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NANOCATALYSTS BASED ON PALLADIUM(II), COPPER(II) AND ACID-MODIFIED VERMICULITE COMPOUNDS FOR THE OXIDATION OF CARBON MONOXIDE WITH ATMOSPHERIC OXYGEN

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In this work, the physicochemical properties of natural vermiculite, its acid-modified forms, and copper–palladium catalysts based on it were investigated. Acid-modified forms of vermiculite were obtained by refluxing with nitric acid solutions (0.25; 0.5; 1.0; 3.0; 4.0; 6.0; and 8.0 mol/L) for one hour. Nanocatalysts were prepared by the impregnation method at moisture capacity, followed by drying at 100^0C for 3 hours. The initial vermiculite, the acid-modified samples, and the catalysts were characterized by X-ray phase analysis, IR spectroscopy, and nitrogen adsorption. Catalyst samples were tested in the reaction of carbon monoxide oxidation with oxygen under the following conditions: initial concentration of 300 mg/m^3, temperature of 20^0C, relative humidity of the gas–air mixture of 67%, and volumetric flow rate of 1 L/min. It was established that the natural material is polyphase and, in addition to the main vermiculite phase (52 wt.%), contains impurity phases of muscovite, cordierite, and sepiolite, each with a content not exceeding 14–18 wt.%. The deposited palladium(II) and copper(II) compounds were well homogenized on the surface of the carrier and did not undergo phase transformations. The crystallites of the vermiculite phase were nanosized. IR spectroscopy showed that under the action of nitric acid (C_{HNO3}>4 mol/L) and upon fixation of palladium(II) and copper(II) compounds, the layered structure of vermiculite was altered, its amorphization increased, and nanosilica was formed. As a result of acid modification, the specific surface area of vermiculite samples increased from 4.49 m^2/g to 282.0 m^2/g. Testing of the nanocatalyst samples showed that CO oxidation occurred in a stationary mode only when the carrier had been modified at C_{HNO3}>4 mol/L, with the degree of carbon monoxide conversion reaching 88%.

Keywords: natural and modified vermiculite, nanocatalysts, carbon monoxide, catalytic oxidation, palladium(II), copper(II).

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Introduction

Carbon monoxide (CO) is the most common environmental pollutant that negatively affects human health. In the workplaces of many enterprises, the maximum permissible concentration (MPC=20 mg/m^3) is exceeded, which requires the constant use of personal respiratory protective equipment (PPE) by workers. Carbon monoxide is oxidized by oxygen in the air only in the presence of catalysts. The development of low-temperature CO oxidation catalysts (LTCO) for PPE is of current interest. Analysis of research in the field of LTCO development has shown that metal complex catalysts (MCCs) of the Wacker type, fixed on various carriers, containing palladium(II) and copper(II) salts and other additives, are promising [1,2]. The activity of such catalysts is regulated by changing the composition of palladium(II) and copper(II) precursors, introducing additional components that affect mainly the composition of the coordination sphere of the named metals, as well as the nature of the supports and the method of obtaining the catalyst. In contrast to the works in which expensive supports were used, we have shown the prospects of developing and using catalysts based on palladium(II) and copper(II) complexes supported on cheap natural sorbents of Ukraine of various mineralogical and chemical composition, namely, zeolites, bentonites, dispersed silicas (tripolis), basalt tuffs [1] and phlogopite [3]. Among the potential natural supports of copper-palladium complexes, the promising layered aluminosilicate vermiculite (Vrm), which has a 2:1 structure similar to montmorillonite and phlogopite [3]. The wide availability of vermiculite, its low cost, thermal stability and the possibility of functionalizing its physicochemical properties determine its various areas of application. Vermiculite and organovermiculite are widely used in wastewater treatment technologies for heavy metal ions [4] and as a carrier of oxide and reduced forms of metals (Ni, Fe, Cu) – catalysts for high-temperature reactions of carbon monoxide oxidation, selective NO_x reduction [5], and oxidation of organic pollutants in wastewater [6]. Information on metal complex catalysts fixed on vermiculite is very limited. It is known that mercury(II) chloride fixed on chemically swollen vermiculite exhibits catalytic properties in the gas-phase hydrochlorination of acetylene [7].

The aim of the work is to investigate the effect of acid treatment conditions (varying the concentration of nitric acid) on the structural and textural properties of vermiculite and the activity of copper-palladium catalysts based on it in the oxidation reaction 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 vermiculite (Vrm) supplied by Ukrvermikulit was used as a starting material.

Methods

Samples preparation

Modification nature vermiculite (N-Vrm) was performed by 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=1:6 (at the rate of 1 g of carrier per 6 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 100^0C to constant weight. The samples were conventionally designated as $\overline{X}H-Vrm-1$, where $\overline{X}$ is the concentration of nitric acid ($\overline{X}$=0.25; 0.5; 1.0; 3.0; 4.0; 6.0; and 8.0 mol/L). Bimetallic compositions K_2PdCl_4-$Cu(NO_3)_2$-KBr/$\overline{X}H-Vrm-1$ were prepared by the method of incipient wetness impregnation of the carrier. 10 g of acid-modified vermiculite was impregnated with 10 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 by temperature 100^0C for 3 hours. The content of components in the catalyst samples was constant and amounted to: $C_{Pd(II)}=2.72{\cdot}10^{-5}$; $C_{Cu(II)}=5.9{\cdot}10^{-5}$; and $C_{KBr}=1.02{\cdot}10^{-4}$ mol/g.

Physical characterization

X-ray phase analysis was carried out using a Siemens D500 (Siemens, Germany) powder diffractometer in copper radiation (CuK_α, λ=1.54178 Å), with a secondary beam graphite monochromator. To record the diffractograms, the test samples were thoroughly grinded in an agate mortar and placed in a glass cuvette with a working volume of 2×1×0.1 cm^3. The obtained diffraction patterns were processed by the Rietveld method using the PDF database.

Samples were examined by IR spectroscopy using FT-IR Spectrometer Frontier (400–4000 cm^{-1}, with a resolution of 4 cm^{-1}) (Perkin Elmer, USA). The spectra were registered in KBr tablets obtained at a ratio of 1 mg of substance per 200 mg of KBr.

Nitrogen adsorption/desorption measurements were performed by a volumetric method on a Sorptomatic adsorption instrument (Thermo Electron Corporation) (Carlo Erba, Israel) at liquid-nitrogen temperature (≈–196^0C). Before the measurements, samples were outgassed at 200^0C for 5 hours. The samples (10 g) of K_2PdCl_4-$Cu(NO_3)_2$-KBr/$\overline{X}H-Vrm-1$ 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), of 300 mg/m^3 and the following GAM parameters: temperature of 20^0C; relative humidity of 67%; a volume flow rate, *w*, of 1 L/min; and a linear velocity, *U*, of 4.2 cm/s. By monitoring final CO concentrations and , C_{CO}^{in}, 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 [3]:

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

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

Results and discussion

Phase analysis

Figure 1 presents the diffraction patterns of natural (N-Vrm) (*a*), acid-modified (6H-Vrm-1) (*b*) vermiculite and the copper-palladium catalyst Pd(II)-Cu(II)/6H-Vrm-1 (*c*).

It can be seen that all samples are crystalline. The most intense reflection d_{001}=14.3973 Å (2θ=6.134^0) belongs to the vermiculite phase and corresponds to the presence of a layer of two water molecules [8,9]. The following reflections of different intensities are identified d_{004}=7.1987 Å, d_{006}=4.7999 Å, d_{021}=4.5684 Å, d_{008}=3.5993 Å, d_{0010}=2.8715 Å, d_{0014}=2.0568 Å, d_{0020}=1.4397 Å, d_{060}=1.5423 Å, the values of which correlate for natural vermiculite from other deposits in the world [10]. The reflection d_{060}=1.5423 Å indicates the trioctahedral structure of vermiculite. Among the impurity phases, muscovite, cordierite, and sepiolite are determined. The reflections from the impurity phases are of very low intensity. It should be noted that vermiculite, muscovite and sepiolite have the same structure and belong to layered aluminosilicates [11]. Cordierite is a magnesium aluminosilicate with a hexagonal crystal lattice [12]. The diffractogram of the catalyst (Fig. 1*c*) does not contain additional reflections that would indicate the formation of new phases PdO, Pd^0, CuO, Cu_2O, Cu^0. This indicates that the deposited palladium(II) and copper(II) compounds are well homogenized on the surface of the support and have not undergone phase transformations.

Analysis of the results (Table 1) shows that the mineralogical composition of these samples is heterogeneous, but the vermiculite phase prevails, the content of impurity phases in the original N-Vrm sample varies within 14–18 wt.%. At the same time, in the 6H-Vrm-1 sample, the content of muscovite and cordierite decreases and the content of sepiolite increases almost 2 times. In the samples of the Pd(II)-Cu(II)/6H-Vrm-1 catalyst, the muscovite phase disappears and a new richterite phase appears. The crystallites of the main vermiculite phase are nanosized; the average crystallite size decreases from 60 nm to 33 nm in the acid-modified sample and to 14 nm in the catalyst. The crystallites of the impurity phases, except for the cordierite, are also nanosized. The parameters of the first reflex (d_{001}) and the volume of the unit cell (V_{cell}) for the studied samples change characteristically (Table 1).

Under the action of nitric acid, interlayer cations (Mg^{2+}, K^+) are leached, which leads to compression of the layers (Δd_{001}=−0.0745 Å) and to a decrease in the volume of the unit cell due to the removal of cations (Al^{3+}, Fe^{3+}, Mg^{2+}) in the octahedral network. A similar effect was observed when modifying vermiculite with 1 M hydrochloric acid at 80^{0}C for 2 hours [13]. For the catalyst, due to doping with Pd(II) and Cu(II), the interlayer distance increases (Δd_{001}=+0.0599 Å) and the volume of the unit cell also increases.

FT-IR spectroscopy

Figure 2 presents fragments of FT-IR spectra of samples of natural (1), acid-modified (*2*, *3*, *4*) vermiculite and catalysts (*5*, *6*, *7*). Analysis of the obtained spectra indicates their correspondence to the literature data [14]. During acid treatment of vermiculite and formation of copper-palladium

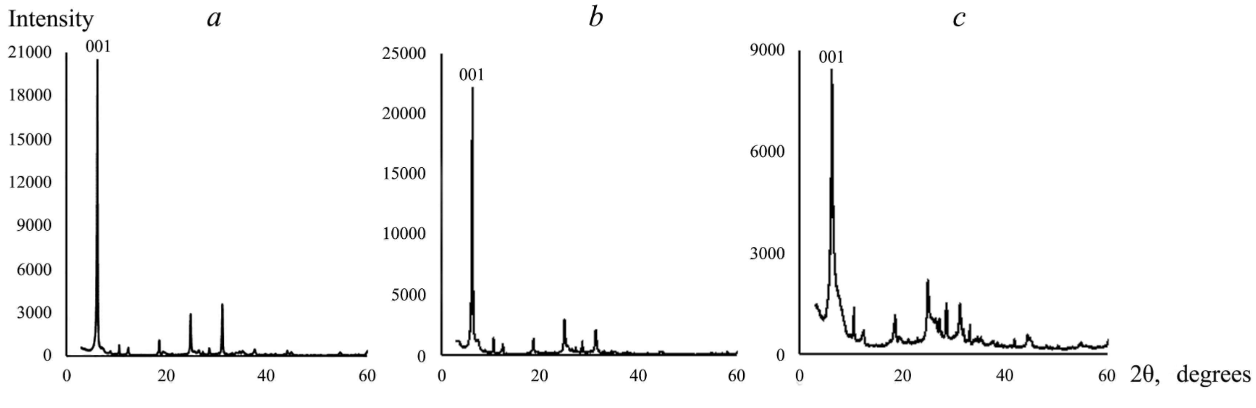

Fig. 1. X-ray diffraction patterns of samples of natural vermiculite N-Vrm (*a*); acid-modified vermiculite 6H-Vrm-1 (*b*); and Pd(II)-Cu(II)/6H-Vrm-1 catalyst (*c*)

catalysts, the largest changes are observed in the region of 1200–800 cm^{-1}. For the sample N-Vrm (*1*), a very intense absorption band of the Si-O fragment is recorded at 994 cm^{-1} with a weakly pronounced shoulder at 1073 cm^{-1}, which indicates the presence of amorphous silica. In the case of samples 4H-Vrm-1 (*2*), 6H-Vrm-1 (*3*) and 8H-Vrm-1 (*4*), the absorption band at 994 cm^{-1} does not change, but the shoulder at 1073 cm^{-1} is separated into a separate band, which corresponds to Si–O vibrations in amorphous silica. The absorption band in the region of 808–814 cm^{-1} is characteristic of vibrations of the siloxane group Si–O–Si in amorphous silica. The deformation vibrations of the Si–O–Si fragment do not depend on the concentration of nitric acid and are characterized by a constant value 458 cm^{-1}. In the spectra of catalysts Pd(II)-Cu(II)/H-Vrm-1 (*5*, *6*, *7*), significant changes occur in the region of vibrations of the Si–O group: the absorption bands at 1075 cm^{-1} and 1082 cm^{-1}, which characterize the Si–O vibrations in amorphous silica, are separated from the 1010 cm^{-1} band and undergo broadening, which indicates an increase in the amorphization of the catalyst samples. In the region of the stretching vibrations of the OH group in the associated water molecules for the catalysts, a high-frequency shift is observed relative to the corresponding carrier by 12 and 16 cm^{-1}, which indicates the interaction of palladium and copper ions with the carrier surface through a system of hydrogen bonds. Thus, under the action of nitric acid and palladium(II) and copper(II) compounds, the layered structure of vermiculite changes and its amorphization with the formation of nanosilica is enhanced.

Table 1

Phase composition of natural N-Vrm and acid-modified 6H-Vrm-1 vermiculite and Pd(II)-Cu(II)/6H-Vrm-1 catalyst

Sample	Phase	Composition, wt. %	Crystallites size, nm	d_{001}, Å	Δd_{001}, Å	V_{cell}, Å^3
N-Vrm	Vermiculite2M_C2/c	52.0	60	14.3928	–	1425
	Muscovite1M_C2/m	18.0	28	–	–	–
	Cordierite_Cccm	16.0	183	–	–	–
	Sepiolite_Pncn	14.0	23	–	–	–
6H-Vrm-1	Vermiculite2M_C2/c	52.7	33	14.3228	–0.0745	1417
	Muscovite1M_C2/m	12.0	34	–	–	–
	Cordierite_Cccm	8.7	183	–	–	–
	Sepiolite_Pncn	26.6	23	–	–	–
Pd(II)-Cu(II)/6H-Vrm-1	Vermiculite2M_C2/c	49.2	14	14.3827	+0.0599	1431
	Cordierite_Cccm	9.3	133	–	–	–
	Sepiolite_Pncn	28.4	14	–	–	–
	Richterite_C2/m	13.1	106	–	–	–

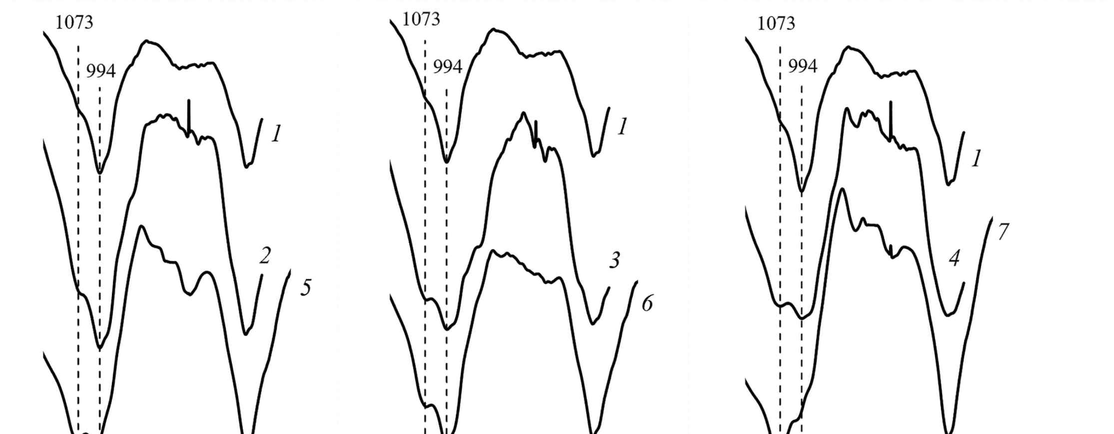

Fig. 2. FT-IR spectra of samples of natural vermiculite N–Vrm (*1*), acid-modified forms $\bar{X}$H - Vrm -1(*2*, *3*, *4*) and catalysts Pd(II)-Cu(II)/$\bar{X}$H - Vrm -1 (*5*, *6*, *7*) where $\bar{X}$ mol/L): 2 – 4.0; 3 – 6.0; and 4 – 8.0

Texture characteristics

Figure 3 shows the adsorption/desorption isotherms of nitrogen by samples of natural N-Vrm (*1, 12*), acid-modified 6H-Vrm-1 (*2, 22*) vermiculite and catalyst Pd(II)-Cu(II)/6H-Vrm-1 (*3, 32*). It is seen that the shape of the adsorption isotherms changes in the case of modification of natural vermiculite. Thus, according to the IUPAC classification, the nitrogen adsorption isotherm by the sample N-Vrm is classified as type III and is characteristic of non-porous materials. The desorption branch of the isotherm is characterized by hysteresis, hysteresis type H3, the width of the hysteresis loop is insignificant, which also indicates a minimal contribution of micropores to the structure of natural vermiculite. The results of the processing of adsorption isotherms using the BET, t-plot (standard D4641-87), and BJH (Barrett-Joyner-Halenda) methods [15] are summarized in Table 2.

The natural vermiculite sample has an undeveloped internal surface area S_{BET}=4.49 m^2/g, which is within the range of those determined for vermiculite from various world deposits [6]. Acid treatment significantly affects the textural characteristics of vermiculite. The shape of the adsorption/desorption isotherm of the acid-modified sample 6H-Vrm-1 (*2, 2'*) changes, the adsorption isotherms belong to type II, the hysteresis type H3 indicates the appearance of a microporous structure; the volume of micropores increases by almost two orders of magnitude, which contributes to an increase in the specific surface area of the samples. The average pore diameter is 2.6 nm for 6H-Vrm-1.

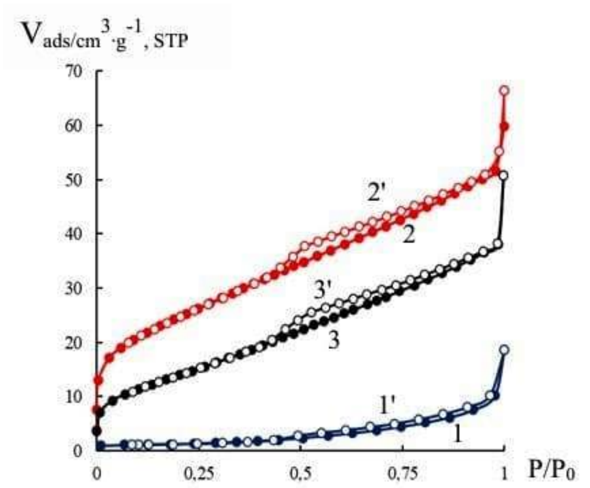

Fig. 3. Nitrogen adsorption/desorption isotherms by samples: N-Vrm (*1,1'*); 6H-Vrm-1 (*2,2'*); and Pd(II)-Cu(II)/6H-Vrm-1 (*3,3'*)

Catalyst testing

Catalysts K_2PdCl_4-$Cu(NO_3)_2$-KBr/ $\overline{X}H-Vrm-1$ was studied under constant conditions, namely $C_{CO}^{in}=300$ mg/m^3, t=20^{0}C, relative humidity of gas air mixture φ_{GAM}=65% (RH=65%), and linear speed U=4.2 cm/s. The results of testing the catalyst samples are presented in Fig. 4 and summarized in Table 3. It should be noted that catalysts based on natural vermiculite, as well as those modified with nitric acid C_{HNO3}=0.25; 0.5; 1.0; 3.0 mol/L did not show catalytic activity at the reactor outlet $C_{CO}^{f}=C_{CO}^{in}$.

Kinetic data reflect the change in the final concentration of CO over time during the oxidation of carbon(II) oxide by atmospheric oxygen in the

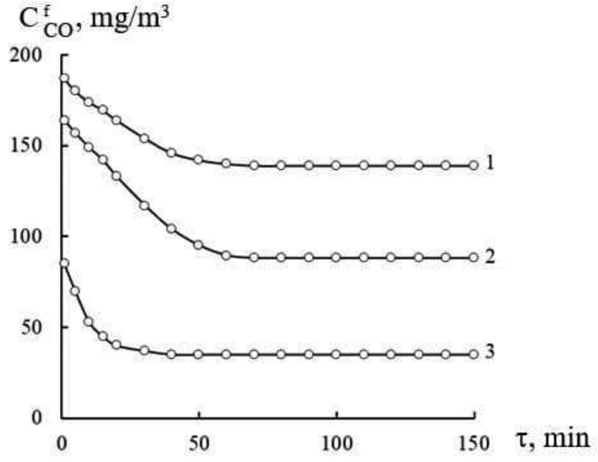

Fig. 4. Dependence of the final CO concentration on time in the oxidation reaction of carbon(II) oxide with air oxygen in the presence of a catalyst K_2PdCl_4-$Cu(NO_3)_2$-KBr/ . $\overline{X}H-Vrm-1$: 1 – 4H-Vrm-1; 2 – 6H-Vrm-1; 3 – 8H-Vrm-1. $C_{Pd(II)}$=2.72·10^{-5}; $C_{Cu(II)}$=5.9·10^{-5}; C_{KBr}=1.02·10^{-4} mol/g; $C_{CO}^{in}=300$ mg/m^3; t=20^{0}C

Table 2

Structural and adsorption characteristics of samples of natural (N-Vrm), acid-modified (6H-Vrm-1) vermiculite and catalyst Pd(II)-Cu(II)/6H-Vrm-1

Sample	S_{BET}, m^2/g	S_{ext}, m^2/g	S_{mi}, m^2/g	V_{Σ}, cm^3/g	V_{mi}, cm^3/g	D_m, nm
N-Vrm	4.49	2.65	1.84	0.0234	7.94?10^{-4}	20.9
6H-Vrm-1	282.0	22.92	259.0	0.1833	0.1310	2.60
Pd(II)-Cu(II)/6H-Vrm-1	279.0	28.95	250.05	0.1804	0.1300	2.89

presence of catalysts in which the carriers are acid-modified forms of vermiculite $\overline{X}H\text{-}Vrm\text{-}1$, where $\overline{X}$ =4.0; 6.0; 8.0 M HNO_3. The profiles of the kinetic curves are typical for such catalysts [1–3]: the concentration of CO at the reactor outlet decreases within 20–50 min and reaches a constant value; the degree of conversion of carbon monoxide in the steady-state mode increases from 54% to 88%.

The delamination of vermiculite under the action of nitric acid 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 layer (h). The increase in h is especially noticeable in the case of 6H-Vrm-1 and 8H-Vrm-1 carriers. Therefore, at a constant linear velocity of the HPS, the effective contact time τ_{eff} of the GAM with the catalyst increases, which causes an increase in the degree of conversion of carbon monoxide. Protonation of the surface centers of vermiculite causes an increase in the acidity of the surface. This factor affects the course of surface complexation reactions, which lead to the formation of catalytically active complexes of palladium(II) and copper(II) [1,2].

Conclusions

The phase composition of natural, acid-modified vermiculite and copper-palladium catalyst was investigated in the work. It was found that the mineralogical composition of these samples is heterogeneous, but the vermiculite phase prevails (52 wt.%) and the content of impurity phases (muscovite, cordierite, sepiolite) does not exceed 18 wt.%. Modification of vermiculite with nitric acid (0.25; 0.5; 1.0; 3.0; 4.0; 6.0; and 8.0 mol/L) leads to a decrease in the content of muscovite, cordierite and an increase in the content of sepiolite to 26.6 wt.%. Crystallites of all phases, except for the cordierite phase, are nanosized. The absence of new reflections in the diffractogram of the catalyst indicates that the deposited palladium(II) and copper(II) compounds are well homogenized and have not undergone phase transformations. At the stages of acid treatment of vermiculite and formation of the copper-palladium catalyst, the crystallinity of the samples decreases, their amorphization occurs. The formation of nanosilica was also confirmed by IR spectroscopy. The appearance of a separate absorption band at 1073 cm^{-1} corresponds to Si–O vibrations in amorphous silica. It was established that under the action of nitric acid, vermiculite stratification occurs, which is accompanied by an increase in the volume of the catalyst and an increase in the acidic properties of the surface (the pH of the suspension decreases from 7.72 to 5.62). Based on kinetic studies of the oxidation reaction of carbon monoxide with atmospheric oxygen, it has been proven that the catalytic properties of palladium(II) and copper(II) compounds are manifested when vermiculite samples modified with 4, 6, and 8 M nitric acid act as carriers.

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Table 3

Influence of acid modification conditions on catalyst activity K_2PdCl_4-$Cu(NO_3)_2$-KBr/ $\overline{X}H\text{-}Vrm\text{-}1$: in the oxidation reaction of CO with oxygen $C_{Pd(II)}=2.72\cdot10^{-5}$; $C_{Cu(II)}=5.9\cdot10^{-5}$; $C_{KBr}=1.02\cdot10^{-4}$ mol/g; C^{in}_{CO} = 300 mg/m^3; U=4.2 cm/s; t=20^{0}C

Carrier	h, cm	τ_{eff}, s	pH_{st}^{*}	C^{f}_{CO}, mg/m^3	η_{st}, %
N-Vrm	2.0	0.48	7.72	300	0
0.25H-Vrm-1			7.35	300	0
0.5H-Vrm-1			7.03	300	0
1H-Vrm-1			6.72	300	0
3H-Vrm-1			6.34	300	0
4H-Vrm-1	2.5	0.60	6.21	139	54
6H-Vrm-1	6.0	1.43	5.87	88	71
8H-Vrm-1	6.0		5.62	35	88

Note: * – determined by measuring the pH of the suspension [1].

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НАНОКАТАЛІЗАТОРИ НА ОСНОВІ СПОЛУК ПАЛАДІЮ(II), МІДІ(II) І КИСЛОТНО-МОДИФІКОВАНОГО ВЕРМИКУЛІТУ ДЛЯ ОКИСНЕННЯ МОНООКСИДУ ВУГЛЕЦЮ КИСНЕМ ПОВІТРЯ

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В даній роботі досліджено фізико-хімічні властивості природного вермикуліту, кислотно-модифікованих форм та мідь-паладієвих каталізаторів на його основі. Кислотно-модифіковані форми вермикуліту отримували рефлакс методом при дії нітратної кислоти (0,25; 0,5; 1,0; 3,0; 4,0; 6,0; 8,0 моль/л) впродовж однієї години. Нанокаталізатори були одержані методом імпрегнування по вологоємності з подальшим сушінням при температурі 100^0C впродовж 3 годин. Вихідні, кислотно-модифіковані зразки вермикуліту та каталізаторів охарактеризовані методами рентгенофазового аналізу, ІЧ-спектроскопії і адсорбції азоту. Зразки каталізаторів тестували в реакції окиснення монооксиду вуглецю киснем за умови початкової концентрації 300 мг/м^3, температури 20^0C, відносної вологості газо-повітряної суміші 67% та об'ємної витрати 1 л/хв. Встановлено, що природний матеріал є поліфазним і, окрім основної фази вермикуліту (52 мас.%) містить домішкові фази мусковіту, кордієриту та сепіоліту, вміст кожної фази не перевищує 14–18 мас.%. Нанесені сполуки паладію(II), міді(II) добре гомогенізовані на поверхні носія та не зазнали фазових перетворень. Кристаліти фази вермикуліту є нанорозмірними. ІЧ-спектральні дослідження показали, що під дією нітратної кислоти (C_{HNO3}>4 моль/л) та закріплених сполук паладію(II) і міді(II) змінюється шарувата структура вермикуліту та посилюється його аморфізація з формуванням наносиліки. В результаті кислотного модифікування питома поверхня зразків вермикуліту збільшується з 4,49 м^2/г до 282,0 м^2/г. Тестування зразків нанокаталізаторів показало, що тільки за умови модифікування носія при $C_{HNO3}\geq4$ моль/л відбувається окиснення CO в стаціонарному режимі і ступінь конверсії монооксиду вуглецю досягає 88%.

Ключові слова: природний та модифікований вермикуліт, нанокаталізатори, монооксид вуглецю, каталітичне окиснення, паладій(II), мідь(II).

NANOCATALYSTS BASED ON PALLADIUM(II), COPPER(II) AND ACID-MODIFIED VERMICULITE COMPOUNDS FOR THE OXIDATION OF CARBON MONOXIDE WITH ATMOSPHERIC OXYGEN

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In this work, the physicochemical properties of natural vermiculite, its acid-modified forms, and copper–palladium catalysts based on it were investigated. Acid-modified forms of vermiculite were obtained by refluxing with nitric acid solutions (0.25; 0.5; 1.0; 3.0; 4.0; 6.0; and 8.0 mol/L) for one hour. Nanocatalysts were prepared by the impregnation method at moisture capacity, followed by drying at 100^0C for 3 hours. The initial vermiculite, the acid-modified samples, and the catalysts were characterized by X-ray phase analysis, IR spectroscopy, and nitrogen adsorption. Catalyst samples were tested in the reaction of carbon monoxide oxidation with oxygen under the following conditions: initial concentration of 300 mg/m^3, temperature of 20^0C, relative humidity of the gas–air mixture of 67%, and volumetric flow rate of 1 L/min. It was established that the natural material is polyphase and, in addition to the main vermiculite phase (52 wt.%), contains impurity phases of muscovite, cordierite, and sepiolite, each with a content not exceeding 14–18 wt.%. The deposited palladium(II) and copper(II) compounds were well homogenized on the surface of the carrier and did not undergo phase transformations. The crystallites of the vermiculite phase were nanosized. IR spectroscopy showed that under the action of nitric acid (C_{HNO3}>4 mol/L) and upon fixation of palladium(II) and copper(II) compounds, the layered structure of vermiculite was altered, its amorphization increased, and nanosilica was formed. As a result of acid modification, the specific surface area of vermiculite samples increased from 4.49 m^2/g to 282.0 m^2/g. Testing of the nanocatalyst samples showed that CO oxidation occurred in a stationary mode only when the carrier had been modified at C_{HNO3}>4 mol/L, with the degree of carbon monoxide conversion reaching 88%.

Keywords: natural and modified vermiculite; nanocatalysts; carbon monoxide; catalytic oxidation; palladium(II); copper(II).

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