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SYNTHESIS OF METAL-CONTAINING PRECURSORS AND ESTIMATION OF THEIR INFLUENCE TO THE PROPERTIES FORMS OF COPPER OXIDES IN THE REACTION OF SELECTIVE OXIDATION OF CARBON MONOXIDE

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In order to evaluate the composition of metal containing precursors on the properties of the carbon monoxide selective oxidation catalysts synthesized complex compounds of copper cations with dimethyl sulfoxide (DMSO) and hydrothermal decomposition of crystalhydrate nitrate conducted in copper ethylene glycol medium. The resulting compounds were studied with the use of complex physical and chemical methods (XRD, IR, UV, SEM, elemental and thermal analyzes). The calcined samples were tested in the selective oxidation reaction of carbon monoxide and shows their prospects.

Keywords: *carbon monoxide, dimethyl sulfoxide, ethylene glycol, copper cations, hydrothermal synthesis*

Thermal decomposition of the corresponding metal coordination compounds is a promising method for making of nano-oxide with a controlled composition and particle size. In recent years, such systems are widely used in catalysis.

Catalytic properties of nanoparticles of metal oxides obtained by thermal decomposition of polynuclear complexes have been studied in the reactions of the alkanes and carbon monoxide oxidation [1]. The high catalytic activity of deep oxidation of methane had nanoscale particles of cobalt oxide and copper 26-65 19-38 nm obtained by thermolysis of formate [2]. Copper also activates of soil enzymes [3].

The aim of this work is the synthesis of the complex compound of copper cations with dimethyl sulfoxide (DMSO), and copper compounds obtained by hydrothermal treatment of nitrate in the presence of ethylene glycol, and the study of comparative activity of copper oxides obtained by thermolysis of these compounds in the selective carbon monoxide oxidation reaction. Synthesis of copper compounds, their characteristics and to study the oxidation of carbon monoxide due to their highest activity among individual and studying massive oxides as active components in the process.

Experimental part

Synthesis of complex compounds copper cationswith DMSO carried out as follows: 1.71 g (0.05 mole) $CuCl_2$ • 2H2O under constant stirring at 35-40^{0}C dissolved in 20 ml of ethanol and the resulting solution was poured 10 ml of DMSO (molar ratio 1: 2). This solution was dropped a dark-green crystals. The precipitate was filtered off, washed several times with ethanol, then dried to constant weight in a desiccator over sulfuric acid.

Hydrothermal synthesis conducted in autoclave 80 ml of crystalline copper nitrate aqueous solution in the presence of ethylene glycol at a temperature 220^{0}C. The resulting solid synthesis product calcined at a temperature 500^{0}C.

The composition and chemical structure derived chemicals studied physico-chemical methods of analysis: elemental analysis (İCP-MS); X-ray analysis (D2 Bruker); IR and UV spectra in the spectrometer removed "Nicolet iS10" and "Evolution 60S". SEM image and the elemental analysis was carried out by the scanning Sigma VP electron microscope.

Catalytic properties studied in a quartz flow reactor with a fixed catalyst bed (0.1 cm^3). The reaction temperature is measured at the outlet of the catalyst chromel-alumel thermocouple. The volumetric rate of the gas mixture was 10800h^{-1}. The starting gas composition is as follows: CO concentration in the hydrogen-containing mixture of 1.6 vol. %; the ratio of the CO/O$_2$ = 1.31. Catalyst activity is determined by the degree of carbon monoxide conversion.

Results and discussion

To assess the effect of composition on the properties of precursor copper oxide obtained in the carbon monoxide selective oxidation reaction of copper oxide was synthesized in two steps. The first stage was synthesized precursors, which were in the reaction products with copper cations and DMSO hydrothermal treatment products copper nitrate mixture with ethylene glycol. The second - the compounds obtained after thermolysis to form finely divided copper oxide. For the targeted synthesis of a particular structure of the active ingredient necessary to investigate the phase composition of intermediate chemical compounds.

The interaction of $CuCl_2$ • $2H_2O$ with DMSO leads to the formation of the complex type adduct by the following reaction:

$$CuCL_2 \cdot 2(H_2O) + 2(CH_3)_2S{=}0 \xrightarrow[-2(H_2O)]{} \left[(CH_3)_2S{=}0\right]_2 CuCl_2 \quad (1)$$

Noteworthy is the fact that under the reaction conditions-solvate strong donor properties of the ligand DMSO contribute very easy removal of water molecules from the coordination environment of the hydrated $CuCl_2$. Elemental composition of $[(CH_3)_2S{=}O]_2CuCl_2$: found: Cu-21.99; Cl-24.39; S-22.10; calculated: Cu-21.90; Cl-24.30; S-22.20

Figure 1 shows the spectra of the synthesized compound and free ligand in the infrared absorption region. Comparative analysis of the obtained spectra shows a clear formation of the complex. So, before the formation of the adduct (Fig. 1a) absorption bands with maxima at Vs = o2994.97 cm^{-1} and Vs = 2911.63 cm^{-1}, characteristic of the sulfoxide group, as well as the absorption spectra of stretching vibrations water molecules associated co-ordinated with the cations copper peaked at V_{H_2O} = 3439.32 cm^{-1}. After the reaction of coppercations with DMSO spectra (Fig. 1 b), the characteristic stretching vibrations of water molecules disappear, and the nature and intensity of the absorption spectrum changes with DMSO peak shift to VS = 2965.16cm^{-1}.

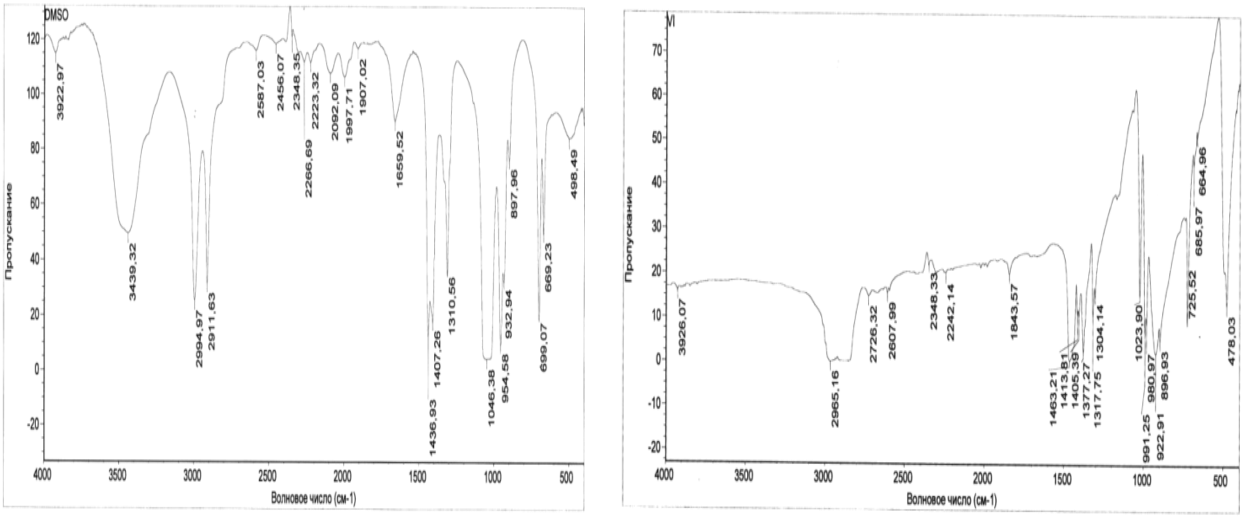

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Fig.1. IR spectra of:

a) The XRD pattern of the complex $[(CH_3)_2S{=}O]_2CuCl_2\,H_2O$;
b) complex $[(CH_3)_2S = O]_2CuCl_2$

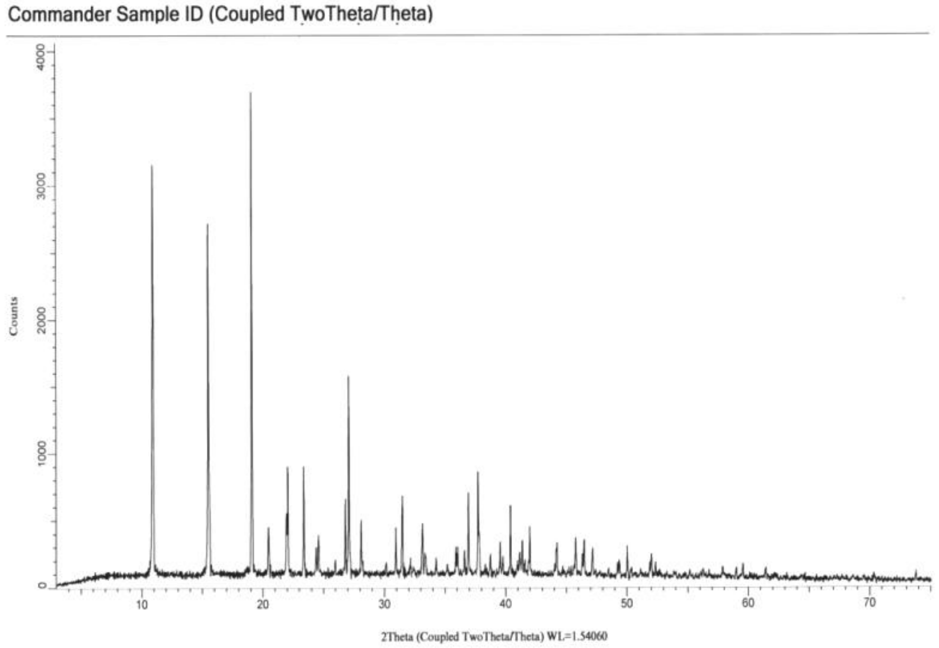

Fig. 2. The XRD pattern of the complex $[(CH_3)_2S{=}O]_2CuCl_2$

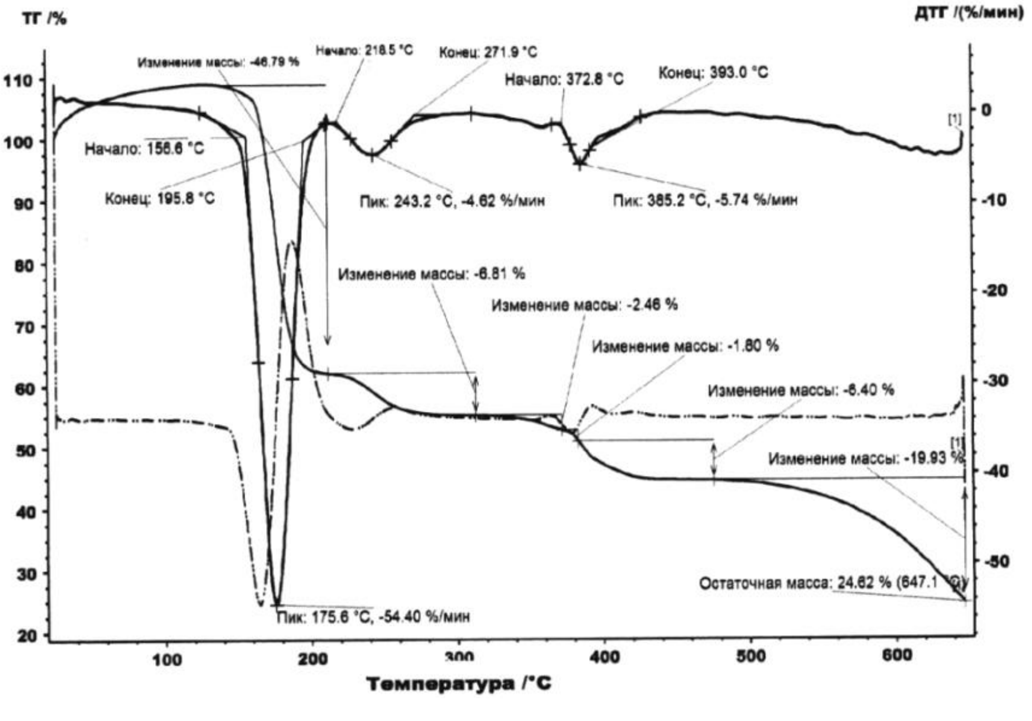

Fig. 3. Shows the results of gravimetrical analysis

Figure 2 shows the result of X-ray analysis of the product synthesis. Interpretation of the data also confirms the formation of the complex $[(CH_3)_2S{=}O]_2CuCl_2$.

Thermolysis synthesized complex begins at 156^0C and takes place in several stages. As can be seen from derivatograms, the first phase of weight loss begins with the 156^0C, the maximum rate of weight fall at the same time observed during 175^0C, and this step is completed by the 210^{0}C, which corresponds to 46.79 wt.% of the weight loss. This is the main stage of weight loss. Next, there are still a few small losses occurring at a much slower rate, and the last stage of weight drop begins at 500^{0}C and thus loss is 19.93 wt.%. The residual mass of the complex is 24.62%. Interpretation of the XRD research results and thermolysis final product showed that it is a copper oxide.

Further work carried out to obtain a catalyst in a closed system by hydrothermal decomposition of copper nitrate in ethylene glycol medium that meets the environmental requirements of the mass of catalyst preparation. Furthermore, these systems are so high dispersion particles [4, 5]

To identify the nature of the substances present in the reaction solution, the reaction spectra of aqueous residues in the IR and UV regions of the spectrum have been removed. Figure 4 shows the UV spectrum of the residual reaction solution. The absorption bands in the region 200-220 nm meet $n \rightarrow \pi^{*}$transition in carboxylic acids, an excess of 230 to 280 nm with a maximum at 260 nm corresponds to π^{*}-electron excitation of the free electron pair of the oxygen of the carbonyl group C=O. The presence of copper oxalate is confirmed by IR spectroscopy (Fig. 5) peak at a wave number of 1636 cm^{-1}. Thus, analysis of the reaction solutions residues reveals that they contain oxalates, which are known, are not stable and decompose under reaction conditions to form an oxide.

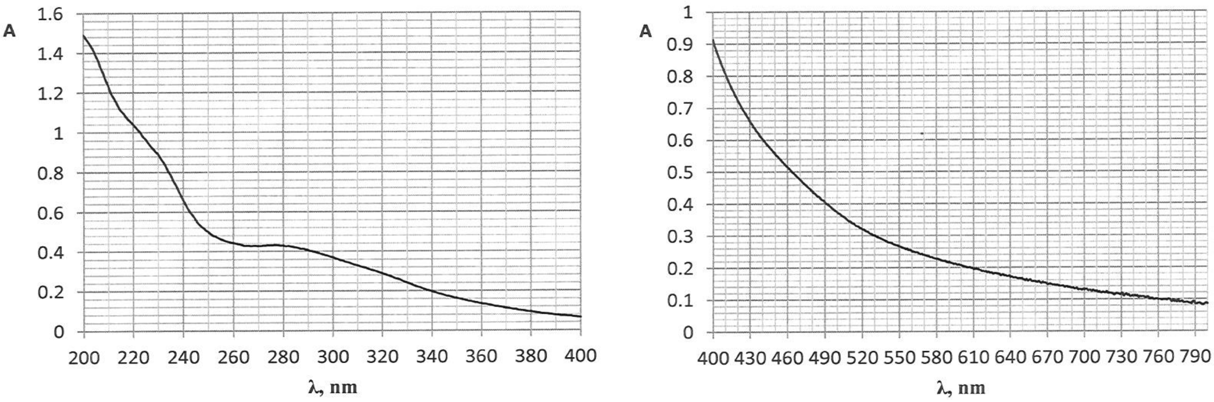

Fig. 4. The UV and visible light region of the reaction solution hydrothermal synthesis

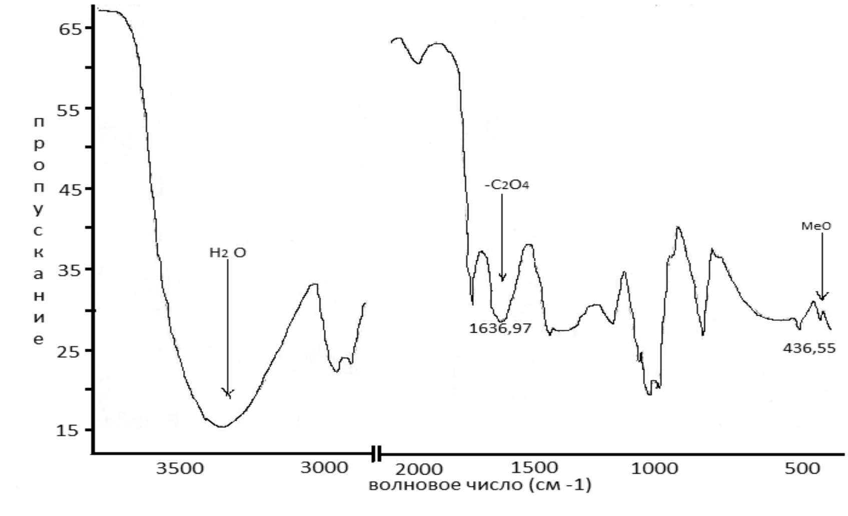

Fig. 5. IK-spectra reaction solution hydrothermal synthesis

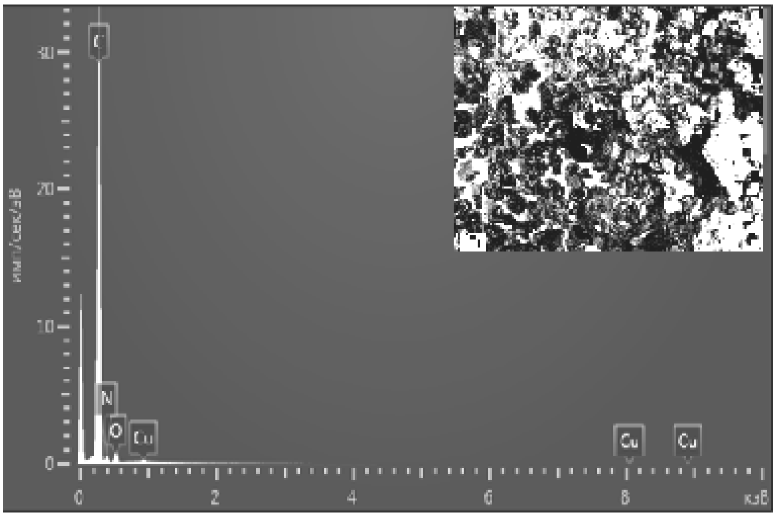

Fig. 6. Elemental analysis and SEM image of the products of hydrothermal decomposition of crystalline copper nitrate in ethylene glycol medium

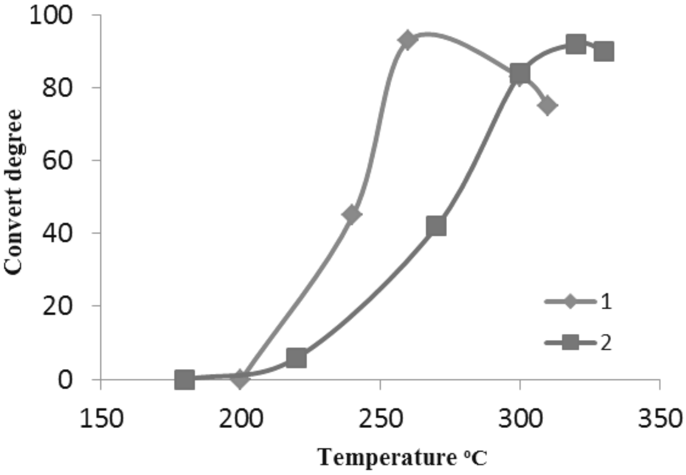

Fig. 7. The catalytic activity in the reaction of selective oxidation of carbon monoxide copper oxide samples obtained from precursors. 1- hydrothermal synthesis products; 2 complex $[(CH_3)_2S{=}O]_2CuCl_2$

Figure 6 shows an SEM image of a solid hydrothermal decomposition and elemental analysis showing the presence of free carbon.

After heat treatment the intermediate product at a temperature 500^0C (1h) formed fluffy black powder. X-ray diffraction analysis, it was found that this product is identified as a copper oxide, the corresponding cards № 01 080 1916 in base ICPDS diffraction data.

The resulting catalysts were tested in a carbon monoxide selective oxidation reaction under the above conditions. Figure7 shows the temperature dependence of the activity of copper oxide derived from precursors with different surface nature. Maximum conversion of carbon monoxide occurs at temperatures in the catalyst 260^0C sample obtained from the hydrothermal synthesis products, whereas it is substantially higher than the other sample.

It is known that the activity of the catalyst depends on the amount of excess energy stored in the defects and which affect the catalytic properties of a substance through a change in the thermodynamic potential. This amount is determined by the physical and chemical nature of the catalytically active sites. The most active catalyst pattern may have an optimum combination of these properties.

Conclusions

1. Samples of copper oxides with different physical and chemical nature of the surface by heat treatment reaction products of $CuCl_2 \cdot 2H_2O$ DMSO decomposition of copper nitrate and in the presence of ethylene under hydrothermal conditions.

2. The methods of X-ray diffraction, thermal analysis showed that the interaction of $CuCl_2 \cdot 2H_2O$ with DMSO leads to the formation of $[(CH_3)_2S = O]_2CuCl_2$

3. Physico-chemical methods of investigation found that the hydrothermal decomposition of copper nitrate in ethylene glycol medium proceeds with the formation of oxalates, which are not stable and decompose under the reaction conditions with the formation of copper oxide.

4. The calcined samples were examined these compounds in the carbon monoxide selective oxidation reaction. It is shown that the most active catalyst sample obtained by heat-treating a product of hydrothermal synthesis.

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METALSAXLAYAN PREKURSORLARIN SİNTEZİ VƏ KARBON MONOOKSİDİN SELEKTİV OKSİDLƏŞMƏ REAKSİYASINDA ƏMƏLƏ GƏLƏN MİS OKSİDLƏRİNƏ ONLARIN TƏRKİBİNİN XASSƏLƏRƏ TƏSİRİNİN QİYMƏTLƏNDİRİLMƏSİ

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Karbon monooksidin selektiv oksidləşməsində metalsaxlayan prekursorların, katalizatorların xassələrinə təsirini öyrənmək məqsədilə mis kationlarının DMSO ilə kompleksi sintez edilmişdir. Eləcə də etilenqlikol mühitində mis kristallohidrat nitratın parçalanması aparılmışdır. Sintez olunmuş birləşmələr müasir fiziki-kimyəvi (RFA, İQ, SEM, element və termiki analiz) metodların köməyilə tədqiq olunmuşdur. Közərdilmiş nümunələr karbon monooksidin selektiv oksidləşməsində öyrənilmiş və perspektivləri göstərilmişdir.

Açar sözlər: *karbon monooksid, dimetilsulfooksid, etilenqlikol, mis kationu, hidrotermal sintez*

СИНТЕЗ МЕТАЛЛСОДЕРЖАЩИХ ПРЕКУРСОРОВ И ОЦЕНКА ВЛИЯНИЯ ИХ СОСТАВА НА СВОЙСТВА ОБРАЗУЮЩИХСЯ ОКСИДОВ МЕДИ В РЕАКЦИИ СЕЛЕКТИВНОГО ОКИСЛЕНИЯ МОНООКСИДА УГЛЕРОДА

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С целью оценки состава металлсодержащих прекурсоров на свойства катализаторов селективного окисления монооксида углерода синтезированы комплексные соединения катионов меди с диметилсульфоксидом (ДМСО), а также проведено гидротермальное разложение кристаллогидратанитарата меди в среде этиленгликоля. Полученные соединения исследованы с применением комплекса физико-химических методов (РФА, ИКС, УФ, СЭМ, элементный и термические анализы). Прокаленные образцы исследованы в реакции селективного окисления монооксида углерода и показана их перспективность.

Ключевые слова: *монооксид углерода, диметилсульфоксид, этиленгликоль, катионов меди, гидротермальный синтез*