

# Physicochemical Properties of Manganese-Containing Oxides with a Spinel Structure Prepared with the Use of Ammonium Nitrate and Their Catalytic Activity in Carbon Monoxide Oxidation

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**Abstract**—Oxide catalysts with the spinel structure with the molar ratios between components  $\text{Co}/\text{Mn} = 1 : 2$ ,  $\text{Cu}/\text{Mn} = 1 : 2$ , and  $\text{Cu}/\text{Co}/\text{Mn} = 2 : 2 : 3$  (samples **I–III**, respectively) have been prepared by the decomposition of metal nitrate hydrate solutions in an ammonium nitrate melt. Sample **IV** with the ratio  $\text{Cu}/\text{Co}/\text{Mn} = 2 : 2 : 3$  containing 80%  $\gamma\text{-Al}_2\text{O}_3$  is obtained by the addition of  $\gamma\text{-Al}_2\text{O}_3$  powder to the initial melt. The catalysts are characterized using X-ray diffraction analysis, electron microscopy, and local X-ray analysis. Catalytic activity in the reaction of CO oxidation increased in the order **I** < **II** < **III** < **IV**. The proposed method is simple, and the synthesis is rapid. Oxides with the spinel structure homogeneous in composition and morphology without any impurities can be prepared by this method. These oxides exhibited high catalytic activity in the reaction of carbon monoxide oxidation.

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The development of efficient catalysts for the removal of environmentally hazardous pollutants such as carbon monoxide, hydrocarbons, and nitrogen oxides from fuel combustion products and, in particular, automobile exhaust emissions is of considerable current interest. A promising solution to this problem is the use of catalysts based on 3d-metal oxides with the spinel structure. Oxides with the spinel structure exhibit a number of advantages over well-known catalysts such as platinum group metals and perovskites. In particular, they are relatively inexpensive and, as a rule, have a more developed specific surface area. In a number of studies, it has been found that oxide catalysts with the spinel structure are highly active not only in the oxidation reactions of hydrocarbons and CO but also in the reduction of nitrogen monoxide [1, 2].

A great number of publications on the use of spinels as catalysts for the oxidation of CO and hydrocarbons are available. Unlike other oxides, spinels are characterized by easy structural rearrangements, the presence of structural defects, and the possibility of electron exchange between neighboring ions [3].

Spinels containing 3d metals that can occur in various oxidation states (Cr, Mn, Co, Ni, and Cu) are the most active [3]. According to published data (for example, [4]), octahedrally coordinated metal ions play a specific role because they are primarily arranged on the crystalline surface of spinel; thus, they are responsible for its catalytic activity. A comparison between the cat-

alytic activities of a number of 3d-metal cobaltites in the reactions of hydrogen and methane oxidation demonstrated [5] that  $\text{Co}_3\text{O}_4$  and  $\text{CuCo}_2\text{O}_4$  spinels are the most active, whereas the  $\text{MnCo}_2\text{O}_4$  manganese cobaltite exhibits the lowest activity. Yang *et al.* [6], who synthesized a series of spinels containing Co, Cu, and Mn, came to an analogous conclusion. The activity of the resulting samples in the reaction of CO oxidation decreased in the order  $\text{Co}_3\text{O}_4 \approx \text{CoCu}_2\text{O}_x \approx \text{CuCoO}_x > \text{MnCuO}_x \approx \text{MnCuCoO}_x$ . In the latter two samples, the surface concentration of manganese was much higher than the average manganese concentration. A decrease in the activity of catalysts containing manganese oxides was explained [5, 6] by the fact that  $\text{Mn}^{2+}$  ions can be readily oxidized to form  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$  ions, which are prone to octahedral coordination and displace more active ions from the octahedral positions of spinel to tetrahedral positions. Thus, the composition of manganese cobaltite is more accurately described by the formula  $\text{Co}_x^{\text{II}}\text{Mn}_{1-x}^{\text{II}}[\text{Mn}_x^{\text{III}}\text{Co}_{2-x}^{\text{III}}]\text{O}_4$  [5], whereas the stable form of copper manganite corresponds to the formula  $\text{Cu}^{\text{I}}[\text{Mn}^{\text{IV}}\text{Mn}^{\text{III}}]\text{O}_4$  [7].

On the other hand, amorphous copper manganite is one of the most active catalysts for CO oxidation. It is a constituent of hopcalite and catalyzes carbon monoxide oxidation even at room temperature [6]. It was found that crystalline copper manganite exhibits high

activity in the reaction of CO oxidation. Thus, Akhundova and Belen'kii [8] found that the catalytic activity of various spinels in CO oxidation increases in the order  $\text{MnCr}_2\text{O}_4 < \text{MnFe}_2\text{O}_4 < \text{Co}_3\text{O}_4 \approx \text{CuCr}_2\text{O}_4 < \text{CuMn}_2\text{O}_4$ .

Thus, published data on the catalytic activity of manganese-containing spinels in the reaction of CO oxidation are contradictory. Of course, not only the composition but also the morphology of samples, as well as the degree of crystallinity and the presence of particular impurities, which mainly depend on the synthetic method used, should be taken into account in the consideration of this problem. The synthesis of oxide catalysts by the decomposition of salt solutions in the melts of alkali metal nitrates is a promising method; however, this method is imperfectly understood. With the use of this method, it is possible to prepare in a single step various simple and complex oxides; oxo salts, for example, molybdates; and complex materials, for example, zirconium polymolybdate supported on zirconium oxide [9]. A disadvantage of this method is that the final products should be washed for the removal of alkali metal salts; in this case, alkali metal impurities cannot be completely removed even by repeated washing. In a number of cases, these impurities may exert a negative effect on catalytic activity. For example, Veprek *et al.* [7] found that the segregation of a potassium salt impurity on the surface of a commercial  $\text{CuMn}_2\text{O}_4$  sample is responsible for a decrease in the activity of copper manganite upon calcination.

The replacement of alkali metal nitrates by ammonium nitrate allowed us to prepare pure oxide samples without the step of washing because, in the course of the heating of a salt solution in molten  $\text{NH}_4\text{NO}_3$ , the solvent was completely removed as a result of evaporation and decomposition. Previously [10], it was found that oxide samples with a high activity in the reaction of deep methane oxidation can be obtained by the decomposition of 3d-metal nitrate solutions in ammonium nitrate. In this work, we applied this method to the preparation of manganese-containing oxides with a spinel structure—catalysts for the reaction of CO oxidation.

## EXPERIMENTAL

The nitrate hydrates  $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , and  $\text{NH}_4\text{NO}_3$  (all of chemically pure grade), as well as  $\gamma\text{-Al}_2\text{O}_3$  (Engelhard de Meern B.V., Chem. Catalysts division; specific surface area of  $185 \text{ m}^2/\text{g}$ ), were used as starting reagents. The amount of water in crystal hydrates was determined more accurately based on weight losses upon the decomposition of nitrates to oxides.

To prepare oxide samples, the hydrates of 3d-metal nitrates in the molar ratios  $\text{Cu/Mn} = 1 : 2$  (sample **I**),  $\text{Co/Mn} = 1 : 2$  (sample **II**), and  $\text{Cu/Co/Mn} = 2 : 2 : 3$  (samples **III** and **IV**) were mixed with a fivefold molar

excess of  $\text{NH}_4\text{NO}_3$  with respect to the total metal amount. Unlike sample **III**, 80%  $\gamma\text{-Al}_2\text{O}_3$  powder with respect to the total oxide weight was added to the starting nitrate mixture in the preparation of sample **IV**. The resulting mixtures were heated in a glass beaker using a sand bath with a gradual increase in the temperature from 353 to 523 K for 30 min. In the course of heating of the starting mixtures, a melt was formed, which boiled and decomposed. To compare the synthesis used in this work with a traditional synthetic approach, a sample with  $\text{Cu/Co/Mn} = 2 : 2 : 3$  was also prepared by the direct decomposition of a nitrate mixture without the addition of ammonium nitrate (sample **V**). All of the resulting samples were annealed in air at 773 K for 2 h.

The thermal decomposition of 3d-metal nitrate hydrate solutions in ammonium nitrate, which were taken in ratios corresponding to samples **I–III**, was studied by thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) with the use of a Derivatograph Q-1500 D instrument. The catalysts were placed in a quartz crucible and heated in a flow of nitrogen to 873 K at a rate of 5 K/min.

The X-ray diffraction (XRD) analysis of samples was performed on an FR-552 instrument using  $\text{CuK}_{\alpha 1}$  radiation and germanium as the internal standard. Phases were identified with the use of the PCPDFWIN database [11].

The morphology and surface composition of catalysts was studied using a Supra 50vp scanning electron microscope (Leo, Germany). To perform electron-probe X-ray microanalysis, an INCA X-Sight microanalysis detector (Oxford Instruments, the United Kingdom) for the electron microscope was used. Powdered samples were pressed in pellets, onto the surface of which gold was sputtered to provide the required conductivity.

The specific surface area of catalysts was determined by the thermal adsorption of nitrogen on a GKh-1 instrument.

The catalytic activity of samples was studied in a flow system. A quartz tube-in-tube reactor was equipped with a Schott filter, onto which a catalyst of volume  $0.3 \text{ cm}^3$  was placed. Before a reaction, the sample was preexposed in a flow of helium ( $25 \text{ cm}^3/\text{min}$ ) at 573 K for 1.5 h in order to remove adsorbed  $\text{H}_2\text{O}$  and  $\text{CO}_2$  molecules from the surface. After cooling to room temperature, the flow of helium was replaced by a reaction mixture of the following composition (vol %): CO, 4;  $\text{O}_2$ , 2; and He, to 100. In all of the experiments, the space velocity of the reaction mixture was  $10000 \text{ h}^{-1}$ .

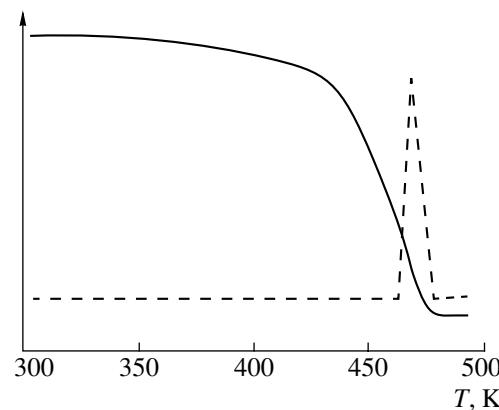
The concentrations of reactants and reaction products were determined using a Chrom 5 chromatograph with a katharometer as a detector. Two columns ( $3000 \times 3 \text{ mm}$ ) were used; one of them was packed with molecular sieves  $5 \text{ \AA}$  ( $\text{O}_2$ ; CO), and the other was packed with Porapak Q (air;  $\text{CO}_2$ ). Helium was a carrier gas ( $30 \text{ cm}^3/\text{min}$ ). The accuracy of the determination of the main components of a gas mixture was 10 rel %.

## RESULTS AND DISCUSSION

On heating the starting mixtures of  $3d$ -metal nitrate hydrates with an excess of ammonium nitrate, the formation of a homogeneous melt was observed even at  $\sim 373$  K. An increase in the temperature to 413 K was accompanied by the dehydration and partial hydrolysis of the melt, whereas the melt completely decomposed with strong gas evolution upon heating to 453–503 K. Figure 1 shows the TG curve for the decomposition of a mixture of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  with excess  $\text{NH}_4\text{NO}_3$  (1 : 2 : 9). The main weight loss occurred in a single step over the temperature range 445–473 K. In the TG and DTA curves, this step is manifested as an almost vertical weight loss and a great exotherm at 468 K, respectively. As the temperature was further increased to 873 K, the TG and DTA curves did not indicate any events and the total weight loss was no higher than 5%. The TG and DTA curves of the decomposition of the other nitrate mixtures were analogously shaped. This character of decomposition facilitated the formation of oxide samples with a homogeneous distribution of components and a developed specific surface area, which essentially depends on catalyst preparation procedures. Thus, the specific surface areas of samples **III** and **V** differed by a factor of more than 2 (see the table).

Upon the addition of powdered  $\gamma\text{-Al}_2\text{O}_3$  to the starting mixture, the decomposition of salts occurred less vigorously (the synthesis of sample **IV**). This was likely due to the absorption of a portion of heat released in the course of melt decomposition by aluminum oxide particles to result in a decrease in the degree of sample agglomeration and in an increase in the dispersity of  $3d$ -metal oxides. This conclusion was supported by the XRD and electron-microscopic studies of the resulting samples.

The XRD analysis of catalysts was complicated by diffuse lines in the XRD patterns. Samples **I** and **II** were the spinels  $\text{CoMn}_2\text{O}_4$  and  $\text{CuMn}_2\text{O}_4$ , respectively (see the table). Based on a similarity between the XRD patterns of sample **III** and the ternary spinel  $\text{CuCoMnO}_x$  (face-centered cell;  $a = 8.20(1)$  Å [6]), indexing was performed and the parameter of the cubic unit cell was found (8.25(1) Å). The XRD patterns of samples **III**



**Fig. 1.** Thermoanalytical curves for the mixture of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , and  $\text{NH}_4\text{NO}_3$  ( $v(\text{Co})/v(\text{Mn})/v(\text{NH}_4) = 1:2:9$ ).

and **V** were fully coincident. Although the ratios between  $3d$  metals in samples **III** and **IV** were equal, the XRD pattern of sample **IV**, which was prepared by the decomposition of the starting nitrate mixture in the presence of  $\gamma\text{-Al}_2\text{O}_3$  powder, did not exhibit reflections corresponding to any  $3d$ -metal oxides. This is indicative of a decrease in the size of crystallites in sample **IV**, as compared with that in sample **III**.

With the use of electron microscopy, we found that samples **I–III**, prepared by nitrate decomposition in an ammonium nitrate melt, had similar morphologies, which remained unchanged in the course of a catalytic experiment (Fig. 2a). The samples consisted of partially agglomerated particles of size 10–20 nm. The micrograph of sample **V**, which was prepared without the use of  $\text{NH}_4\text{NO}_3$ , was noticeably different (Fig. 2b). In this case, individual crystals of sizes up to 0.5  $\mu\text{m}$  can be seen along with small particles. With the use of local X-ray analysis, we found a uniform distribution of metals in all of the catalysts; in this case, the surface and bulk concentrations were practically equal. Thus, for example, the atomic fractions of metals on the surface of sample **III** measured at five points were equal to 27.0(2.2), 27.6(1.1), and 45.4(1.8)% for Cu, Co, and Mn, respectively (standard deviations from the average

Phase composition and specific surface area ( $S_{\text{sp}}$ ) of oxide samples and the temperature of 50% CO conversion into  $\text{CO}_2$  ( $T_{50\%}$ )

Sample	Metal ratio in the sample, at %	Phase composition	$S_{\text{sp}}$ , $\text{m}^2/\text{g}$	$m_{\text{Cat}}$ , g	$T_{50\%}$ , K
<b>I</b>	$\text{Co/Mn} = 1:2$	$\text{CoMn}_2\text{O}_4(77-0471)***$	29.9	0.300	412
<b>II</b>	$\text{Cu/Mn} = 1:2$	$\text{CuMn}_2\text{O}_4(84-0543)***$	12.3	0.287	383
<b>III</b>	$\text{Cu/Co/Mn} = 2:2:3$	$\text{Cu}_2\text{Co}_2\text{Mn}_3\text{O}_x$	27.8	0.350	351
<b>IV</b>	$\text{Cu/Co/Mn} = 2:2:3*$	–	140	0.343	340
<b>V</b>	$\text{Cu/Co/Mn} = 2:2:3**$	$\text{Cu}_2\text{Co}_2\text{Mn}_3\text{O}_x$	12.5	0.352	410

\* Sample containing 80 wt %  $\gamma\text{-Al}_2\text{O}_3$ .

\*\* Sample prepared by the decomposition of nitrates with no addition of  $\text{NH}_4\text{NO}_3$ .

\*\*\* X-ray diffraction pattern number from the PCPDFWIN database [11].

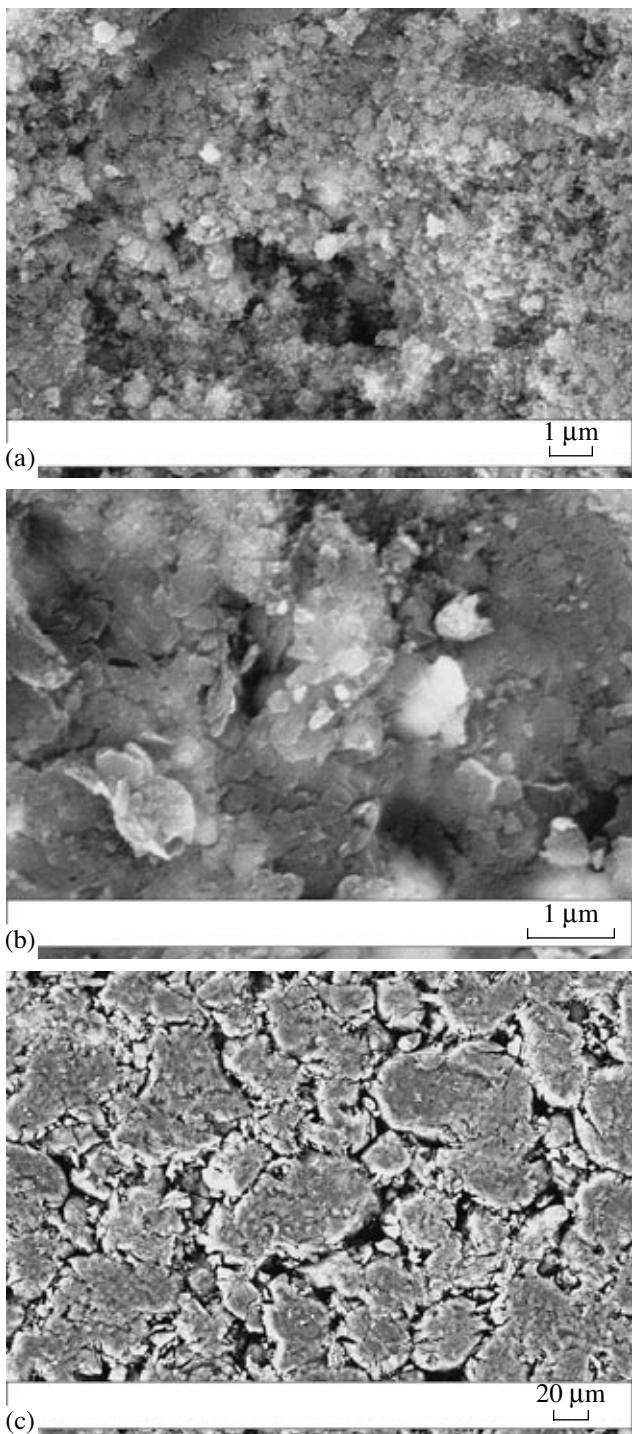


Fig. 2. Micrographs of samples (a) III, (b) V, and (c) IV.

are given in parentheses), whereas the average concentrations of these components in the bulk of the sample were 28.5, 28.5, and 43%, respectively.

The micrograph of sample IV shows parent  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> particles of size 20–80  $\mu$ m (Fig. 2c). According to local X-ray analysis data, the concentration of aluminum was 50–72 at % with respect to the concentration of 3d met-

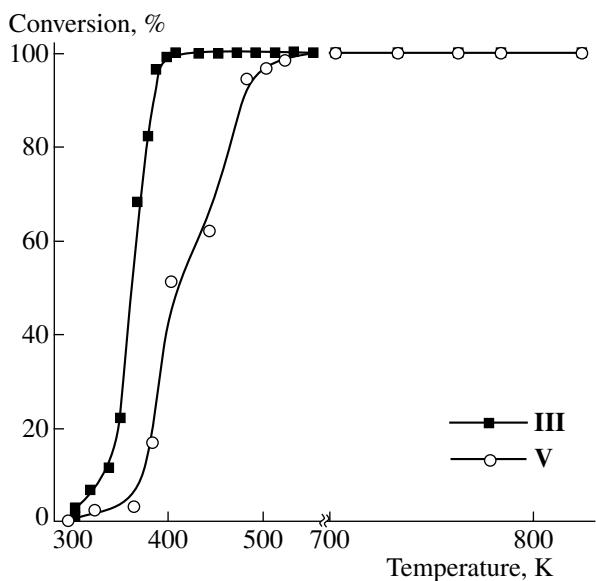


Fig. 3. The temperature dependence of CO conversion in the presence of Cu<sub>2</sub>Co<sub>2</sub>Mn<sub>3</sub>O<sub>x</sub> samples prepared in an ammonium nitrate melt (III) and by the decomposition of a nitrate mixture (V).

als; this suggests the formation of a film of 3d-metal oxides about 1  $\mu$ m in thickness on the surface of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. According to data measured at four points, the relative concentrations of Cu, Co, and Mn on the surface of alumina were 29.6(1.4), 34.2(2.7), and 36.2(3.3) at %, respectively, which are somewhat different from the average values (28.5, 28.5, and 43%, respectively). At the same time, the measurement at a single point gave an overestimated concentration of Mn (Cu/Co/Mn = 23 : 25 : 52) at a relatively low concentration of Al (51 at %). This suggests that copper and cobalt oxides were primarily concentrated on the surface of Al<sub>2</sub>O<sub>3</sub>, whereas the concentration of manganese in sample segments that are more distant from the surface of alumina increased.

From data given in the table and Figs. 3 and 4, it follows that catalysts synthesized in molten ammonium nitrate were more active in the reaction of carbon monoxide oxidation than samples prepared by other methods. Thus, sample V, which was prepared by the decomposition of a nitrate mixture in the absence of NH<sub>4</sub>NO<sub>3</sub>, ranks below chemically analogous sample III, which was synthesized by the method proposed in this work, in activity (Fig. 3). Yang *et al.* [6] prepared spinels by coprecipitation from an alcoholic solution of nitrates with ammonia at  $-30^{\circ}\text{C}$  followed by the thermal decomposition and annealing of the resulting precipitate at 773 K for 12 h. The calculations of conversion per gram of catalyst demonstrated that samples I–III prepared in this work were more active than the spinels MnCuO<sub>x</sub> and MnCuCoO<sub>x</sub> synthesized by Yang *et al.* [6] by a factor of 5–10.

According to the experimental data, the samples can be arranged in the following order of decreasing catalytic activity: **IV** (20%  $\text{Cu}_2\text{Co}_2\text{Mn}_3\text{O}_x/\text{Al}_2\text{O}_3$ ) > **III** ( $\text{Cu}_2\text{Co}_2\text{Mn}_3\text{O}_x$ ) > **II** ( $\text{CuMn}_2\text{O}_4$ ) > **I** ( $\text{CoMn}_2\text{O}_4$ ) (the compositions of the resulting samples are specified in parentheses) (table; Fig. 4). The spinel  $\text{CuMn}_2\text{O}_4$  ( $T_{100\%} = 482$  K) is more active than  $\text{CoMn}_2\text{O}_4$  ( $T_{100\%} = 502$  K); this is consistent with the well-known fact that hopcalite is highly active in the reaction of CO oxidation. The higher activity of the ternary spinel (sample **III**,  $T_{100\%} = 382$  K) is consistent with data published by Yang *et al.* [6], who found that the activity of catalysts with the spinel structure based on Mn, Co, and Cu oxides in the reaction of CO oxidation increased as the concentration of Mn was decreased. Indeed, the average Mn content of samples **I** and **II** was 66.7 at %, whereas it was equal to 43% in sample **III**. Moreover, an increase in activity on going from a binary spinel to a ternary spinel can be explained based on the facts and hypotheses given below.

Previously [3], it was found that redox couples playing a key role in catalytic oxidation are formed on the surface of mixed spinels containing atoms in variable oxidation states. Thus, the equilibrium  $\text{Cu}^{2+} + \text{Mn}^{3+} = \text{Cu}^{1+} + \text{Mn}^{4+}$  [6, 7] was considered for the Cu–Mn spinel, and  $\text{Co}^{3+} + \text{Mn}^{2+} = \text{Co}^{2+} + \text{Mn}^{3+}$  [6] and  $\text{Co}^{3+} + \text{Mn}^{3+} = \text{Co}^{2+} + \text{Mn}^{4+}$  [5] were considered for Co–Mn spinels. In addition to electron disordering due to electron exchange, defects can also be formed because of a rearrangement of polyhedrons and changes in the M/O ratio [3]. It is likely that, on passing from a binary spinel to a ternary spinel, new opportunities appear for various electron transitions and defect formation; this has a positive effect on the catalytic activity of samples.

Sample **IV**, which was prepared by the decomposition of a mixture of 3d-metal nitrates and ammonium nitrate in the presence of  $\gamma\text{-Al}_2\text{O}_3$ , was found to be even more active in CO oxidation than sample **III** with the same ratio between 3d metals (table; Fig. 4), although the total concentration of active components (3d-metal oxides) in catalyst **IV** was lower by a factor of 5. Thus, the introduction of a prepared support ( $\gamma\text{-Al}_2\text{O}_3$ ) into a nitrate solution resulted in an increase in the activity of the catalyst; this was likely due to an increase in the dispersity of the sample.

Thus, as a result of our experiments, we found that the proposed synthetic method based on the decomposition of 3d-metal nitrate solutions in molten ammonium nitrate is simple and rapid. This method allowed us to prepare samples that are free of any impurities and homogeneous in composition and morphology. These samples exhibited high catalytic activity in the reaction of carbon monoxide oxidation.

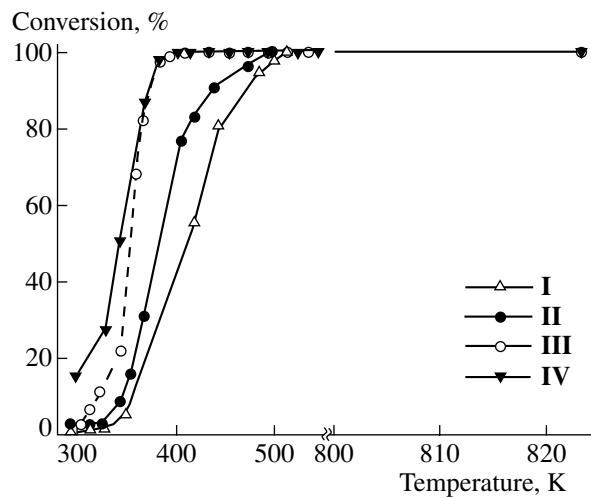


Fig. 4. Catalytic activity of samples **I** ( $\text{CoMn}_2\text{O}_4$ ), **II** ( $\text{CuMn}_2\text{O}_4$ ), **III** ( $\text{Cu}_2\text{Co}_2\text{Mn}_3\text{O}_x$ ), and **IV** (20 wt %  $\text{Cu}_2\text{Co}_2\text{Mn}_3\text{O}_x/\gamma\text{-Al}_2\text{O}_3$ ) in the reaction of CO oxidation.

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