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*T.O. Kiose<sup>a</sup>, T.L. Rakytska<sup>a</sup>, K.O. Holubchyk<sup>b</sup>***Pd(II)–Cu(II) COMPOSITIONS FIXED ON DISPERSED SILICA FROM AMMONIA SOLUTIONS FOR CARBON MONOXIDE OXIDATION WITH AIR OXYGEN**<sup>a</sup> Odesa I.I. Mechnikov National University, Odesa, Ukraine<sup>b</sup> Odesa National Medical University, Odesa, Ukraine

The samples of dispersed silica, tripoli from the Konoplyansky deposit, were used in this work. Pd(II)–Cu(II) compounds fixed on dispersed silica for the oxidation of carbon monoxide with air oxygen were obtained by impregnation of the carrier, which was previously boiled in distilled water for one hour, through NH<sub>3</sub>-coordination in the presence of ethyl alcohol, followed by maturation of the catalyst at 20°C for 20 hours and drying at 300°C for 4 hours. The initial and chemically modified samples of tripoli were characterized by X-ray phase analysis, IR-spectral and thermogravimetric research methods and tested in the reaction of low-temperature oxidation of carbon monoxide with oxygen. The degree of CO conversion in the stationary mode was used to estimate the activity of the catalyst. It was established that the activity of copper-palladium catalysts is significantly affected by the method of catalyst preparation, namely: the sequence of mixing the starting solutions, the drying temperature, and the content of the catalyst components. The catalyst with the highest activity contained all the components, such as K<sub>2</sub>PdCl<sub>4</sub>, Cu(NO<sub>3</sub>)<sub>2</sub>, NH<sub>4</sub>OH, KBr, and C<sub>2</sub>H<sub>5</sub>OH, mixed beforehand in the specified sequence. It provides air purification from CO to a concentration that is 5 times lower than the maximum permissible concentration for the working area (MPC<sub>CO</sub>=20 mg/m<sup>3</sup>). The degree of CO oxidation reaches 98.6%. With other variations of the method of the catalyst preparation, the samples show much lower activity, which indicates the formation of surface complexes of different composition, responsible for the oxidation of carbon monoxide by air oxygen.

**Keywords:** carbon monoxide, tripoli, oxidation, copper-palladium catalyst, NH<sub>3</sub>-coordination.

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**Introduction**

The analysis of research in the field of development of Wacker-type catalysts for low-temperature oxidation of carbon monoxide showed that the attention of researchers was mainly focused on the search for new carriers and methods of their modification, as well as on the justification of palladium(II) and cuprum(II) precursors, which are basic catalyst components [1,2]. Traditionally, to prepare such catalysts, the method of impregnation based on the moisture content of the carrier with an aqueous or aqueous alcohol solution of palladium(II) and copper(II) compounds was used according to one-stage [1–3] or two-stage [4] schemes. For instance,

the PdCl<sub>2</sub>–CuCl<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst obtained by the two-stage impregnation method had higher activity and stability for 30 hours than the catalyst obtained by the one-stage method [5]. In recent years, a method of impregnating the carrier with Pd(II) and Cu(II) compounds by moisture content in the presence of ammonia was proposed [6–9]. The method is based on the reaction of ammonia surface complexation with palladium(II) and copper(II) followed by calcination of such a composition in an oxygen-containing environment at 300°C for 4 hours. It should be noted that catalysts based on Al<sub>2</sub>O<sub>3</sub> were mainly obtained using the ammonia method, which showed activity even at negative temperatures (–30°C÷–10°C)

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[7]. However, the example [5] shows that the PdCl<sub>2</sub>–CuCl<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst exhibits greater activity and stability in the absence of ammonia. Only one case is described about using the ammonia method for the synthesis of a copper–palladium catalyst on a natural attapulgite support [8]. The activity of such a catalyst was extremely low.

Therefore, the issue of further improvement of the ammonia method for obtaining Wacker-type catalysts fixed on various carriers and the detection of the influence of various factors on their activity in the carbon monoxide oxidation reaction is of great research interest.

The aim of the work is to produce copper–palladium compositions on dispersed silica by the ammonia method under different conditions and determine their activity towards the reaction of carbon monoxide oxidation by air oxygen.

#### Materials and methods

We used the samples of dispersed silica N-Tr(K-I) (Konoplyanske deposit, batch I, according to the Ukrainian technical requirements TU U 14.2-00374485-004). Natural tripoli was boiled in distilled water for one hour; the solid phase was dried at a temperature of 110°C to a constant weight. Modified tripoli H<sub>2</sub>O-Tr(K-I) was used as a carrier ( $\bar{S}$ ) of catalytic compositions for the oxidation of carbon monoxide (Table 1).

The method of medium impregnation through NH<sub>3</sub>-coordination (coordination-impregnation, CI) in the presence of ethyl alcohol (Et) was worked out. A carrier weighing 10 g was impregnated by moisture content with a solution, containing components of the Wacker-type catalyst K<sub>2</sub>PdCl<sub>4</sub>, Cu(NO<sub>3</sub>)<sub>2</sub>, KBr and auxiliary components NH<sub>4</sub>OH and ethyl alcohol C<sub>2</sub>H<sub>5</sub>OH. The loose material was kept at 20°C for 20 hours, and then dried at 300°C for 4 hours. Samples IK-NH<sub>3</sub>-Et – IIIK-NH<sub>3</sub>-Et were obtained under

different mixing sequences of the starting solutions. The sample IVK-NH<sub>3</sub> was obtained without the addition of ethyl alcohol, and the sample VK-Et did not contain ammonia. When varying the drying temperature, the composition of the IIIK-NH<sub>3</sub>-Et sample was taken as a basis. The samples were dried at a temperature of 110°C, in two stages of 110°C/300°C, 300°C and 600°C. Samples of this series are marked as IIIK-NH<sub>3</sub>-Et-110<sup>0</sup>, IIIK-NH<sub>3</sub>-Et-110<sup>0</sup>/300<sup>0</sup>, IIIK-NH<sub>3</sub>-Et-300<sup>0</sup> and IIIK-NH<sub>3</sub>-Et-600<sup>0</sup>. The resulting samples have a constant composition: C<sub>Pd(II)</sub>=1.02·10<sup>-5</sup>; C<sub>Cu(II)</sub>=5.9·10<sup>-5</sup>; C<sub>KBr</sub>=1.0·10<sup>-4</sup>; C<sub>NH<sub>4</sub>OH</sub>=6.5·10<sup>-4</sup> mol/g.

X-ray phase analysis was carried out on a Siemens D500 powder diffractometer in copper radiation (CuK<sub>α</sub>(λ=1.54178 Å)) with a graphite monochromator on the secondary beam. To record diffractograms, after grinding in a mortar, the samples were placed in a glass cuvette with a working volume of 2×1×0.1 cm<sup>3</sup>. Diffractograms were measured in the range of angles 3<sup>0</sup><2θ<70<sup>0</sup> with a step of 0.03<sup>0</sup> and an accumulation time of 60 seconds at each point.

IR spectra of tableted samples were recorded on a Perkin Elmer FT-IR Spectrometer Frontier (wavenumber range of 400–4000 cm<sup>-1</sup>, and resolution of 4 cm<sup>-1</sup>). The mixture in the ratio of 1 mg of the substance per 200 mg of KBr was pressed under a pressure of 7 t/cm<sup>2</sup> for 30 seconds.

Thermogravimetric studies of the samples were carried out using a Paulik, Paulik and Erdey derivatograph. The weight of the sample was 0.25 g. The furnace temperature was increased with a linear heating rate of 10°C/min in the temperature range of 25–1000°C. The measurement error was ±5%.

#### Sample testing

Gas air mixture with a CO concentration of 300 mg/m<sup>3</sup> was obtained by diluting the concentrated gas (98–99 vol.% CO) with purified air. The initial

Table 1

Samples of catalytic compositions and conditions of their receiving

No.	Designation of samples	Composition	Method of obtaining
0	$\bar{S}$	H <sub>2</sub> O-Tr(K-I)	the carrier ( $\bar{S}$ ) was boiled for 1 hour; dried to a constant mass at 110°C
1	IK-NH <sub>3</sub> -Et	Pd(II)-NH <sub>4</sub> OH-Cu(II)-KBr-C <sub>2</sub> H <sub>5</sub> OH	impregnation with an ammonia alcohol solution under the condition of a different sequence of mixing the starting solutions
2	IIK-NH <sub>3</sub> -Et	Cu(II)-NH <sub>4</sub> OH-Pd(II)-KBr-C <sub>2</sub> H <sub>5</sub> OH	
3	IIIK-NH <sub>3</sub> -Et	Pd(II)-Cu(II)-NH <sub>4</sub> OH-KBr-C <sub>2</sub> H <sub>5</sub> OH	
4	IVK-NH <sub>3</sub>	Pd(II)-Cu(II)-NH <sub>4</sub> OH-KBr-H <sub>2</sub> O	impregnation with ammonia aqueous solution according to moisture content
5	VK-Et	Pd(II)-Cu(II)-KBr-C <sub>2</sub> H <sub>5</sub> OH	impregnation with aqueous alcohol solution according to moisture content
6	IIIK-NH <sub>3</sub> -Et-110 <sup>0</sup>	Pd(II)-Cu(II)-NH <sub>4</sub> OH-KBr-C <sub>2</sub> H <sub>5</sub> OH	dried at 110°C
7	IIIK-NH <sub>3</sub> -Et-110 <sup>0</sup> /300 <sup>0</sup>	Pd(II)-Cu(II)-NH <sub>4</sub> OH-KBr-C <sub>2</sub> H <sub>5</sub> OH	dried in two stages: I – 110°C; II – 300°C
8	IIIVK-NH <sub>3</sub> -Et-600 <sup>0</sup>	Pd(II)-Cu(II)-NH <sub>4</sub> OH-KBr-C <sub>2</sub> H <sub>5</sub> OH	dried at 600°C

*Pd(II)–Cu(II) compositions fixed on dispersed silica from ammonia solutions for carbon monoxide oxidation with air oxygen*

( $C_{CO}^{in}$ ) and final ( $C_{CO}^f$ ) concentrations of carbon monoxide were determined using a gas analyzer 621EX04 («Analytprilad», Ukraine) with sensitivity of 2 mg/m<sup>3</sup>.

The reaction rate was calculated by the formula:

$$W = \frac{\omega(C_{CO}^{in} - C_{CO}^f)}{m_k}, \text{ mol}/(\text{g}\times\text{s}),$$

where  $\omega=1.67\cdot 10^{-2}$  is the volume consumption, L/s;  $C_{CO}^{in}$  and  $C_{CO}^f$  are the initial and final CO concentrations, respectively, mol/L; and  $m_k$  is the weight of the composition sample, g. The degree of CO conversion in the steady state ( $\eta_{st}$ ) was determined by the following formula:

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

### Results and discussion

#### X-ray phase analysis

It can be seen from the X-ray patterns (Fig. 1) that the samples of dispersed silica, natural (N-Tr(K-I)) and modified ( $H_2O$ -Tr(K-I)) tripoli are crystalline, but with a certain degree of amorphization. The highest differences are observed in the region  $2\theta$  of  $20^\circ$  to  $27^\circ$  which is caused by a change in the ratio of the content of siliceous phases:  $\alpha$ -quartz,  $\beta$ -cristobalite, and  $\alpha$ -tridymite. Identification of phases and calculations of the crystallites size in each phase were carried out according to the Rietveld method (Table 2).

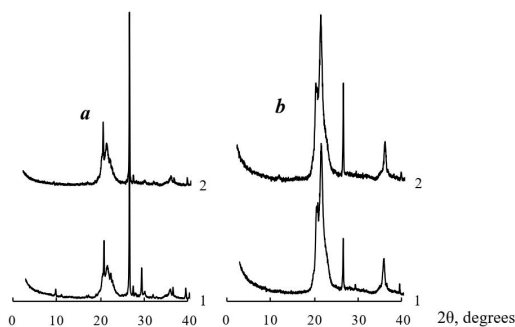


Fig. 1. Diffractograms of natural and modified tripoli (1) and Pd(II)-Cu(II)-catalysts (2) based on them: a – N-Tr(K-I); b –  $H_2O$ -Tr(K-I)

The impurity phase is calcite, the content of which decreases in the  $H_2O$ -Tr(K-I) sample. No additional reflections are observed on the diffractograms of catalytic compositions (Fig. 1,a,b, curve 2), which indicates a high degree of homogenization of the catalyst components.

#### IR spectra

Figure 2 presents the IR spectra of the  $H_2O$ -Tr(K-I) carrier (1) and the IIIK-NH<sub>3</sub>-Et catalyst (2). The spectra were identified taking into account the data for N-Tr(K-I) [10], a free and coordinated NH<sub>3</sub> molecule. According to ref. [11], the valence vibrations  $\nu(NH_3)$  are detected at 3411 and 3336 cm<sup>-1</sup> for a free (uncoordinated) ammonia molecule; the deformation doubly degenerate  $\delta_d(NH_3)$  and  $\delta_s(NH_3)$  are detected at 1628 cm<sup>-1</sup> and 950 cm<sup>-1</sup>, respectively. For the  $[Cu(NH_3)_4]Cl_2$  complex, the following vibrations are detected:  $\nu(NH_3)=3270$  cm<sup>-1</sup>;  $\delta_d(NH_3)=1596$  cm<sup>-1</sup>,  $\delta_s(NH_3)=1245$  cm<sup>-1</sup>,  $\rho(NH_3)(fan)=709$  cm<sup>-1</sup> and  $\nu(Cu-N)=420$  cm<sup>-1</sup>; and for ammonium complexes of palladium(II), the following vibrations are detected  $\nu(Pd-N)=498$  cm<sup>-1</sup>.

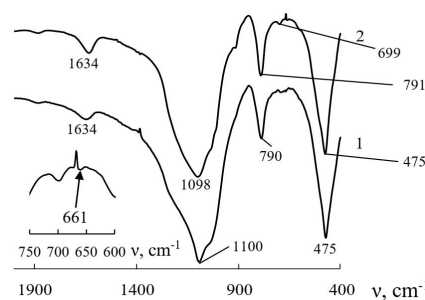


Fig. 2. IR spectra of samples: 1 –  $H_2O$ -Tr (K-I); 2 – IIIK-NH<sub>3</sub>-Et

Taking into account the listed values of wave numbers, the overlap of the bands of valence vibrations of ammonia complexes Pd(II) and Cu(II) can be expected when they are fixed on the  $H_2O$ -Tr(K-I) carrier, which determines the identity of the spectra (Fig. 2), except for the region 600–680 cm<sup>-1</sup>, where a very weak absorption band is observed at 661 cm<sup>-1</sup> for IIIK-NH<sub>3</sub>-Et, at 674 cm<sup>-1</sup> for VIIK-NH<sub>3</sub>-Et and at 607 cm<sup>-1</sup> for VIK-NH<sub>3</sub>-Et. A similar IR spectrum was observed by Zienkiewicz-Strzalka and Pikus [12]

Table 2

Content of main phases in samples of natural and modified Tripoli (K-I) and crystallite size

Sample	Phase							
	$\alpha$ -SiO <sub>2</sub>		$\beta$ -cristobalite		$\alpha$ -tridymite		calcite	
	Content, %	D, nm	Content, %	D, nm	Content, %	D, nm	Content, %	D, nm
N-Tr(K-I)	31.9	248	30.8	11	22.2	11	4.3	105
$H_2O$ -Tr(K-I)	4.24	103	37.8	9	55.6	18	0.76	79

for the  $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$  complex incorporated into the structure of the mesoporous silicate MSM-41; a broad band was detected at  $615\text{ cm}^{-1}$ .

#### Thermochemical properties

DTG profiles of carrier samples  $\text{H}_2\text{O-Tr(K-I)}$  and  $\text{Pd(II)-Cu(II)}$ -compositions are presented in Fig. 3. The results of processing the thermograms are summarized in Table 3. It can be seen that only one  $T_m$  value at  $100^\circ\text{C}$  is observed for the  $\text{H}_2\text{O-Tr(K-I)}$  sample, which corresponds to the removal of physically adsorbed water. Since samples of catalysts obtained by the ammonia method were calcined at  $300^\circ\text{C}$ , the preliminary deammonization took place by approximately 50% [13]. Such samples demonstrate two more maxima on DTG, for which the values of  $T_m$  differ slightly, depending on the order of mixing the solutions of the catalyst components.

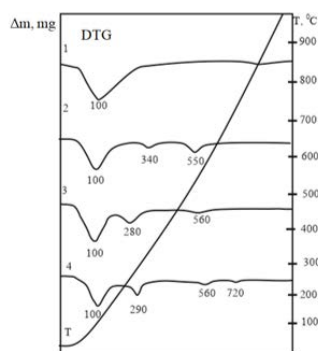
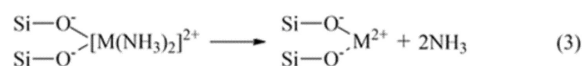
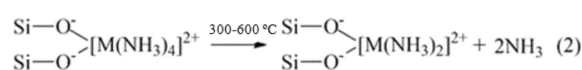
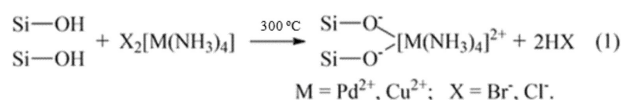


Fig. 3. Derivatograms of samples of chemically modified tripoli: 1 –  $\text{H}_2\text{O-Tp(K-I)}$ ; 2 –  $\text{IK-NH}_3\text{-Et}$ ; 3 –  $\text{IIK-NH}_3\text{-Et}$ ; and 4 –  $\text{IIIK-NH}_3\text{-Et}$

Sequential cleavage of amino ligands continues in the indicated temperature interval of  $280^\circ\text{C}$ – $560^\circ\text{C}$ , which is proven by studies of UV spectra of diffuse reflection of  $[\text{Pd}(\text{NH}_3)_4]^{2+}/\text{NaY}$  samples in the temperature range of  $100^\circ\text{C}$ – $500^\circ\text{C}$  [14]. Anchoring of  $[\text{Pd}(\text{NH}_3)_4]\text{X}_2$  ( $\text{X}=\text{Cl}^-$ ,  $\text{Br}^-$ ) complexes on zeolite

matrices [13,14], layered aluminosilicate (montmorillonite) [15] occurs by the ion-exchange mechanism. Besides of  $\text{NH}_3$ -ligands cleavage, their oxidation and autoreduction (self-reduction) of  $\text{Pd}^{2+}$  to  $\text{Pd}^0$  is possible with increasing temperature. However, studies [14,15] testify to the advantage of the first process. Taking into account the results and obtained data [13–15], we can propose the following scheme of transformations of palladium(II) and copper(II) ammonia complexes on the surface of dispersed silica with  $\text{SiOH}$  functional groups:



Complexes  $[\text{M}(\text{NH}_3)_4]\text{X}_2$ , where  $\text{M}=\text{Pd}^{2+}$ ,  $\text{Cu}^{2+}$ ;  $\text{X}=\text{Cl}^-$ ,  $\text{Br}^-$ , exchange protons with  $\text{SiOH}$  groups of dispersed silica (tripoli) according to reaction (1). Removal of  $\text{HX}$  from the reaction medium occurs already at temperature  $120^\circ\text{C}$ – $130^\circ\text{C}$  [1]. Deammonization of surface complexes leads to the fact that at  $T>500^\circ\text{C}$ , only the  $\text{M-O}$  bond with oxygen atoms of the silica matrix is realized. A similar conclusion was also made in papers [13–15].

Therefore, depending on the calcination temperature, the composition of surface complexes changes, the activity of which in the carbon monoxide oxidation reaction will differ.

#### Testing catalysts in the carbon monoxide oxidation reaction

Results of kinetic studies (Fig. 4, Table 4) of catalyst samples  $\text{IK-NH}_3\text{-Et}$  (1),  $\text{IIK-NH}_3\text{-Et}$  (2),  $\text{IIIK-NH}_3\text{-Et}$  (3), obtained under conditions of

Table 3

Thermochemical properties of  $\text{H}_2\text{O-Tr(K-I)}$  carrier samples and of  $\text{Pd(II)-Cu(II)}/\bar{\text{S}}$  compositions

Sample	$T_m, ^\circ\text{C}$	Absolute weight loss, %			
		25–100 $^\circ\text{C}$	100–300 $^\circ\text{C}$	300–600 $^\circ\text{C}$	Total weight loss
$\text{H}_2\text{O-Tr(K-I)}$	100	2.0	1.2	0.4	4.8
$\text{IK-NH}_3\text{-Et}$	100	1.6	0.8	1.6	6.4
	340				
	550				
$\text{IIK-NH}_3\text{-Et}$	100	1.6	3.4	2.0	8.0
	280				
	560				
$\text{IIIK-NH}_3\text{-Et}$	100	1.2	2.4	1.6	6.4
	290				
	560				

different mixing sequence of initial solutions, and samples that do not contain ethyl alcohol IVK-NH<sub>3</sub> (4) or ammonia VK-Et (5), testify to the significant influence of these factors on the activity of catalysts. Thus, the IIIK-NH<sub>3</sub>-Et catalyst (Fig. 4, curve 3), which includes all the components, namely K<sub>2</sub>PdCl<sub>4</sub>, Cu(NO<sub>3</sub>)<sub>2</sub>, NH<sub>4</sub>OH, KBr, C<sub>2</sub>H<sub>5</sub>OH, mixed in advance in the indicated sequence (Table 1), showed the greatest activity. Such a catalyst provides air purification from CO to a concentration that is 5 times lower than the maximum permissible concentration for the working area (MPC<sub>CO</sub>=20 mg/m<sup>3</sup>). The degree of CO oxidation reaches 98.6%.

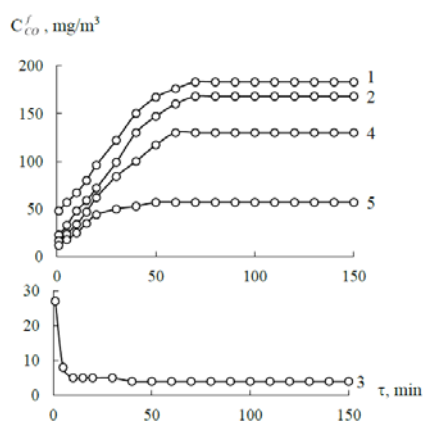


Fig. 4 The change in  $C_{CO}^f$  over time during the carbon monoxide oxidation by oxygen in the presence of catalysts obtained by the method of impregnation with an ammonia solution (Table 1): 1 – IK-NH<sub>3</sub>-Et; 2 – IIK-NH<sub>3</sub>-Et; 3 – IIIK-NH<sub>3</sub>-Et; 4 – IVK-NH<sub>3</sub>; and 5 – VK-Et

With other variations of the catalyst obtaining method (Table 1; Fig. 4, curves 1, 2, 4, and 5), the samples showed much lower activity, which indicates the formation of surface complexes of different composition, responsible for the oxidation of carbon monoxide by air oxygen.

Table 4

**The results of testing Pd(II)–Cu(II)/  $\bar{S}$  compositions obtained by the method of impregnation with ammonia solution in the reaction of carbon monoxide oxidation with air oxygen\***

Composition	$W_{st} \cdot 10^9$ , mol/(g·s)	$C_{CO}^f$ , mg/m <sup>3</sup>	$\eta_{st}$ , %
IK-NH <sub>3</sub> -Et	7.02	183	39.0
IIK-NH <sub>3</sub> -Et	7.92	168	44.0
IIIK-NH <sub>3</sub> -Et	17.76	4	98.6
IVK-NH <sub>3</sub>	10.20	130	81.0
VK-Et	12.42	53	69.0

Note: \* –  $C_{Pd(II)}=1.02 \cdot 10^{-5}$ ;  $C_{Cu(II)}=5.9 \cdot 10^{-5}$ ;  $C_{KBr}=1.0 \cdot 10^{-4}$ ;  $C_{NH_4OH}=6.5 \cdot 10^{-4}$  mol/g.  $C_{CO}^i=300$  mg/m<sup>3</sup>;  $U=4.2$  cm/s;  $d_g=0.75$  mm.

The drying temperature of the catalyst affects the kinetics and degree of carbon monoxide oxidation in the stationary mode (Fig. 5, Table 5). Composition IIIK-NH<sub>3</sub>-Et-110<sup>0</sup> does not show catalytic properties and  $C_{CO}^f = C_{CO}^i$  after 50 min. The catalyst providing the highest degree of carbon monoxide conversion (98.6%) was obtained by drying the compositions at 300<sup>0</sup>.

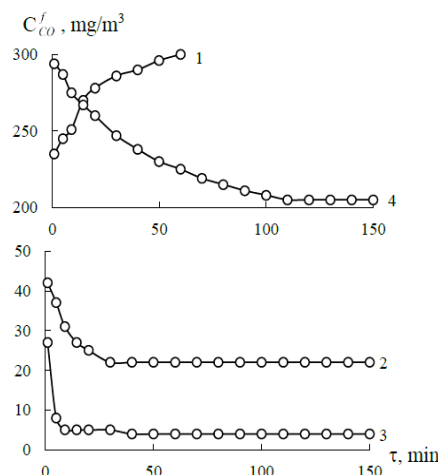


Fig. 5. The change in  $C_{CO}^f$  over time during the carbon monoxide oxidation by oxygen in the presence of the IIIK-NH<sub>3</sub>-Et catalyst obtained at different drying temperatures: 1 – 110°C; 2 – 110/300°C; 3 – 300°C; and 4 – 600°C

Table 5

**The results of testing the IIIK-NH<sub>3</sub>-Et composition in the reaction of carbon monoxide oxidation with air oxygen obtained at different drying temperatures\***

Composition	$W_{st} \cdot 10^9$ , mol/(g·s)	$C_{CO}^f$ , mg/m <sup>3</sup>	$\eta_{st}$ , %
IIIK-NH <sub>3</sub> -Et-110 <sup>0</sup>	–	300	–
IIIK-NH <sub>3</sub> -Et-110 <sup>0</sup> /300 <sup>0</sup>	16.68	22	92.7
IIIK-NH <sub>3</sub> -Et-300 <sup>0</sup>	17.76	4	98.6
IIIVK-NH <sub>3</sub> -Et-600 <sup>0</sup>	5.70	205	31.4

Note: \* –  $C_{Pd(II)}=1.02 \cdot 10^{-5}$ ;  $C_{Cu(II)}=5.9 \cdot 10^{-5}$ ;  $C_{KBr}=1.0 \cdot 10^{-4}$ ;  $C_{NH_4OH}=6.5 \cdot 10^{-4}$  mol/g.  $C_{CO}^i=300$  mg/m<sup>3</sup>;  $U=4.2$  cm/s;  $d_g=0.75$  mm.

A decrease in the degree of CO conversion to 92.7% is observed in the case of the catalyst calcination in two stages: drying at 110°C to a constant weight, then calcination at 300°C. The catalyst fired at 600°C does not exhibit catalytic properties during the first minutes of contact with the gas mixture, but the degree of CO conversion increases over time and reaches 31.4% in stationary state. The obtained results correlate with DTG data (Fig. 3 and Table 2) and confirm the presence of surface complexes of different composition, the formation of which occurs according to schemes (1)–(3).

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### КОМПОЗИЦІЇ Pd(II)–Cu(II), ФІКСОВАНІ НА ДИСПЕРСНОМУ КРЕМНЕЗЕМІ З РОЗЧИНІВ АМІАКУ ДЛЯ ОКИСЛЕННЯ МОНООКСИДУ ВУГЛЕЦЮ КИСНЕМ ПОВІТРЯ

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В роботі використовували зразки дисперсного кремнезему – трепелу Конопляньського родовища. Закріплені на дисперсному кремнеземі Pd(II)–Cu(II)-композиції для окиснення монооксида вуглецю киснем повітря одержували методом імпрегнування носія, який попередньо кип'ятили в дистильованій воді впродовж однієї години, через NH<sub>3</sub>-координацію в присутності етилового спирту з подальшим визріванням катализатора при 20°C впродовж 20 годин та сушінням при температурі 300°C впродовж 4 годин. Вихідні та хімічно-модифіковані зразки трепелу охарактеризовані рентгенофазовим аналізом, ІЧ-спектральним і термогравіметричним методами дослідження та тестовані в реакції низькотемпературного окиснення монооксида вуглецю киснем. Показником активності катализатора є ступінь перетворення CO у стаціонарному режимі. Встановлено, що на активність мідь-паладієвих катализаторів суттєво впливає спосіб одержання катализатора, а саме: послідовність змішування вихідних розчинів, температура сушіння та вміст компонентів катализатора. Найбільшу активність виявив катализатор, до складу якого входять усі компоненти, а саме K<sub>2</sub>PdCl<sub>4</sub>, Cu(NO<sub>3</sub>)<sub>2</sub>, NH<sub>4</sub>OH, KBr, C<sub>2</sub>H<sub>5</sub>OH, змішані попередньо в зазначеній послідовності. Він забезпечує очищення повітря від CO до концентрації, яка в 5 разів нижче за гранично-припустиму концентрацію для робочої зони (ГПК<sub>CO</sub>=20 мг/м<sup>3</sup>). Ступінь окиснення CO досягає 98,6%. При інших варіаціях способу виготовлення катализатора зразки виявляють набагато нижчу активність, що свідчить про утворення різних за складом поверхневих комплексів, відповідальних за окиснення монооксида вуглецю киснем повітря.

**Ключові слова:** монооксид вуглецю, трепел, окиснення, мідь-паладієвий катализатор, NH<sub>3</sub>-координація.

### Pd(II)–Cu(II) COMPOSITIONS FIXED ON DISPERSED SILICA FROM AMMONIA SOLUTIONS FOR CARBON MONOXIDE OXIDATION WITH AIR OXYGEN

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The samples of dispersed silica, tripoli from the Konoplyansky deposit, were used in this work. Pd(II)–Cu(II)

compounds fixed on dispersed silica for the oxidation of carbon monoxide with air oxygen were obtained by impregnation of the carrier, which was previously boiled in distilled water for one hour, through  $\text{NH}_3$ -coordination in the presence of ethyl alcohol, followed by maturation of the catalyst at 20°C for 20 hours and drying at 300°C for 4 hours. The initial and chemically modified samples of tripoli were characterized by X-ray phase analysis, IR-spectral and thermogravimetric research methods and tested in the reaction of low-temperature oxidation of carbon monoxide with oxygen. The degree of CO conversion in the stationary mode was used to estimate the activity of the catalyst. It was established that the activity of copper-palladium catalysts is significantly affected by the method of catalyst preparation, namely: the sequence of mixing the starting solutions, the drying temperature, and the content of the catalyst components. The catalyst with the highest activity contained all the components, such as  $\text{K}_2\text{PdCl}_4$ ,  $\text{Cu}(\text{NO}_3)_2$ ,  $\text{NH}_4\text{OH}$ ,  $\text{KBr}$ , and  $\text{C}_2\text{H}_5\text{OH}$ , mixed beforehand in the specified sequence. It provides air purification from CO to a concentration that is 5 times lower than the maximum permissible concentration for the working area ( $\text{MPC}_{\text{CO}}=20 \text{ mg/m}^3$ ). The degree of CO oxidation reaches 98.6%. With other variations of the method of the catalyst preparation, the samples show much lower activity, which indicates the formation of surface complexes of different composition, responsible for the oxidation of carbon monoxide by air oxygen.

**Keywords:** carbon monoxide; tripoli; oxidation; copper-palladium catalyst;  $\text{NH}_3$ -coordination.

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