Catalyst containing natural nanosilica, palladium(II) and copper(II) salts in oxidation of carbon monoxide with oxygen

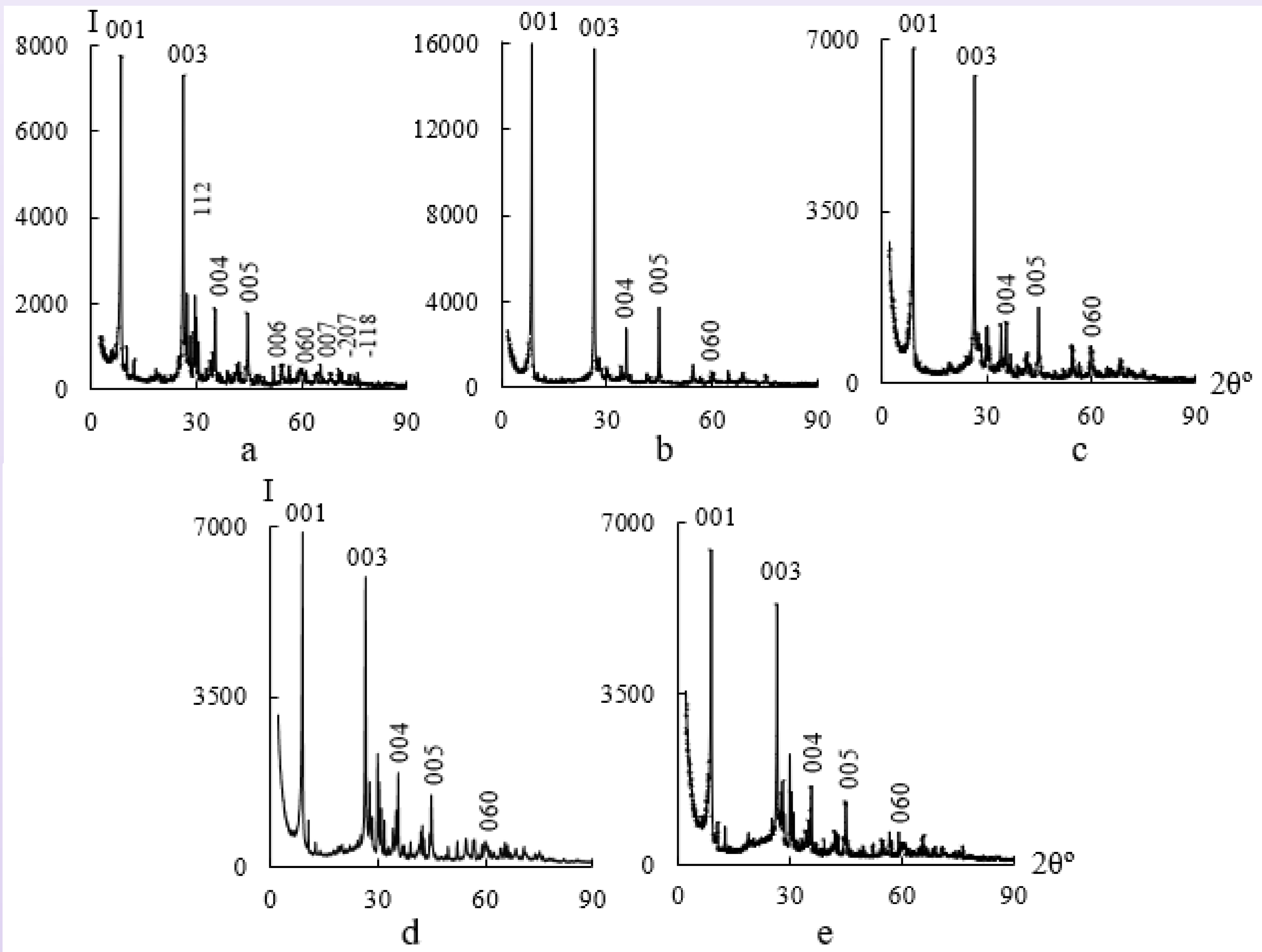
Rakitskaya T.L., Nazar A.P.*, Kiose T.O.

Faculty of Chemistry and Pharmacy, Odesa I.I. Mechnikov National University, 2, St. Dvoryanska, 65082, Odesa, Ukraine.

**E-mail: annnzr1401@gmail.com*

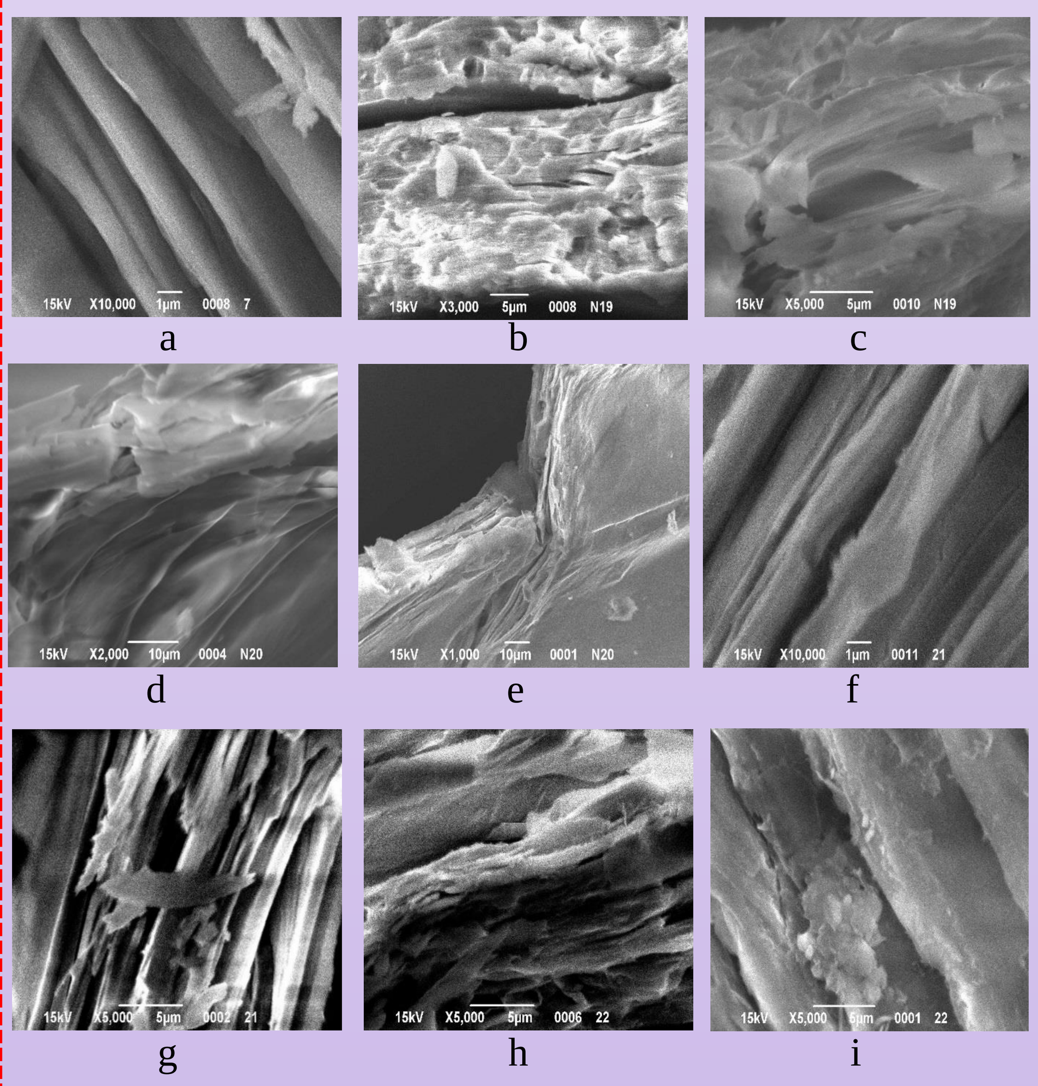
The paper presents original results regarding the effect of long-term treatment of phlogopite concentrate with nitric acid on the phase ratio, chemical composition, and catalytic activity of copper-palladium complexes in the reaction of carbon monoxide oxidation with air oxygen. The phlogopite composite is polyphasic and contains phases of phlogopite, clinochlore, diopside, and tremolite. Samples were modified with 8H HNO_3 at room temperature for 1; 24; 48; 72 hours (8H-Phl-τ). Samples of 8H-Phl-τ ($\bar{S}$) and Pd(II)–Cu(II)/$\bar{S}$ catalysts were characterized by XRD, SEM, FT-IR spectroscopy and pH metric methods. It is shown that the content of the phlogopite phase decreases in a number of these samples, while the content of the clinochlore phase increases. The content of diopside and tremolite phases varies irregularly and decreases within the limits for the original sample. Long-term acid modification (72 hours) leads to amorphization of the sample, and an increase in the silicon content to 92 mass % to the formation of nanosilica, which ensures a high degree of CO conversion.

Phase analysis



Diffraction patterns of samples of natural (a) and acid-modified phlogopite: 8H-Phl-1(b); 8H-Phl-24(c); 8H-Phl-48(d); 8H-Phl-72(e)

SEM characterization

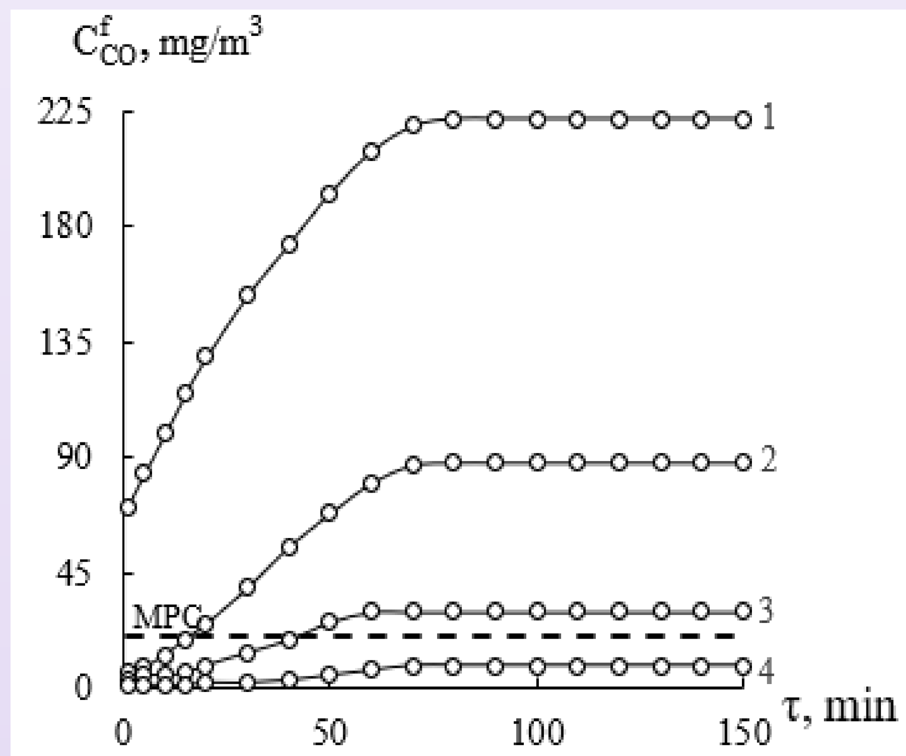


SEM images of samples of natural (a) and acid-modified phlogopite: 8H-Phl-1 (b, c); 8H-Phl-24(d,e); 8H-Phl-48(f, g); 8H-Phl-72(h, i).

Natural phlogopite (Fig. a) shows a typical lamellar morphology. Individual lamellae have a smooth surface without obvious pores. The presence of impurity phases in the form of agglomerates of various shapes and sizes is noted. When exposed to 8M HNO_3 even for one hour, the initially smooth surface of the lamella loosens (Fig. b) and porous formations begin to form (Fig. c). As the duration of contact of the samples with acid increases, phlogopite delamination intensifies (Fig. d), but the main changes occur on the end face (Fig. e). The separation of individual bands (lamellas) (Fig. f) and partial destruction (Fig.g) are characteristic of sample 8H-Phl-48.

The surface structure of sample 8H-Phl-72 changes significantly: the destruction of lamellae leads to the formation of irregular cavities (cracks, holes) (Fig. h), as well as to the formation of agglomerates similar to globules (Fig. i).

Catalytic properties



Dependence of the final concentration of CO on time τ in the reaction of oxidation of carbon monoxide by air oxygen in the presence of a catalyst K_2PdCl_4-$Cu(NO_3)_2$-KBr/8H-Phl: 1 – 8H-Phl-1; 2 – 8H-Phl-24; 3 – 8H-Phl-48; 4 – 8H-Phl-72

The influence of the duration of carrier treatment at room temperature on the K_2PdCl_4-$Cu(NO_3)_2$-KBr/8H-Phl system

(C^{in}_{CO}=300 mg/m³; **U = 4,2 cm/s;** t = 20°C; **m = 10 g.**)

$C_{Pd(II)} = 2{,}72\cdot10^{-5}$; $C_{Cu(II)} = 5{,}9\cdot10^{-5}$; $C_{KBr} = 1{,}02\cdot10^{-4}$ mol/g

№	Sample	h, cm	τ′, s	W·10⁹, mol/(g·s)		$C^f_{CO,1}$, mg/m³	$C^f_{CO,st}$, mg/m³	η_{st}, %
				W_{in}	W_{st}			
1	8H-Phl-1	3,3	0,79	13,74	4,68	71	222	26
2	8H-Phl-24	3,3	0,79	17,64	12,72	6	88	71
3	8H-Phl-48	3,3	0,79	17,82	16,20	3	30	90
4	8H-Phl-72	4,0	0,95	17,94	17,46	1	9	97

Protolytic properties

Characteristics of the surface acidity of natural and modified forms of phlogopite at room temperature

№	Sample	pH_0	pH_{st}	ΔpH_s
1	N-Phl	7,03	6,66	-0,37
2	8H-Phl-1	5,33	5,63	0,30
3	8H-Phl-24	5,26	5,55	0,29
4	8H-Phl-48	5,18	5,50	0,32
5	8H-Phl-72	5,10	5,43	0,33

The sign of the suspension effect $\Delta pHs = pH_{st} - pH_0$ indicates the mechanism of protolysis of water molecules on the acid-base centers of the surface.

Based on the fact that for the sample N-Phl $\Delta pHs < 0$, it can be concluded that the Lewis acid center is involved in the protolysis of the water molecule: $E^+ + HOH \leftrightarrow E – OH + H^+$.