl), mordenite (Mord), bentonite (Bent), trepel (Tr), basaltic tuff (BT)). Among the listed catalysts, only two catalysts based on acid-modified clinoptilolite and trepel are used in RPE.²

Thus, research that will contribute to the creation of new low-temperature carbon monoxide oxidation catalysts for equipping multifunctional respiratory devices is relevant. Wacker-type catalysts are promising for solving problematic issues in this area. The advantages include the ability to vary the activity of the catalyst by changing the nature of the carrier provided the basic components are the same, as well as a simplified production technology. It was established that the carrier not only affects the equilibria of surface complex formation,^{1,2} but also changes the degree of palladium oxidation and the phase state of the copper(II) salt.¹²⁻¹⁷ Due to the presence of many factors that affect the activity of Pd(II)-Cu(II)/ \mathbb{S} (\mathbb{S} – carriers of different origin) catalysts, there is a need to optimize the properties of the carrier, the method of obtaining and determining the operational characteristics of the catalyst in RPE.

The purpose of the work is to investigate the influence of non-woven carbon fiber material on the state of the catalyst basic components - palladium(II) and copper(II) salts and the influence of other factors on the protective properties of carbon monoxide oxidation catalyst.

2. Experimental

In the work, non-woven carbon fiber material (CFM) Carbofon B-Active-200-65-A, which precursor was hydrated cellulose, was used as a carrier of the basic components of the Wacker-type CO oxidation catalyst, namely K_2PdCl_4 , $Cu(NO_3)_2$, and KBr. Table 1 summarizes the CFM technical specifications provided by the supplier SvitlogorskKhimvolokno, belarus.

Table 1. Technical characteristics of non-woven CFM Carbofon

Characteristics	Value
Surface density, g/m^2	145
Bulk density, g/dm^3	81
Thickness, mm	1.9
Adsorption activity by MB *, mg/g	370
The maximum volume of sorption space for benzene vapors, cm^3/g	0.56
Mass fraction of ash, %	3.4

MB * – methylene blue

The CFM carrier was pre-dried at $T = 383$ K to a constant mass. The carrier weighing 0.5–2.5 g was impregnated according to its moisture content with a water-alcohol solution containing precursors of palladium and copper in the form of K_2PdCl_4 , $Cu(NO_3)_2$, and the auxiliary component KBr in given ratios. The ratio of the solid phase to the liquid phase was 1:10. The concentration of the initial solutions was: for palladium(II) – $16.95 \cdot 10^{-2}$ mol/L; for copper(II) – 1.17 mol/L; for bromide ions – 2.0 mol/L. The wet mass was kept in a closed Petri dish under conditions of 293–298 K for 20-24 h, then dried in an oven in air at 383 K to a constant mass. The samples were cooled in a desiccator to room temperature. The content of the catalyst components in the samples was constant and consisted of: $C_{Pd(II)} = 1.7 \cdot 10^{-4}$; $C_{Cu(II)} = 4.68 \cdot 10^{-4}$; $C_{Br^-} = 6.0 \cdot 10^{-4}$ mol/g. The catalyst was conventionally designated Pd(II)-Cu(II)/CFM.

X-ray phase analysis was carried out on a Siemens D500 powder diffractometer in a copper radiation with a graphite monochromator on the secondary beam. To record diffraction patterns, samples after grinding in a mortar were placed in a glass cuvette with a working volume of $2 \times 1 \times 0.1$ cm^3 . Diffractograms were measured in the range of angles $3^\circ < 2\theta < 70^\circ$ with a step of 0.03° and an accumulation time of 60 s at each point.

Desorption of Pd(II) and Cu(II) from compositions prepared on the basis of carbon fiber material was carried out by the elution method under static conditions. Distilled water, HCl or HNO_3 acids were used as eluents. Aqua regia, a mixture of concentrated acids HCl and HNO_3 in a ratio of 3:1 was used for the desorption of palladium. Desorption was carried out at temperatures of 293 K, 373 K, the contact time of the sample with the desorbent was 90 and 10 min. The content of Pd(II) and Cu(II) in the solutions was determined by the atomic absorption method using an atomic absorption spectrophotometer AAS-1N of Carl Zeiss Jena (Germany). The determination was made using the flame version of the method (propane-butane-air). In order to eliminate the interfering effect of the matrix components of the solution, the additive method with a background correction was applied. In particular, the wavelength of resonance radiation during measurement of the palladium concentration was equal to 247.6 nm with the background correction at $\lambda = 246.7$ nm, and determination of copper concentration was carried out at $\lambda = 324.8$ nm with the background correction at $\lambda = 323.1$ nm. The error of determination of Pd(II) and Cu(II) was ± 5 %.

Catalyst samples were tested in a flow-through gas thermostated at 293 K installation in an “along” type reactor with a fixed catalyst layer provided that:

– initial CO concentration, mg/m^3 – 50; 100; 200; 300;

- volume flow rate of GAM, L/min – 1.0;
- GAM linear speed, cm/s – 2.1;
- the diameter of the “along in the light” (working zone), cm – 3.5;
- catalyst mass, g – 0.5; 1.0; 1.5; 2.0; 2.5;
- temperature, K – 293;
- relative humidity, % – 65.

Taking into account the criteria in the “along” type reactor, regimes of ideal displacement and the course of the process in the kinetic region are realized. The conditions of absence of elongated diffusion are fulfilled. $\bar{d}_f/h \ll 1$ ($\bar{d}_f = 6 \cdot 10^{-6}$ m – average width of elementary fiber,¹⁸ $h = 1 \cdot 10^{-2}$ m – the height of the catalyst layer) and the lack of wall effect $d_r/\bar{d}_f \geq 30$ ($d_r = 3.5 \cdot 10^{-2}$ m – the inner diameter of the reactor). When varying the linear speed from 2.1 to 5.3 cm/s, the degree of CO conversion almost does not change.

GAM with a given concentration of CO was obtained by a diluting concentrated gas (98-99 vol. % CO) with purified air to the required concentration of 50; 100; 200; 300 mg/m³. The initial (C_{CO}^{in}) and final (C_{CO}^f) concentrations of carbon monoxide were determined using a gas analyzer 621EX04 (“Analitprilad”, Ukraine) with a sensitivity of 2 mg/m³.

The degree of conversion of CO in the stationary mode (η_{st}) was calculated according to:

$$\eta_{st} = \frac{(C_{CO}^{in} - C_{CO}^f)}{C_{CO}^{in}} \cdot 100, \%$$

3. Results and Discussion

3.1. X-Ray Phase Analysis

On the basis of the diffractogram of the Pd(II)-Cu(II)/CFM sample (Fig. 1), the following conclusions can be drawn: i) next to amorphous carbon, there are graphitized fibers, for which reflections [002] and [001] are indicative;¹⁹ ii) reflexes at $2\theta = 16.2^\circ$, 32.1° , 39.8° and 53.5° refer to the paratacamite $Cu_2(OH)_3Cl$ phase [IPCDs 25-1427]; iii) there is no reflection of any palladium salt forms, Pd or PdO, which may indicate a high level of their dispersion on the CFM surface, or their content is below the limit of detection by XRD. The obtained results correlate with the data of the authors,¹⁷ which relate to the identification of the $Cu_2(OH)_3Cl$ phase. At the same time, there is a possibility of the presence of a PdO phase on Busofit brand CFM.¹⁷ The authors did not detect any of the crystalline forms of palladium PdO, or Pd⁰, or PdCl₂ in the PdCl₂-CuCl₂/Al₂O₃ catalyst,²⁰ at the same time, the $Cu_2(OH)_3Cl$ phase is present in samples with the in-

creased moisture content. Paratacamite phase is formed on the basic centers of the carbon carrier²¹ provided that the pH value of the hydrated surface layer is increased, which in the case of CFM is 7.63.

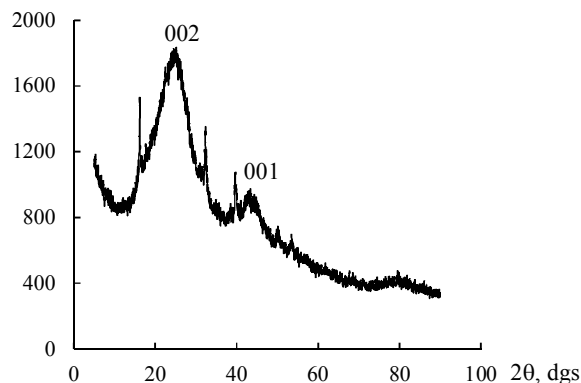


Fig. 1. Catalyst sample diffractogram Pd(II)-Cu(II)/CFM

3.2. The Influence of Order of the Catalyst Components Application on Its Activity in the Reaction of CO Oxidation by Air Oxygen

The order of application of catalyst components can affect its activity. One- and two-stage impregnation was used in the work. In the first case, all components of the catalyst K_2PdCl_4 - $Cu(NO_3)_2$ - KBr /CFM (1) are applied from a water-alcohol solution simultaneously. In the second method, the catalyst components are applied separately: K_2PdCl_4 / $Cu(NO_3)_2$ - KBr /CFM (2); $Cu(NO_3)_2$ / K_2PdCl_4 - KBr /CFM (3); KBr / K_2PdCl_4 - $Cu(NO_3)_2$ /CFM (4).

Tests of samples 1-4 in the reaction of carbon monoxide oxidation with air oxygen (Fig. 2) showed that the profile of the kinetic curves does not depend on the method of application of the catalyst components: the final concentration of CO at the reactor outlet increases and becomes constant after about 40-50 min. The stationary mode of the reaction is maintained for a long time, which is a necessary condition for the use of the catalyst in respiratory devices. The degree of CO conversion in the stationary mode, although insignificant, depends on the order of application of the catalyst components. In the case of separate deposition of K_2PdCl_4 and $Cu(NO_3)_2$ (curves 2 and 3), C_{CO}^f in the stationary mode decreases, compared to the catalyst obtained in one stage (curve 1). In the case of a separate application of KBr, C_{CO}^f in the stationary increases (curve 4).

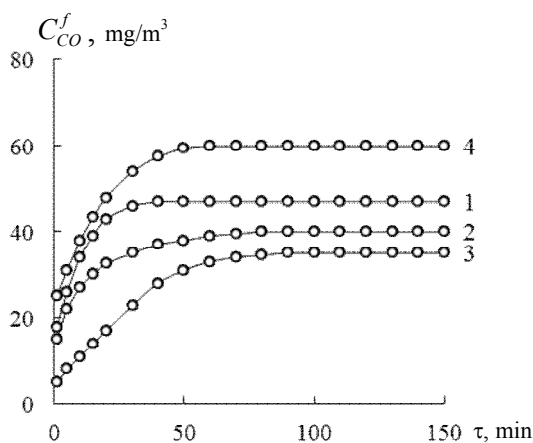


Fig. 2. C_{CO}^f change in time during carbon monoxide oxidation by oxygen in the presence of catalysts obtained by single-stage (1) and separate (2-4) impregnation methods

3.3. The state of the basic components in the Pd(II)-Cu(II)/CFM catalyst

To determine the state and relative strength of the connection of the catalyst components with the carbon surface, a simple chemical method was used, based on the desorption of the catalyst components by various eluents and comparing the activity of the catalyst model sample with the activity of the control sample.^{22,23}

Table 2 summarizes the results of palladium and copper desorption from samples containing only palladium (No. 1) or copper (No. 2), as well as both components together (No. 3).

Analysis of palladium desorption data leads to the following conclusions:

- palladium is not desorbed by water from the samples No. 1 and No. 3;

- the degree of desorption of palladium by HCl acid is only 0.4 % for composition No. 1 and increases for composition No. 3;

- with the use of aqua regia, the extraction degree of palladium is 55.5 % at 293 K and 58.4 % at 373 K.

The obtained data indicate that the initial complex forms of palladium(II), when applied to a carbon surface, are reduced to Pd⁰, which is held fairly firmly by the surface (it is not desorbed by water and HCl) and dissolves in aqua regia, oxidizing to palladium(II), its content in the solution was determined by the AAS method. Apparently, the degree of palladium extraction can be increased by increasing the temperature and contact time of the sample with aqua regia.

According to XRD data (Fig. 1), on a carbon surface at pH 7.8, copper(II) nitrate in the presence of chloride ions (introduced due to the K₂PdCl₄ complex salt) transforms into the Cu₂(OH)₃Cl (paratacamite) phase.

Table 2. The results of copper-palladium components catalyst desorption

No.	Sample	Eluent	Contact time, min	Temperature, K	Desorbed Pd mg/g (%)	Desorbed Cu mg/g (%)
1	K ₂ PdCl ₄ -KBr/CFM C _{Pd} =18 mg/g	H ₂ O	90	293	Not revealed	–
		H ₂ O	10	373	Not revealed	–
		1.5M HCl	90	293	0.076 (0.4)	–
		aqua regia	90	293	10.0 (55.5)	–
		HCl+HNO ₃ (3:1)	10	373	10.52 (58.4)	–
2	Cu(NO ₃) ₂ -KBr/CFM C _{Cu} =30 mg/g	H ₂ O	90	293	–	2.8 (9.3)
		H ₂ O	10	373	–	22.1 (73.6)
		HNO ₃ (1:1)	90	293	–	15.0 (50.0)
		1.5M HCl	90	293	–	16.0 (53.3)
3	K ₂ PdCl ₄ - Cu(NO ₃) ₂ - KBr/CFM C _{Pd} =18 mg/g C _{Cu} =30 mg/g	H ₂ O	90	293	Not revealed	1.3 (4.3)
		H ₂ O	10	373	Not revealed	4.8 (16)
		HNO ₃ (1:1)	90	293	0.64 (3.5)	14.8 (49.3)
		1.5M HCl	90	293	0.26 (1.4)	16.2 (54.0)

Table 3. The results of testing the control and model samples of the catalyst

*No.	Sample	C_{CO}^f , mg/m ³	η_{st} , %	$\Delta\eta_{st}$ %
1	Control sample K ₂ PdCl ₄ -Cu(NO ₃) ₂ -KBr/CFM	47	84	0
Model samples		Pd(II) desorption		
2	K ₂ PdCl ₄ / Cu(NO ₃) ₂ - KBr /CFM	27	91	+7
		Cu(II) desorption		
3	Cu(NO ₃) ₂ / K ₂ PdCl ₄ - KBr /CFM	71	76	-8
		KBr desorption		
4	KBr/ K ₂ PdCl ₄ -Cu(NO ₃) ₂ /CFM	79	74	-10

* The ordinal number corresponds to the number of the kinetic curve in Fig. 3

Unlike palladium, copper(II) is desorbed by water and with increasing temperature, the degree of copper(II) desorption increases from 9.3 to 73.6 % for composition No. 2 and from 4.3 to 16.0 % for composition No. 3. Individual acids HNO₃ and HCl even at room temperature provide a degree of copper(II) extraction of 50-54 %, both for No. 2 and No. 3 compositions. These data are consistent with the results of copper(II) desorption applied to natural aluminosilicates^{22,23} and prove that copper(II) on the carbon surface does not change the degree of oxidation.

The kinetic method makes it possible to evaluate the effect of the catalyst components desorption on its activity. For this, model samples were prepared by the method of separate impregnation, following the sequence: i) the stage of the carrier impregnation with K₂PdCl₄-C₂H₅OH solution (I), or Cu(NO₃)₂-C₂H₅OH (II), or KBr-C₂H₅OH (III); drying at 373 K; ii) water desorption stage (293 K) of palladium from sample (I), or copper from sample (II), or potassium bromide from sample (III); drying at 373 K; iii) impregnation stage after desorption of sample (I) with a solution of Cu(NO₃)₂-KBr-C₂H₅OH, sample (II) with a solution of K₂PdCl₄-KBr-C₂H₅OH, sample (III) with a solution of K₂PdCl₄-Cu(NO₃)₂-C₂H₅OH; drying at 373 K (Table 3). Fig. 3 presents the kinetic curves profiles of C_{CO}^f change in time during the CO oxidation by air oxygen in the presence of a control sample of the catalyst (curve 1) and model samples (curves 2-4). As can be seen, the model sample (curve 2), for which palladium desorption was not detected (Table 3), shows even higher activity than the control sample (curve 1). This effect is caused by the influence of the catalyst components application order on its activity (Fig. 2).

The model sample (curve 3), for which desorption of copper(II) was detected, reduces its activity by 8 % compared to the control sample (Table 3), which is due to a decrease in the content of copper(II) in the catalyst.

Desorption of potassium bromide from the sample (III) also leads to a decrease in the catalytic activity of the model sample by 10 % (curve 4) compared to the control sample.

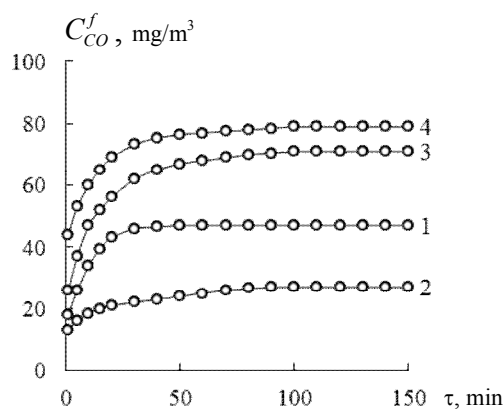


Fig. 3. C_{CO}^f change in time during carbon monoxide oxidation with air oxygen in the presence of control sample K₂PdCl₄-Cu(NO₃)₂-KBr/CFM (curve 1) and model catalyst samples after desorption of palladium (curve 2), copper (curve 3) and potassium bromide (curve 4). $C_{CO}^{in} = 300$ mg/m³; $C_{Pd(II)} = 1.7 \cdot 10^{-4}$; $C_{Cu(II)} = 4.68 \cdot 10^{-4}$; $C_{Br^-} = 6.0 \cdot 10^{-4}$ mol/g

Thus, the kinetic results of the control and model samples of the catalyst study in the reaction of CO oxidation with oxygen, a set of data characterizing the ability of the catalyst components to desorption, and X-ray phase studies showed that the initial compounds of copper(II) and palladium(II) change their state: palladium in the catalyst is in the form of X-ray amorphous Pd⁰, and copper(II) is in the form of the paratacamite Cu₂(OH)₃Cl crystalline phase.

3.4. Protective properties of the Pd(II)-Cu(II)/CFM catalyst

Catalyst samples for this series of experiments were obtained by the method of one-stage impregnation. At initial concentrations of carbon monoxide of 50, 100, 200, 300 mg/m³ and a constant linear speed of the GAM ($U = 2.1$ cm/s), the effective contact time of the catalyst with the GAM varied from 0.09 to 0.45 s (Fig. 4).

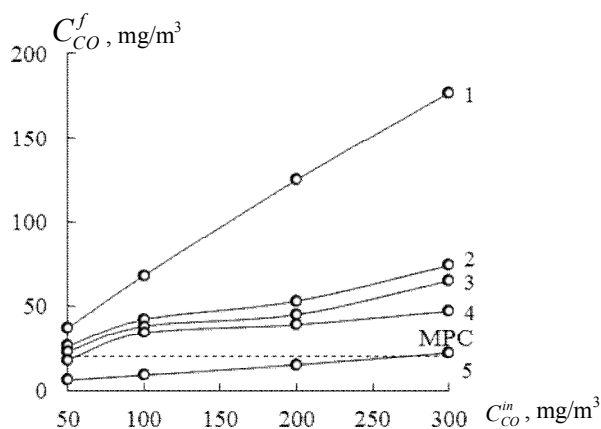


Fig. 4. Dependence of C_{CO}^f in the steady-state carbon monoxide oxidation by oxygen in the presence of the Pd(II)-Cu(II)/CFM catalyst on the initial concentration of CO in the GAM at different effective contact times τ_{ef} : 1 – 0.09; 2 – 0.18; 3 – 0.27; 4 – 0.36; 5 – 0.45. $U = 2.1$ cm/s; $T = 293$ K; $C_{Pd(II)} = 1.7 \cdot 10^{-4}$; $C_{Cu(II)} = 4.68 \cdot 10^{-4}$; $C_{Br^-} = 6.0 \cdot 10^{-4}$ mol/g

The kinetics of the CO oxidation reaction at different τ_{ef} and C_{CO}^{in} shows the similarity of the kinetic curves, which indicates the same reaction mechanism. Based on the obtained data, a dependence was constructed that reflects the influence of the CO initial concentration on C_{CO}^f in the stationary mode at different effective contact times. It was established that, under the condition of 50 to 300 mg/m³, air purification from carbon monoxide to MPC is ensured only at $\tau_{ef} = 0.45$ s.

4. Conclusions

A catalyst for carbon monoxide low-temperature oxidation with oxygen was obtained by the method of impregnation on carbon fiber material with a water-alcohol solution containing precursors of palladium and copper in the form of K_2PdCl_4 and $Cu(NO_3)_2$ and the auxiliary component KBr in given ratios. With the help of a set of research methods (X-ray phase, desorption, kinetic) it was established that the initial compounds of palladium(II) and copper(II) change their state under the action of a carbon fiber carrier. Palladium is reduced to X-ray amorphous Pd^0 , and copper(II) is in the form of a crystalline phase $Cu_2(OH)_3Cl$.

The protective properties of the catalyst, which characterize its ability to provide air purification from CO to the maximum permissible concentration for the working area (MPC = 20 mg/m³), were studied. Catalyst samples were tested under the condition of varying the effective contact time (τ_{ef}) of the catalyst with the gas-air mixture from 0.09 to 0.45 s and the initial CO concentra-

tion (C_{CO}^{in}) from 50 to 300 mg/m³. It was established that the catalyst exhibits protective properties under the condition of $\tau_{ef} = 0.45$ s and $C_{CO}^{in} \leq 300$ mg/m³. The catalyst can be used in human respiratory protection from carbon monoxide.

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СКЛАД ТА АКТИВНІСТЬ КУПРУМ-ПАЛАДІЄВОГО КАТАЛІЗАТОРА НА ВУГЛЕЦЕВОМУ ВОЛОКНИСТОМУ МАТЕРІАЛІ ДЛЯ ОЧИЩЕННЯ ПОВІТРЯ ВІД МОНООКСИДУ КАРБОНУ

Анотація. Сукупність методів дослідження (рентгенофазовий, десорбційний, кінетичний) використовували для встановлення стану базових компонентів K₂PdCl₄ і Cu(NO₃)₂ в каталізаторі окиснення монооксиду карбону киснем. Встановлено, що вихідні сполуки паладію (II) і купруму (II) під дією вуглецевого волокнистого носія змінюють свій стан. Паладій відновлюється до рентгеноаморфного Pd⁰, а купрум (II) перебуває у формі кристалічної фази Cu₂(OH)₃Cl. Встановлено, що каталізатор проявляє захисні властивості в межах початкових концентрацій монооксиду карбону ≤ 300 мг/м³ та ефективного часу контакту 0,45 с, і його можна застосовувати в засобах захисту органів дихання людини.

Ключові слова: монооксид карбону, вуглецеві волокнисті матеріали, каталізатори, окиснення, респіраторні пристрої.