

INFLUENCE OF ACID MODIFICATION OF NATURAL PHLOGOPITE ON CATALYTIC ACTIVITY OF SUPPORTED Pd(II)-Cu(II) COMPLEXES IN THE REACTION OF OXIDATION OF CARBON MONOXIDE BY ATMOSPHERIC OXYGEN

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Abstract. The paper presents original results on the effect of nitric acid concentrations on structure, morphology, protolytic properties and the activity of low-temperature carbon monoxide oxidation catalysts based on acid-modified phlogopite (\bar{X} H-Phl-1) and K_2PdCl_4 , $Cu(NO_3)_2$, KBr base components. Samples (supports and catalysts) were characterized by XRD, SEM, FT-IR spectroscopy and pH metric method. It was found that only at $\bar{X} \geq 3.0$ mol/L, the phlogopite samples undergo structural and morphological changes and the pH of the suspension decreases, contributing to the achievement of such a catalyst activity, which ensures stable air purification from CO to a concentration below the $MPC_{CO} = 20$ mg/m³ for the working area. The catalyst Pd(II)-Cu(II)/8H-Phl-1 can be recommended for use in respiratory devices.

Keywords: phlogopite, acid treatment, carbon monoxide, low temperature oxidation, Wacker-type catalyst.

Received: 14 March 2022/ Revised final: 09 June 2022/ Accepted: 12 June 2022

Introduction

Carbon monoxide with the maximum permissible concentration in the working area is 20 mg/m³ ($MPC_{CO} = 20$ mg/m³), is a danger to the environment and humans. Although carbon monoxide is a strong reducing agent ($\varphi_{CO_2/CO} = -0.12$ V) [1,2], direct reaction with oxygen due to steric hindrance is either at high temperature, or in the presence of catalysts. As catalysts may be used oxides, metals and metal complexes, and according to their temperature characteristics they may be divided into low-temperature and high-temperature catalysts [1].

The development of catalysts for low-temperature oxidation of CO (SMCC-CO) for personal protective equipment of the respiratory system is an urgent issue. Respiratory catalysts must ensure stable air purification to a CO concentration lower than or equal to the MPC_{CO} at ambient temperature and high humidity of the gas-air mixture (GAM). Analysis of research in the field of development of SMCC-CO showed that Wacker-type metal-complex catalysts deposited on various carriers, containing Pd(II), Cu(II) salts and other additives, have high application potential [3].

A feature of such catalysts is the ability to vary their activity by changing the nature of the support. Al_2O_3 [4,5], activated carbon [6,7], and carbon fiber materials [8,9] were studied as carriers. High potential carriers are cheaper and more accessible materials of natural origin, including dispersed silicas (tripoli) [1,3], framed (clinoptilolite [10,12,13], mordenite [1,3]) and layered (montmorillonite in bentonite [11,14], palygorskite [15]). Phlogopite is mica mineral with a 2:1 structure. The structure, morphology, adsorption and other physicochemical properties of phlogopite have been studied in many works [16-18]. However, the adsorption and catalytic properties of phlogopite have hardly been studied. It was shown that phlogopite effectively adsorbs Th(IV) [19], Cs(I) and Sr(II) [20-22]. Acid-modified and intercalated phlogopite were studied in the reaction of selective oxidation of ammonia to N_2 [23,24] and hydrogenation of alkenes [25]. There are no data in the literature on the use of phlogopite as a carrier of metal complex compounds that catalyze redox processes with the participation of gaseous toxic substances of inorganic nature. Studies have shown that, in many cases, the preparation of an active catalyst requires

a preliminary acid modification of the carrier [10-15]. The basic components of the catalysts are K_2PdCl_4 and $Cu(NO_3)_2$, and the maximum catalytic activity is achieved in the presence of potassium bromide [1,3].

The aim of this work was to study the effect of the concentration of the modifying acid on the structure, morphology of phlogopite, and the catalytic activity of the deposited Pd(II)-Cu(II) complexes in the reaction of low-temperature oxidation of carbon monoxide with atmospheric oxygen.

Experimental

Materials

KBr, $Cu(NO_3)_2 \cdot 3H_2O$, $PdCl_2$, KCl, HNO_3 (p.a. grade, Sigma-Aldrich, U.S.A.) and a commercial concentrate of phlogopite from Uzbekistan (N-Phl) supplied by Ukrvermikulit was used as a starting material.

Methods

Samples preparation

To improve the surface properties of natural carriers that affect the processes of surface complexation, the method of acid modification by hydrochloric or nitric acids is used [1,3,12,13].

Modification of phlogopite was performed by the reflux method for 1 hour using nitric acid. The acid concentration was varied from 0 to 8 mol/L. The ratio of solid and liquid phases was S:L= 1:2 (at the rate of 1 g of carrier per 2 mL of acid). The precipitate was separated, repeatedly washed with boiling water until a negative reaction to nitrate ion with diphenylamine reagent, and dried in an oven in air at 100°C to constant weight. The samples were conventionally designated $\bar{X}H$ -Phl-1, \bar{X} - the concentration of nitric acid; \bar{X} = 0; 0.5; 1.0; 3.0; 4.0; 6.0; 8.0 mol/L.

The Pd(II)-Cu(II)/ $\bar{X}H$ -Phl-1 catalysts were prepared by the method of incipient wetness impregnation of the carrier. Acid-modified phlogopite (10 g) was impregnated with 5 mL of an aqueous solution containing K_2PdCl_4 ($PdCl_2 + KCl$), $Cu(NO_3)_2$, and KBr in specified ratios. Excessive moisture was removed by sample drying in an oven in air at 100°C for 3 hours. The content of components in the catalyst samples was constant and amounted to: $C_{Pd(II)} = 2.72 \times 10^{-5}$; $C_{Cu(II)} = 5.9 \times 10^{-5}$; $C_{KBr} = 1.02 \times 10^{-4}$ mol/g.

Physical characterization

The diffractograms of powder samples of carrier and catalyst were performed on a Siemens D500 diffractometer (CuK_α radiation, $\lambda = 1.54178 \text{ \AA}$) with a secondary beam graphite monochromator. To record the diffractograms, the test samples were thoroughly grinded in an agate

mortar were placed into a glass cell with an enclosed volume of $2 \times 1 \times 0.1 \text{ cm}^3$. XRD patterns were measured in the angle range of $3^\circ < 2\theta < 70^\circ$ with the pitch of 0.03° and acquisition time of 60 s for each position.

The phlogopite samples were also characterized by scanning electron microscopy using a JEOL-JSM5410 scanning microscope with an AZtech Energy X-max 50 energy dispersive spectrometer. An accelerating voltage was 15 kV.

The infrared spectroscopic analysis in the range from 4000 cm^{-1} to 400 cm^{-1} was carried out using a Perkin Elmer FT-IR spectrometer. All spectra were recorded using pellets consisting of 1 mg of the material under study and 200 mg of KBr.

Protolytic properties of the phlogopite surface were estimated by measurement of equilibrium pH, pH_{eq} , values in aqueous suspensions of 0.2 g N-Phl in 20 mL of distilled water under continuous stirring of the suspensions at 20°C. The change in the pH of the suspension with time was monitored using a pH-340 instrument with an ESL 43-07 glass electrode and an EVL 1M3 silver chloride electrode.

The samples (10 g) of K_2PdCl_4 - $Cu(NO_3)_2$ -KBr/ $\bar{X}H$ -Phl-1 compositions were tested in a gas-flow setup with a fixed-bed glass reactor at an initial CO concentration in the gas-air mixture (GAM), C_{CO}^{in} , of 300 mg/m^3 and the following GAM parameters: temperature of 20°C, relative humidity, of 67%, a volume flow rate, w , of 1 L/min, a linear velocity, U , of 4.2°cm/s . By monitoring final CO concentrations, C_{CO}^f , a carbon monoxide conversion, η (%), was determined and η in a steady state mode, η_{st} , serves as a parameter characterizing the catalytic activity of the compositions [13,14].

$$\eta = \frac{(C_{CO}^{in} - C_{CO}^f)}{C_{CO}^{in}} 100, \% \quad (1)$$

where, C_{CO}^{in} , C_{CO}^f are the initial and final CO concentrations, mg/m^3 .

Results and discussion

Phase analysis

Natural phlogopite, depending on the deposit, in addition to the main phase, contains various impurities, for example, calcite, augite, leucite, zeolite (analcime, phillipsite, chabazite), quartz and traces of albite. However, examples are known when a natural mineral is monophasic and contains only phlogopite. Figure 1(a) shows a diffractogram of natural phlogopite confirming

that the sample is crystalline and polyphase in composition. The phases were identified by the Rietveld method [26]. The content of phlogopite in the original sample is 62.7 wt.%.

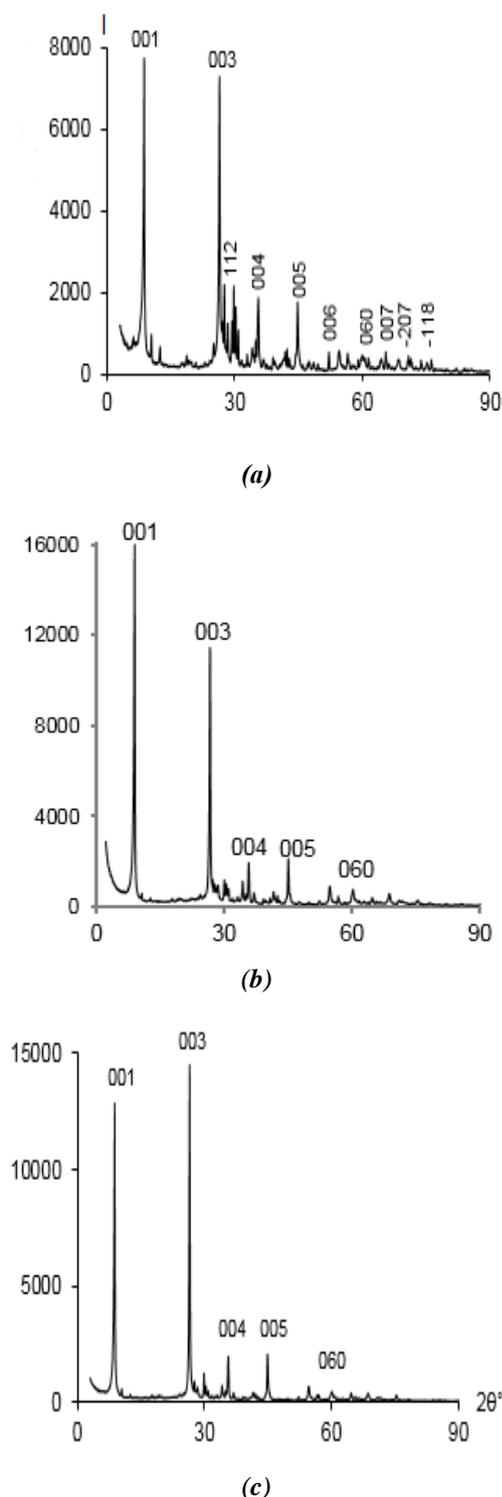


Figure 1. Diffraction patterns of samples of natural phlogopite N-Phl (a), acid-modified phlogopite, 6H-Phl-1 (b), and catalyst Pd(II)-Cu(II)/6H-Phl-1 (c).

For the following interplanar distances d , Å: 10.0929; 5.0464; 3.3643; 3.1514; 2.5232; 2.1814; 2.0136; 1.6821; 1.5406; 1.4418; 1.3703; 1.2675 the phase of phlogopite is uniquely determined. The diffractogram of pure phlogopite shows strong reflections with the following values d , Å: 10.129; 5.022; 3.354; 2.513; 2.171; 2.011; 1.675 Å [27], which ideally coincide for the N-Phl sample under study. The $[hkl]$ indices are indicated on the diffractogram. X-ray spectral characteristics of the studied sample of phlogopite almost completely coincide with those for phlogopite from the Kovdor deposit (Murmansk region, Russia) [28]: d , Å: 10.16; 5.07; 3.39; 2.53; 2.19; 2.03; 1.687; 1.545; 1.443; 1.373; 1.267. It should be noted that two diffraction patterns exhibit characteristic reflection [060] with interplanar spacing (1.5406 and 1.545 Å), which indicates the trioctahedral structure of phlogopite.

Along with the phlogopite phase, the diopside phases $2\theta^\circ$ (d , Å) were identified in the mineral composition: 27.596 (3.2298); 35.430 (2.5315); 49.627 (1.8355); vermiculite $2\theta^\circ$ (d , Å): 6.229 (14.1779); 19.081 (4.6475); 21.261 (4.1757); 25.104 (3.5445). Some other phases such as clinocllore and cordierite give very low reflections.

Phlogopite changes its structural and physicochemical properties as a result of physical and chemical action [29,30]. Results have shown that when exposed to 0.5, 1.0, 3.0, 6.0 mol/L nitric acid, no noticeable changes in the structure of phlogopite are observed, for example, Figure 1(b) for the 6H-Phl-1 sample. One can only note a decrease in the intensity of reflection [060] and a decrease in the interplanar distance to 1.5318 Å in comparison with the initial sample, for which $d = 1.5406$ Å. When Pd(II) and Cu(II) salts are deposited, for example, on a 6H-Phl-1 carrier, additional peaks in the diffractogram Figure 1(c) which would indicate the formation of new phases from the deposited components, are not detected.

Morphology investigations

The obtained results have shown that phlogopite (Figure 2(a)) has a typical lamellar morphology [1,2,30]; however, in the natural sample, along with the main phase, there are impurity phases, which are presented in the form of agglomerates of various shapes and sizes. Individual lamellas (stripes) have a smooth surface with no obvious pores. Under the action of nitric acid, the structure of phlogopite undergoes changes. For example, in the case of the 3H-Phl-1 sample, the lamellar morphology is retained; however, separate destroyed deformed layers with

uneven edges appear, the surface of which is wrinkled and covered with depressions Figure 2(b). In the case of 6H-Phl-1, the stratification is enhanced, cavities of different sizes are formed between the strips; the edges are uneven. When the salts of Pd(II) and Cu(II) are applied to the acid-modified form of 6H-Phl-1, the stratification is enhanced; the lamellae are partially destroyed, the surface is not smooth, wrinkled.

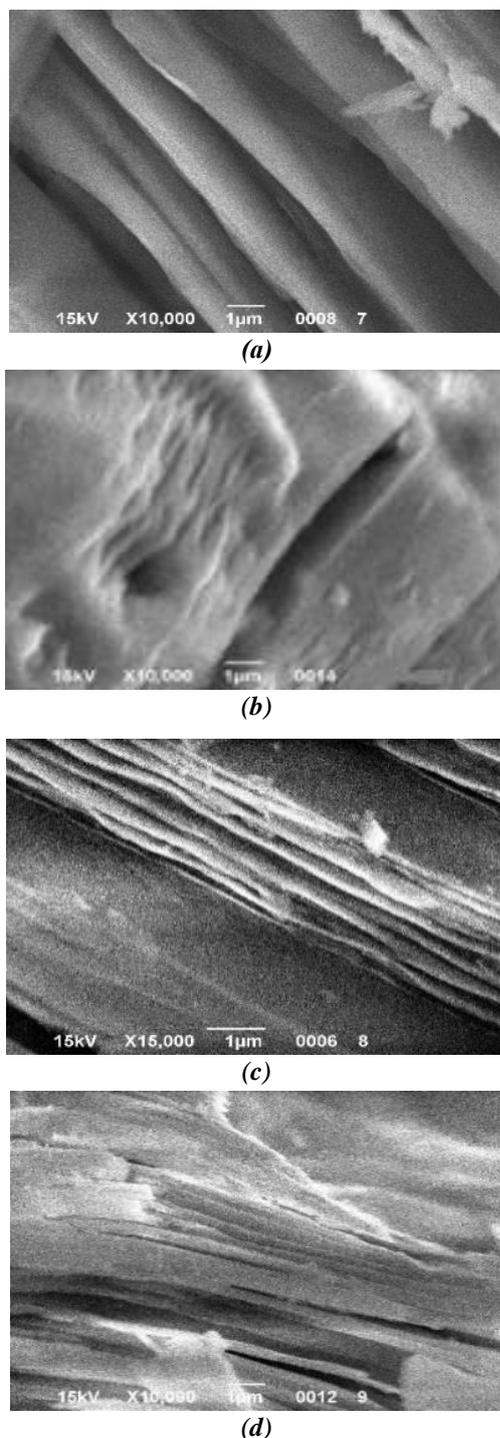


Figure 2. SEM images of samples of natural (a), acid-modified 3H-Phl-1 (b), 6H-Phl-1 (c) phlogopite and catalyst Pd(II)-Cu(II)/6H-Phl-1 (d).

FT-IR spectroscopy results

Identification of spectra of samples N-Phl, \bar{X} H-Phl-1 (\bar{X} = 0.25; 0.5; 1.0; 3.0; 4.0; 6.0 and 8.0 M HNO₃) and catalyst Pd(II)-Cu(II)/6H-Phl-1 were carried out taking into account the latest publications [23,31,32]. Table 1 shows the results of identification of the IR spectra of all samples and some literature data for comparison.

The analysis showed that the FT-IR spectra of the N-Phl and \bar{X} H-Phl-1 samples studied and those presented in previous publications [23,31,32] have similar profile with wavenumbers characterizing the stretching and bending vibrations of structural groups. One should pay attention to the following features. The most intense characteristic Si - O band is in the region of 970–1000 cm⁻¹ and it is somewhat shifted (low frequency shift) compared to other layered aluminosilicates, for example, bentonites [14]. The position of this band does not change with an increase in the concentration of nitric acid used to modify phlogopite. Also, the position of the Si-OH band remains unchanged, which is detected by the bend in the low-frequency component of the characteristic band. Changes in the shape of the characteristic band in the spectra of samples \bar{X} H-Phl-1 (\bar{X} = 3.0; 4.0; 6.0; 8.0 M HNO₃) first begin with the appearance of bends at 1073 and 1066 cm⁻¹ (\bar{X} = 3.0; 4.0 M HNO₃), and then clear maxima at 1069 and 1072 cm⁻¹ (\bar{X} = 6.0; 8.0 M HNO₃). Such changes are due to the partial destruction of the layered structure of phlogopite by the appearance of amorphous SiO₂. In the FT-IR spectrum of the last sample (\bar{X} = 8.0 M HNO₃), a new band appears distinctly at 790 cm⁻¹, which is characteristic of vibrations in the siloxane Si-O-Si group of amorphous silica gel. Attention should be paid to some differences in the position of the absorption band, which corresponds to stretching vibrations ν_{OH} in water molecules. At the same time, deformation vibrations (δ_{H_2O}) are characterized by practically the same value of the wave number. It should be distinguished that the spectrum of the original sample shows an absorption band at 1423 cm⁻¹, which indicates the presence of calcite; the band disappears upon acid treatment.

In the spectrum of the Pd(II)-Cu(II)/6H-Phl-1 catalyst, in comparison with the spectrum of the 6H-Phl-1 carrier, the following features are observed: *i*) high-frequency shift ($\Delta\nu = +11$ cm⁻¹) in the region of OH groups stretching vibrations in associated water molecules, which is caused by the localization of Pd(II) and Cu(II) ions in the system of hydrogen

bonds; *ii*) the amorphization of phlogopite is enhanced under the action of the catalyst components, as evidenced by the appearance of a band at 790 cm^{-1} , which corresponds to Si-O-Si vibrations in amorphous silica gel. The sharp band at 1384 cm^{-1} is due to the presence of Cu(II) nitrate in the catalyst.

Protolytic properties

As a result of acid modification, not only the structure and morphology of phlogopite change, but also the acidic properties of its surface. Phlogopite transforms into the H-form, the content of Bronsted acid sites increases [23]. The change in the acidic properties of the surface was monitored by measuring the pH of an aqueous suspension of natural and acid-modified phlogopite samples after 15 s (pH_0) and upon

reaching an equilibrium value (pH_{st}). In addition, the value of $\Delta\text{pH}_s = \text{pH}_{\text{st}} - \text{pH}_0$ was calculated, which characterizes the suspension effect (Table 2). Under the condition $\Delta\text{pH}_s < 0$, the Lewis acid center attaches the OH group from the water molecule: $\text{E}^+ + \text{HOH} \leftrightarrow \text{E-OH} + \text{H}^+$, which leads to a decrease in the pH of the suspension.

The condition $\Delta\text{pH}_s > 0$ is satisfied for all acid-modified samples of phlogopite, which indicates the progress of the reaction: $\text{E-OH} + \text{HOH} \leftrightarrow \text{E-OH}_2^+ + \text{OH}^-$, which is accompanied by an increase in the pH of the suspension.

The pH value of the suspension for N-Phl is in accordance with the literature data [33]. With an increase in the concentration of nitric acid, the pH_{st} value decreases.

Table 1

Wavenumbers (ν , cm^{-1}) of absorption maxima in FT-IR spectra.

Sample	Structural groups								Source
	$\nu_{\text{H}_2\text{O}}$	$\delta_{\text{H}_2\text{O}}$	$\nu_{\text{Si-O}}$ amorphous SiO_2	$\nu_{\text{Si-O}}$	$\nu_{\text{Si-OH}}$	$\nu_{\text{Si-O-Si}}$ amorphous SiO_2	$\delta_{\text{Si-O-Si}}$	$\nu_{\text{M-O-Si}}$ M=Al, Mg, Fe	
N-Phl	3435	1634	-	994	967 bend	-	457; 440 shoulder	876 bend; 760; 672; 634	this work
0.25H-Phl-1	3435	1636	-	994	962 bend	-	458; 440 shoulder	760; 673; 633	this work
0.5H-Phl-1	3436	1634	-	994	962 bend	-	458; 440 shoulder	760; 673; 634	this work
1H-Phl-1	3437	1634	-	994	962 bend	-	458; 440 shoulder	760; 674; 634	this work
3H-Phl-1	3435	1636	1073 bend	994	962 bend	-	458; 440 shoulder	760; 673; 634	this work
4H-Phl-1	3435	1634	1066 shoulder	993	962 bend	-	458; 440 shoulder	762; 672; 633	this work
6H-Phl-1	3435	1634	1069 shoulder	992	962 bend	-	458; 440 shoulder	871 bend; 764; 672; 633	this work
8H-Phl-1	3435	1635	1072	992	962	790 (clear)	458; 440 shoulder	761; 634	this work
Pd(II)-Cu(II)/ 6H-Phl-1	3446 ($\Delta\nu=11$)	1635	1069 shoulder	994	961	799	460; 440 shoulder	871 bend; 760; 673; 633	this work
Phlogopite (Pietrasecca village, central Italy)	3490	1635	-	1000	950	-	462	-	[31]*
Commercial S&B Industrial Minerals	-	-	1060	980	945	-	-	670	[23]*

*According to [23,31], only those absorption bands are shown that are described in the text of the article.

Table 2
Surface acidity characteristics of samples of natural and modified forms of phlogopite.

No.	Sample	pH_0	pH_{st}	ΔpH_s
1	N-Phl	7.03	6.66	-0.37
2	0.25H-Phl-1	5.73	6.09	0.36
3	0.5H-Phl-1	5.68	6.05	0.37
4	1H-Phl-1	5.45	6.01	0.56
5	3H-Phl-1	5.16	5.72	0.56
6	4H-Phl-1	5.34	5.69	0.35
7	6H-Phl-1	5.26	5.63	0.37
8	8H-Phl-1	5.29	5.57	0.28

Catalyst testing

The results of testing the catalysts $K_2PdCl_4-Cu(NO_3)_2-KBr/\bar{X}H-Phl-1$ are shown in Figure 3 and summarized in Table 3. It should be noted that the samples based on untreated phlogopite, as well as those modified with nitric acid (0.25, 0.5, 1.0 mol/L) did not show catalytic properties either at the outlet of the reactor $C_{CO}^f = C_{CO}^{in}$ (Table 3). Kinetic data reflect the change in the final concentration of CO with time during the oxidation of carbon monoxide with atmospheric oxygen in the presence of catalysts in which the carriers are acid-modified forms of phlogopite $\bar{X}H-Phl-1$, where $\bar{X} = 3.0; 4.0; 6.0$ and 8.0 M HNO_3 . The kinetic curve profiles are typical for such catalysts [10-15]. For catalyst samples based on 3H-Phl-1 and 4H-Phl-1 (curves 1, 2), the concentration at the outlet from the reactor increases and reaches a constant value, but $C_{CO}^f > MPC_{CO}$. For catalyst samples based on 6H-Phl-1 and 8H-Phl-1 (curves 3, 4) for 70 min $C_{CO}^f < MPC_{CO}$, and this condition remains for a long time for the second sample (curve 4).

It is known that the change in the activity of Pd(II)-Cu(II) complexes deposited on natural carriers in the CO oxidation reaction is caused by changes in the structural, morphological, textural and protolytic properties of the carrier under the action of protic acids [10-15]. The data are set out in Figures 1-2, Table 2 prove that at $C_{HNO_3} \geq 3.0$ mol/L phlogopite undergoes structural, morphological changes, and protonation of the surface of the centers leads to a decrease in the pH of the suspension. As reported previously, it is in the pH range of 3.0–5.5 that Pd(II)-Cu(II) complexes deposited on natural carriers are most active in the oxidation of carbon monoxide [3].

However, in the case of phlogopite, one should pay attention to its ability to undergo separation under the action of acid [1,2,32], which is confirmed by SEM images of the samples under study Figure 2.

The layering of phlogopite is accompanied by an increase in the volume of the catalyst, which at constant geometric parameters of the reactor leads to an increase in the height of the catalyst bed.

Table 3
Influence of the effective contact time of the gas-air mixture with the catalyst and the pH of the suspension on the degree of CO conversion in the presence of catalysts $K_2PdCl_4-Cu(NO_3)_2-KBr/\bar{X}H-Phl-1^*$.

Carrier	h , cm	τ_{ef} , s	pH_s	C_{CO}^{fst} , mg/m ³	η_{st} , %
N-Phl	2.0	0.48	6.66	300	0
0.25H-Phl-1	2.1	0.50	6.09	300	0
0.5H-Phl-1	2.1	0.50	6.05	300	0
1H-Phl-1	2.2	0.52	6.01	300	0
3H-Phl-1	2.2	0.52	5.72	140	53
4H-Phl-1	2.3	0.55	5.69	60	80
6H-Phl-1	3.2	0.76	5.63	26	91
8H-Phl-1	3.3	0.79	5.57	15	95

*Conditions: $C_{Pd(II)} = 2.72 \times 10^{-5}$; $C_{Cu(II)} = 5.9 \times 10^{-5}$; $C_{KBr} = 1.02 \times 10^{-4}$ mol/g; $C_{CO}^{in} = 300$ mg/m³; $U = 4.2$ cm/s; $t = 20^\circ C$.

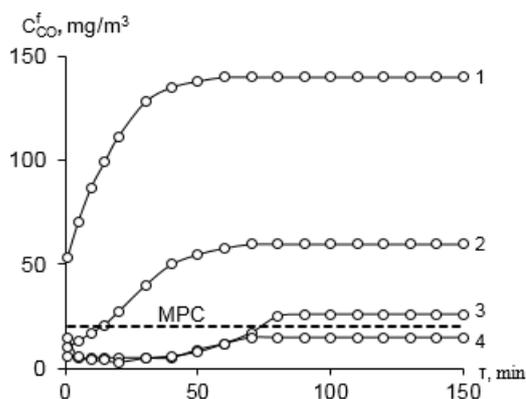


Figure 3. Dependence of the final CO concentration on time τ in the oxidation reaction of carbon monoxide with atmospheric oxygen in the presence of a catalyst $K_2PdCl_4-Cu(NO_3)_2-KBr/\bar{S}$.
 \bar{S} : 1 - 3H-Phl-1; 2 - 4H-Phl-1; 3 - 6H-Phl-1; 4 - 8H-Phl-1.

$C_{Pd(II)} = 2.72 \times 10^{-5}$; $C_{Cu(II)} = 5.9 \times 10^{-5}$;
 $C_{KBr} = 1.02 \times 10^{-4}$ mol/g; $C_{CO}^{in} = 300$ mg/m³;
 $U = 4.2$ cm/s; $t = 20^\circ C$

Table 4

Comparative characteristics of catalysts for low-temperature oxidation of carbon monoxide with air oxygen.

Catalyst	C_{CO}^{in} , mg/m ³	RH, %	τ_{ef} , s	η_{CO} , %	Protective action time, min	Source
K ₂ PdCl ₄ -Cu(NO ₃) ₂ -KBr/8H-Phl-1	300	67	0.79	100-95	>>150	this work
MnO ₂ -CuO/Al ₂ O ₃ Garulite-300 (China)	310	0	0.524	95-100	15-20	[34]
MnO ₂ -CuO/Al ₂ O ₃ Dräger Cat (3Mcompany, U.S.A.)	310	0	0.524	95	15-20	[34]
PdCl ₂ -CuCl ₂ / Al ₂ O ₃ LT-CAT (MST, U.S.A.)	130	-	0.43	39	-	[34,35]
K ₂ PdCl ₄ -Cu(NO ₃) ₂ -KBr/H-Cl TU U 28.2-02071091-003: 2012	300	70	0.61	97	>150	[1]

The increase in h is especially noticeable in the case of 6H-Phl-1 and 8H-Phl-1 carriers. With an increase in the height of the catalyst bed at a constant linear velocity of the gas-air system, the effective contact time τ_{ef} of the gas-air system with the catalyst increases, leading to an increase in the degree of conversion of carbon monoxide.

Table 4 shows the characteristics of the K₂PdCl₄-Cu(NO₃)₂-KBr/8H-Phl-1 catalyst for low-temperature oxidation of carbon monoxide with air oxygen and industrial catalysts used in human respiratory protection equipment.

Despite some progress in the development of catalysts for the oxidation of carbon monoxide, a hopcalite type catalyst is mainly used to equip respiratory devices due to its low price. The time of the protective action of such a catalyst is only 15–20 min at a relative air humidity $RH=0\%$. The basic components of Wacker-type catalysts are Pd(II) and Cu(II) salts. The activity of such catalysts depends substantially on the nature of the support [1,3]. The performance of the K₂PdCl₄-Cu(NO₃)₂-KBr/8H-Phl-1 catalyst is improved compared to the known ones [1,34,35] and it can be used in human respiratory protective equipment.

Conclusions

It is shown that Pd(II) and Cu(II) compounds applied by impregnation to the surface of natural phlogopite do not exhibit catalytic activity in the oxidation of carbon monoxide with oxygen. To change the structural, morphological and acidic properties of phlogopite, the acid leaching method was applied. For these purposes, the original samples by the reflux method were treated for one hour with nitric acid of various concentrations. As a result, a series of samples $\bar{X}H$ -Phl-1 was

obtained, where $\bar{X}=0.25; 0.5; 1.0; 3.0; 4.0; 6.0$ and 8.0 mol/L, which were used to obtain the catalytic compositions of K₂PdCl₄-Cu(NO₃)₂-KBr/ $\bar{X}H$ -Phl-1 type. Carriers and catalysts were characterized by XRD, SEM, FT-IR spectroscopy; for the samples of the initial and acid-modified phlogopite, the pH values of the suspensions were determined under equilibrium conditions. It was found that the oxidation of CO with oxygen with the establishment of a stationary mode is carried out in the presence of catalysts K₂PdCl₄-Cu(NO₃)₂-KBr/ $\bar{X}H$ -Phl-1, when $\bar{X} \geq 3$ mol/L, however, the condition when the concentration of CO at the outlet of the reactor is less than the maximum permissible concentration, observed only at $\bar{X}=8.0$ mol/L. This sample corresponds to the highest degree of amorphization and formation of nanosilicon (XRD and IR spectroscopy), the greatest increase in volume due to phlogopite layering (SEM), and the lowest pH value of the suspension. A catalyst has been obtained that is promising for use in respiratory devices.

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