Journal of the Turkish Chemical Society Section A: Chemistry

TURKISH CHEMICAL SOCIETY

Cobalt-Containing Oxide Catalysts Obtained by The Sol-Gel Method with Auto-Combustion in The Reaction of Low-Temperature Oxidation of Carbon Monoxide

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Abstract: The reaction of low-temperature oxidation of carbon monoxide is important in the context of air purification and reduction of automotive emissions. Along with the search for active catalytic systems for carbon monoxide oxidation, the development of new energy-saving methods of catalyst synthesis also seems important. Cobalt-iron-, cobalt-manganese, cobalt-chromium, cobalt-copper binary and cobalt-manganese-iron, cobalt-copper-iron-containing triple oxide systems for low-temperature oxidation of carbon monoxide into carbon dioxide were synthesized by the sol-gel method with auto-combustion. The samples were analyzed by X-ray diffraction, IR spectral and derivatographic methods of analysis, their specific surface area was measured by the BET method, micro-photographs were taken on a scanning electron microscope. It was established that the resulting binary and ternary cobalt-containing oxide systems are multiphase systems containing ferrites, manganites, and oxides of cobalt, copper, manganese, and iron. The resulting catalysts are active in the low-temperature oxidation of carbon monoxide at 145-180 °C. The activation energy of the CO oxidation reaction on the analyzed oxide systems was revealed by the Arrhenius equation is placed in the range of 17-33 kJ/mol. In the systems, an intensifying effect of the influence of its components on the catalytic activity is observed in the oxide and spinel phases. The Co-Cr=2:1 system, which, along with chromite, also contains cobalt oxide, which is active at a much lower temperature – 145 °C than systems with a Co-Cr=1:1 and 1:2 ratios. A similar dependence was obtained in the Co-Fe=2:1 system, i.e. in a sample that, along with cobalt ferrite, also contains cobalt oxide. On this catalyst, 100% conversion of CO to CO_2 occurs at a temperature of 200 °C, and a Co-Fe = 1: 2 sample with a stoichiometric ratio of metals, in which the ferritization reaction completely occurs, as experiments have shown, is active only at temperatures above 300 °C. The intensifying effect of the influence of the components on its activity is also observed in three-component systems, in which the complete conversion of CO occurs at a temperature of 145-160 °C. The appearance of various structural defects during short-term combustion of the gel without additional heat treatment, which can potentially be considered as catalytically active centers, on the one hand, and the presence of oxide and spinel phases in the composition of catalysts, which exhibit a mutual reinforcing effect, on the other hand, is demonstrative advantage of this method for the synthesis of active catalysts for low-temperature oxidation of carbon monoxide to dioxide.

Keywords: Sol-gel method with auto-combustion, Catalysis, Carbon monoxide oxidation, Cobalt-containing oxide catalysts.

Submitted: March 08, 2023. **Accepted:** May 10, 2023.

Cite this: Zulfugarova SM, Azimova GR, Aleskerova ZF, Tagiev DB. Cobalt-Containing Oxide Catalysts Obtained by The Sol-Gel Method with Auto-Combustion in The Reaction of Low-Temperature Oxidation of Carbon Monoxide. JOTCSA. 2023;10(3):577-588.

DOI: https://doi.org/10.18596/jotcsa.1261839

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1. INTRODUCTION

The problem of utilization of carbon monoxide, which makes a significant contribution to environmental pollution, is relevant to this day. CO emissions are mostly the result of anthropogenic impact on the biosphere. It is known, that most often CO is formed in the process of incomplete combustion of various carbon-containing materials during the operation of internal combustion engines used in various types of land, water and air transport. In addition to transport, CO is a by-product of a number of large-scale production of the chemical industry. Also, the release of significant amounts of CO accompanies the work of metallurgical and a number of other industries. Among the many gas cleaning systems on the market today, the most promising are catalytic conversion systems containing an active monocatalyst or their mechanical mixture, introduced into the carrier by impregnation or deposition. Catalysts used to oxidize carbon monoxide to carbon dioxide can be divided into three classes:

The first class includes noble metals, such as Pt, Pd and Rh on various carriers (CeO, ZrO_2, Al_2O_3, TiO_2, etc.), which have a high catalytic activity in CO oxidation in the temperature range of 150-250 °C and widely used in the disinfection of exhaust gases (1-8). The second class of catalysts includes nanosized gold catalysts used at very low temperatures of CO oxidation to CO_2 (9-13). These catalysts can work under normal conditions, especially in air purification systems, breathing apparatus.

The catalysts of the third class include metal oxides of Fe, Ni, Mn, Cu, Co, Cr, Ni, Ce, etc. Oxides can be used separately or in various combinations of oxides, including ferrites (14-29). In recent years, there are also many works in the literature devoted to the oxidation of CO on catalysts of the spinel structure (30-38).

Currently, the most advanced catalysts for the neutralization of waste and waste gases are catalysts containing noble metals (Pt, Pd, Rh) (1). However, for industrial catalysts containing platinoids, a cost-effective technology for extracting an expensive active phase for reuse has not yet been proposed. From the point of view of the efficiency of the CO oxidation process, it is especially important to carry out the oxidation process at the lowest possible temperatures, i.e., in an energy-saving mode. Therefore, the search for active and stable catalysts for the low-temperature oxidation of CO instead of expensive catalysts containing noble metals remains a priority in research.

From this point of view, many works are devoted to cobalt-containing catalysts, both oxide and more complex (39-48).

Catalysts for the oxidation of carbon monoxide are obtained by various methods - co-precipitation, thermal decomposition of salts, sol-gel method, ceramic, combustion of solutions in a high-temperature stream, plasma-chemical, etc. In all available methods, the formation of the catalyst structure proceeds at high temperature during sintering, which is a solid-phase process and requires long-term heat treatment. Mechanochemistry (49-50), microwave radiation (27, 36, 51-52) are often used to accelerate solid-phase processes.

Along with the search for active catalytic systems, the development of new energy-saving synthesis methods also seems important for heterogeneous catalysis.

To date, among the methods for obtaining highly dispersed catalysts, much attention is paid to the sol-gel method, the main advantage of which is the high homogenization of the initial components with the production of sol and its transformation into gel due to the processes of hydrolysis and condensation, followed by aging, drying and heat treatment.

A variation of the sol-gel method is the sol-gel with auto-combustion. The process of drying and heat treatment in this method occurs in one stage. The method includes an exothermic and self-sustaining redox reaction of a xerogel, which is obtained from an aqueous solution containing metal salts (oxidizing agent) and an organic component (reducing agent), which is also "combustible". The organic component forms complexes with metal ions, which prevents the precipitation of metal salts and thereby improves gelation conditions. In addition to these advantages, as a result of the combustion of the organic component, a large amount of gaseous products is formed, which prevents the solid phase crystallites from sintering - it is obtained in the form of ash or a fine powder. The reaction proceeds quickly and at a sufficiently low temperature. The method is quite simple for practical implementation and economical in terms of time and energy.

Based on the foregoing, this paper presents the results of a study of the reaction of carbon monoxide oxidation on cobalt-containing oxide catalysts obtained by the sol-gel method with auto-combustion, as well as using microwave treatment.

2. EXPERIMENTAL PART

Double cobalt-iron-, cobalt-manganese, cobalt-chromium, cobalt-copper and triple cobalt-manganese-iron, cobalt-copper-iron-containing oxide systems were synthesized by the sol-gel method with auto-combustion.

Precursors for the synthesis of these systems were nitrates of salts of the appropriate metals – $Co(NO_3)_2 \bullet 6H_2O$, $Fe(NO_3)_3 \bullet 9H_2O$, $Cu(NO_3)_2 \bullet 3H_2O$, $Mn(NO_3)_2 \bullet 4H_2O$ and citric acid, glycine, urea as organic reagents. Two-component cobalt-iron oxide systems were synthesized with a ratio of Co:Fe = 1:1, 1:2 and 2:1, cobalt-manganese oxide systems with a ratio of Co-Mn = 1:1, cobalt-copper oxide systems with a ratio of Co- Cu=1:1 and three-component cobalt-manganese-iron-containing oxide compositions with ratio Co:Mn:Fe= 1:1:1, 2:1:1, 1:2:1. Aqueous solutions of the calculated amounts of salts and the organic reagent were mixed on a magnetic stirrer with heating until a gel formed. The resulting gel was placed in an oven heated to 175-190 °C, in which it completely dried and then ignited. Microwave technology has also been used in the synthesis of some catalytic systems.

Microwave sol-gel synthesis was carried out in two ways:

- Gel was subjected to microwave treatment until complete cessation of combustion with the formation of powder within a few minutes.

- Microwave treatment of the gel was stopped at the moment of ignition, i.e. microwave energy was used to ignite the gel without further prolonged irradiation, and even at low magnetron power; this took several seconds.

X-ray phase diffraction analysis of the products was carried out on a Bruker D 2Phazer automatic diffractometer with a CuKα radiation source. IR spectra were recorded on a Bruker FTIR Alfa spectrometer. Measurement of the specific surface of the samples was determined by low-temperature nitrogen adsorption according to the multipoint BET method on SORBI-MS (Russia) device.

Derivatographic analysis was performed on a NETZCH STA 449F3 instrument. Micrographs were taken on a Hitachi TM 3000 electron microscope.
The obtained powders of oxide systems in the amount of 1 gram were mixed with a binder - alumogel, formed into granules, dried in air, further heat treatment was carried out in a drying cabinet and a muffle furnace at a temperature of 135 and 500 °C, respectively.

CO oxidation was carried out by the flow method at a ratio of CO: air = 1:(3-5), a volumetric rate of 6000-12000 h^{-1}. The analysis was carried out on an LKhM chromatograph, in two columns with sorbents CaA and porapak Q. The measure of activity was the temperature of 100% conversion of CO into CO_2.

$$X_{CO} = 100\frac{C_{input} - C_{output}}{C_{input}}$$

Where;
C_{input} is the concentration of CO in the gas mixture at the inlet to the reactor,
C_{output} is the concentration of CO in the gas mixture at the outlet of the reactor,
X_{CO} - CO conversion (%).

3. RESULTS

3.1. Catalytic activity of double cobalt-containing oxide systems in the oxidation of carbon monoxide.

3.1.1. Co-Fe system

X-ray diffraction analysis of the resulting two-component Co-Fe system with a ratio of 1:2 showed the formation of cobalt ferrite $CoFe_2O_4$, as well as a small amount of double iron oxide Fe_3O_4 (Fig. 1, a). In the IR spectrum, a band characteristic of ferrites was also observed at 547.56 cm^{-1}. The phase composition of the sample with the ratio Co-Fe = 1: 1 consists of oxides of cobalt, iron and ferrite, and the sample with the ratio Co-Fe = 2: 1 - from cobalt oxide and ferrite.

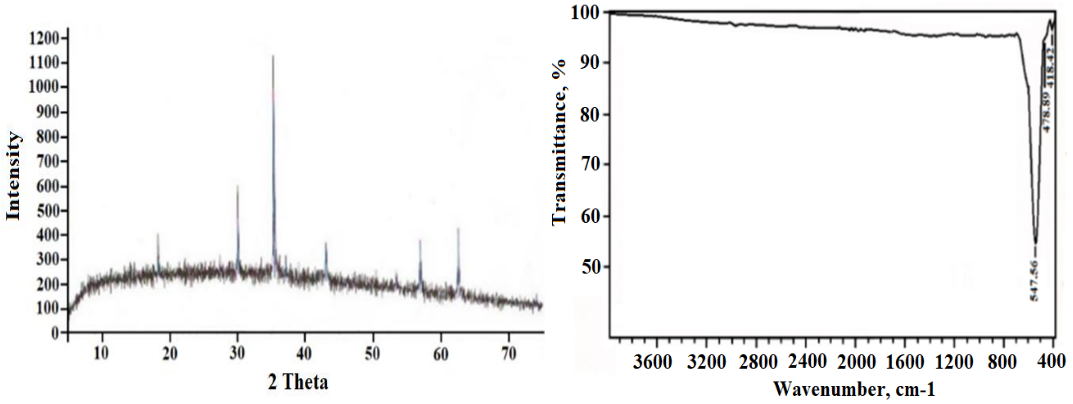

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Figure 1: Diffraction pattern (a) and IR spectrum (b) of the Co-Fe=1:2 sample obtained by the sol-gel method with auto-combustion.

Previously, we carried out the microwave synthesis of cobalt ferrite using a ceramic method from cobalt oxide and magnetite (53). To compare the catalytic activity of cobalt ferrite obtained by various methods, we carried out a microwave sol-gel synthesis; burning the gel in a microwave oven. The diffraction pattern of the resulting sample was identical to the diffraction pattern of the sample obtained by conventional gel combustion.

To elucidate the processes occurring during the combustion of a xerogel during the synthesis of a two-component Co-Fe system by the sol-gel method with combustion, a differential thermal analysis was carried out of a xerogel prepared from metal nitrates and citric acid by heating it to a temperature of 900 °C (Fig. 2).

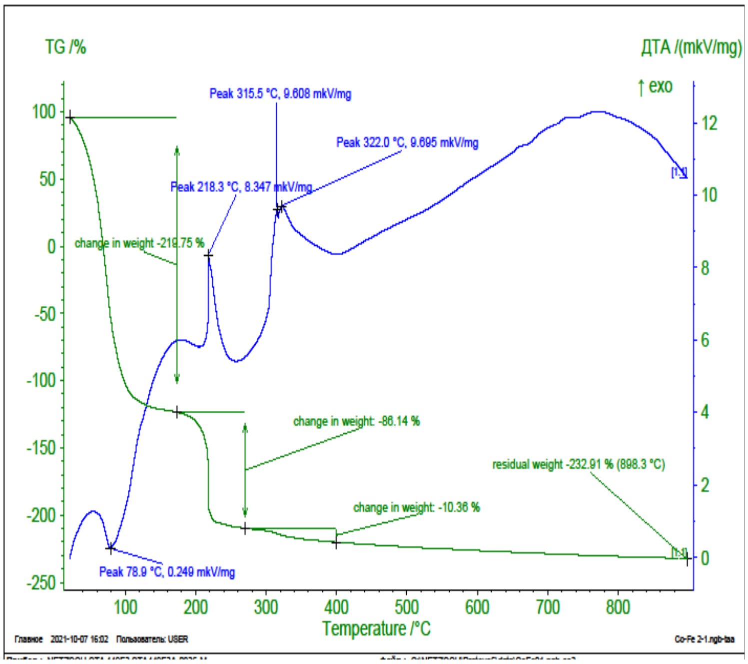

Figure 2: Derivatogram of Co-Fe system

The DTA curve shows an endothermic peak at 80 °C and two exothermic peaks at 218 and 322 °C. C is about 64% due to water evaporation. In the range of 180-280 °C, a chemical reaction occurs between metal nitrates and citric acid due to the ignition of the latter. The weight loss in this case is about 25%. Note that the onset of combustion, i.e., the reaction initiation temperature, was previously recorded during the synthesis of ferrite. The drying of the gel took place in an oven at a temperature of 175-180 °C. Under these conditions, ignition and further combustion of the gel occurred. The exothermic band between 280 and 400 °C with a maximum at 322 °C complies with the combustion of residual amounts of the organic component and the weight loss in this temperature range is 2.7%. With a further increase in temperature, the mass loss is very small.

The catalytic activity of Co-Fe systems prepared by various methods with different ratios of metals was studied in the reaction of oxidation of carbon monoxide to dioxide. The measure of activity was the temperature of 100% conversion of CO to CO_2. The experimental results are shown in Fig.3.

It can be seen from the Fig. 3 that for all the synthesized samples, the complete conversion of carbon monoxide is achieved in the temperature range above 350 °C. The exception is a sample with a ratio of Co-Fe=2:1, on which 100% conversion of CO to CO_2 occurs at a temperature of 200 °C. According to elemental analysis, the content of cobalt in this catalyst is 71, and iron is 29%. It is likely that the presence of Co_3O_4 in samples with a higher ratio of cobalt to iron favors the occurrence of the oxidation reaction as compared to the Co-Fe=1:2 sample with a stoichiometric ratio of metals, in which the ferritization reaction occurs almost completely. On the samples obtained by the microwave sol-gel method and microwave synthesis from oxides, the conversion at 500 °C is 64 and 16%, respectively, so carrying out the reaction on these samples at higher temperatures was of no interest. Samples obtained by "igniting" the gel in a microwave show the same activity as samples obtained by the conventional sol-gel method with combustion. The specific surface area of the samples is shown in Table 1, according to which a relatively long microwave treatment leads to a decrease in the specific surface area, which affects the catalytic activity.

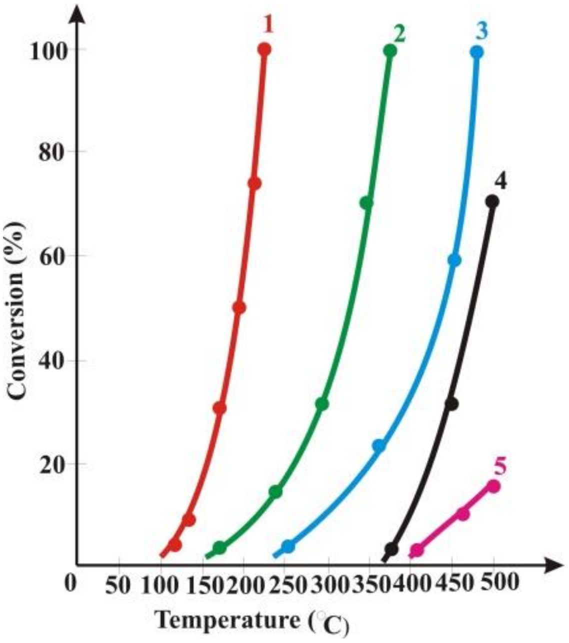

Figure 3: Dependence of carbon monoxide conversion on temperature on the Co-Fe catalytic system synthesized by various methods: sol-gel method with combustion (1 - Co-Fe=2:1; 2 - Co-Fe=1:1; 3 - Co- Fe=1:2), gel combustion in a microwave field (4-Co-Fe=1:2) and microwave synthesis from oxides (5-Co-Fe=1:2).

Table 1: Specific surface area values of synthesized catalysts samples

Catalyst and synthesis method	Specific surface, m^2/g
Co-Fe=1:2, solid phase microwave synthesis from oxides	0.2
Co-Fe=1:2, microwave sol-gel synthesis	1.5
Co-Fe=1:2, sol-gel synthesis with auto-combustion	12
Co-Fe=1:1, « ---------------------------------»	26
Co-Fe=2:1, « --------------------------------- »	28
Co-Mn-Fe, sol-gel synthesis with auto-combustion	28
Co-Mn-Fe, microwave sol-gel synthesis	1.8
Co-Cu-Fe, sol-gel synthesis with auto-combustion	26
Co-Cu-Fe, microwave sol-gel synthesis	2.2

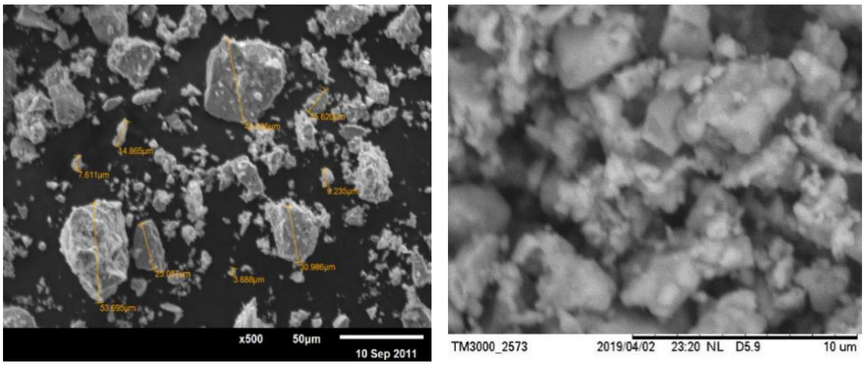

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Figure 4: Micrographs of a Co-Fe=2:1 sample obtained by microwave treatment from oxides (a) and microwave sol-gel synthesis (b).

Fig. 4 shows the data of an electron microscopic study of samples using microwave exposure, from which rather large crystallites are visible, the dimensions of which vary within 500 nm -2 μm. When samples are obtained by solid-phase microwave synthesis from oxides, the time of microwave treatment as compared to gel combustion is rather long and is measured in minutes, since microwave treatment alternates with grinding the initial mixture of oxides. Owing to the high ability of the initial oxides to absorb microwave radiation, a strong rise in temperature occurs which leads to aggregation of the formed particles. This occurs both during the microwave sol-gel synthesis of samples and during additional microwave treatment of the powder obtained after burning the gel. These samples are also characterized by low specific surface area, which is 0.2–1.8 m^2/g, respectively.

In the synthesis of the sol-gel method with combustion, as a result of the release of a large amount of gas, a bulk mass of ash is formed, which, when rubbed, produces a fine powder (Fig. 5). The burning of the gel occurs within a few seconds. The specific surface of the samples obtained by the sol-gel method with combustion is 12–28 m^2/g.

Figure 5: A sample of the catalyst Co-Fe=1:2 obtained sol-gel method with auto-burning.

3.1.2. Co-Mn, Co-Cu and Co-Cr systems

According X-ray diffraction analysis, along with the binary spinel-type oxide, cobalt manganite $CoMn_2O_4$, cobalt and manganese oxides are also formed in the Co-Mn system ($CoMn_2O_4$ - 48%, Mn_3O_4 - 29.5%, Co_3O_4 - 22.5%) (Fig. 6, a). The IR spectrum shows an absorption band at 665 cm^{-1}, which characterizes the Me-O bonds of tetrahedrally coordinated ions in spinels. The absorption bands in the range 900–1400 cm^{-1} (1168.97, 1276.97, 1458.85) are related to Me–OH bending vibrations (19, 30).

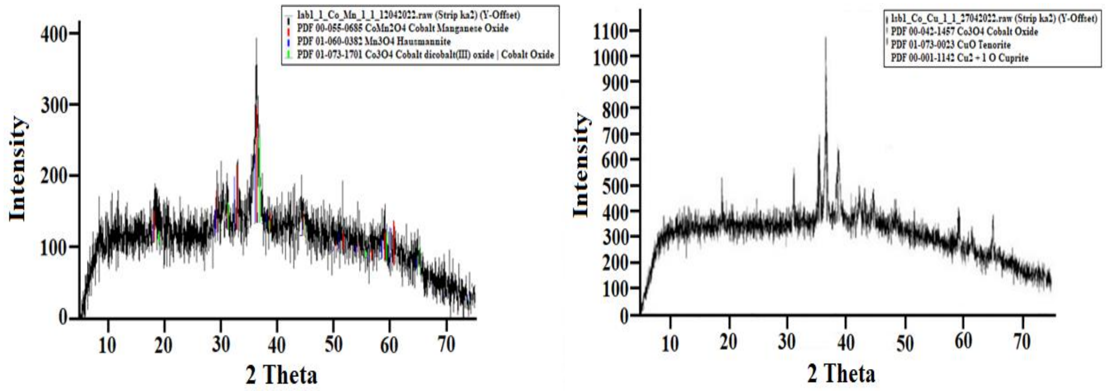

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Figure 6: X-ray diffraction patterns of Co-Mn=1:1 (a) and Co-Cu=1:1 (b) samples

In the Co-Cu (1:1) system, only oxides Co_3O_4, CuO, Cu_2O are formed while in the Co-Cr system there are formed cobalt chromite Co_2CrO_4. The phase composition of double oxide systems is given in Table 2.

Table 2 shows that the complete conversion of carbon monoxide on these systems is achieved within 7-11 minutes of the reaction. The nature of the dependence of the degree of conversion on time at different temperatures for these samples is shown in Fig. 7, from which it can be seen that the relatively higher the reaction temperature, the shorter the time to achieve complete conversion of carbon monoxide.

Table 2: Phase composition of binary oxide system

Catalyst	Reaction temperature,^{0}C	Time to reach 100% conversion, min
Co-Mn=1:1	200	9
Co-Mn=2:1	180	10
Co-Cu=1:1	150	8-9
Co-Cr=1:1	300	9-10
Co-Cr=1:2	280	7-8
Co-Cr=2:1	145	11

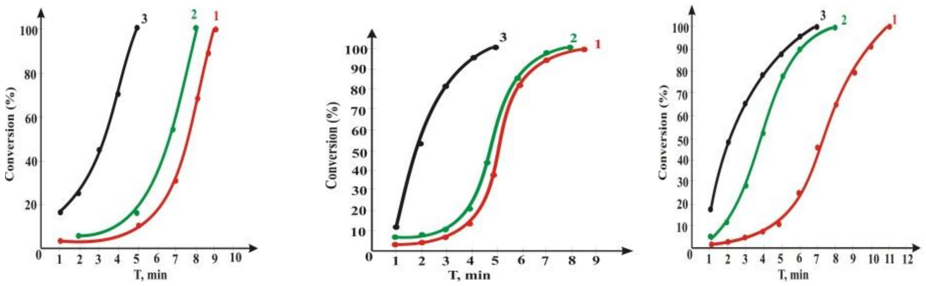

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Figure 7: Dependence of the degree of conversion of carbon monoxide on time in oxide catalytic systems at different temperatures: a) Co-Mn (1-185^{0}C, 2-215 ^{0}C, 3-245^{0}C); b) Co-Cu (1-140^{0}C, 2-150 ^{0}C, 3 - 180^{0}C) and c) Co-Cr (1 - 145^{0}C, 2 - 160 ^{0}C, 3 - 180^{0}C).

3.1.3. Three-component systems Co-Mn-Fe and Co-Cu-Fe

The composition of three-component systems obtained by the sol-gel method with combustion is more complex. Reflections of $CoFe_2O_4$, $CoFe_{0.8}Mn_{1.2}O_4$, Mn_3O_4, Fe_3O_4 are observed in the diffraction pattern of the Co-Mn-Fe-oxide system (Fig. 8,a). Reflections of the following phases are observed on the diffraction pattern of the Co-Cu-Fe-oxide system: $CuFe_2O_4$, $CoFe_2O_4$, $CoCu_2O_3$, CuO (Fig. 8,b). Thus, we see that in the studied 3-component systems obtained by the sol-gel method with auto-combustion, in addition to copper, iron and manganese oxides, the formation of spinels - cobalt ferrite, as in the case of a two-component Co-Fe system, and copper ferrite is observed. These systems can be considered as solid solutions in the same way as binary compositions. And as the composition becomes more complex, various combinations of mixed oxides are possible.

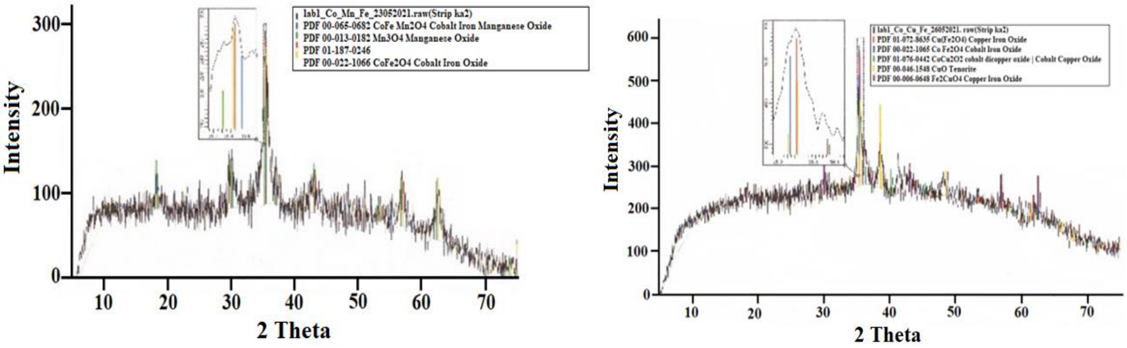

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Figure 8: Diffractograms of X-ray diffraction patterns of Co-Mn-Fe (a) and Co-Cu-Fe (b) systems

Thermogravimetric analysis of the Co-Mn-Fe system (Fig. 9) showed that there are 3 exothermic peaks on the DTA curve of the system, one is pronounced at a temperature of 209 °C, the other two at 401 and 486 °C are less pronounced. In the domain of the first exothermic peak at 209 °C, a sharp weight loss occurs, which corresponds to the ignition of the nitrate-citrate gel, followed by combustion. The weight loss in this case is about 70%. Further, in the range of 350-500 °C, the residual amounts of the organic component burn out, which complies with a weight loss of 12%. The difference in the weight loss between samples of two-component Co-Fe and three-component Co-Mn-Fe systems in the temperature range before ignition of the gel can be related to different moisture content of the initial samples.

The dependence of the degree of conversion of carbon monoxide on time for three-component oxide catalytic systems is shown in Fig.10.

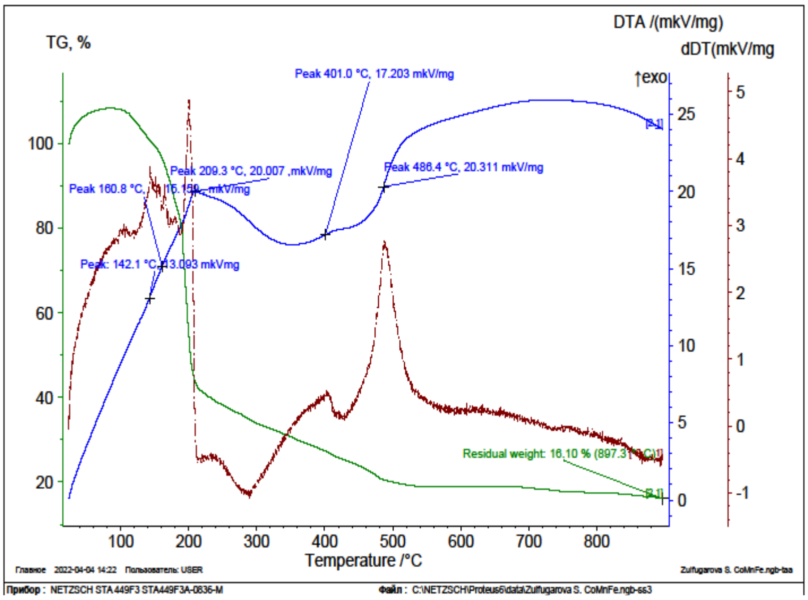

Figure 9: Thermogravimetric analysis of the Co-Mn-Fe system

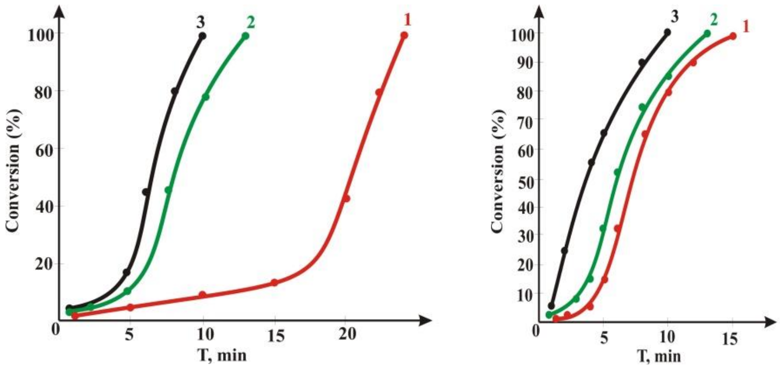

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Figure 10: Dependence of the degree of conversion of carbon monoxide on three-component oxide systems at different temperatures:
a) Co-Mn-Fe (1 – 145 °C, 2 – 165 °C, 3 – 180 °C); b) Co-Cu-Fe (1 – 160 °C, 2 – 170 °C, 3 – 215 °C)

Fig. 10 shows that these ternary systems are also active in the low-temperature oxidation of carbon monoxide. The lower temperature of their activity, at which complete conversion of carbon monoxide is achieved, is 145-160 °C. However, unlike two-component cobalt-containing systems, for which the time to achieve complete CO conversion is 7-11 minutes (Table 2), complete CO conversion on three-component systems is achieved within 15-20 minutes. At higher temperatures, this time is reduced to 10-13 minutes.

The activation energy of the CO oxidation reaction on the studied oxide systems found by the Arrhenius equation lies in the range of 17-33 kJ/mol (Table 3). The CO oxidation reaction proceeds with the lowest activation energy on two-component systems Co-Cu and Co-Cr.

Table 3: Activation energy of the CO oxidation reaction on oxide catalysts

Catalyst	**E, kJ/mol**
Co-Mn=1:1	33
Co-Mn=2:1	31
Co-Cu=1:1	17
Co-Cr= 2:1	25
Co-Mn-Fe=1:1:1	31
Co-Cu-Fe= 1:1:1	30

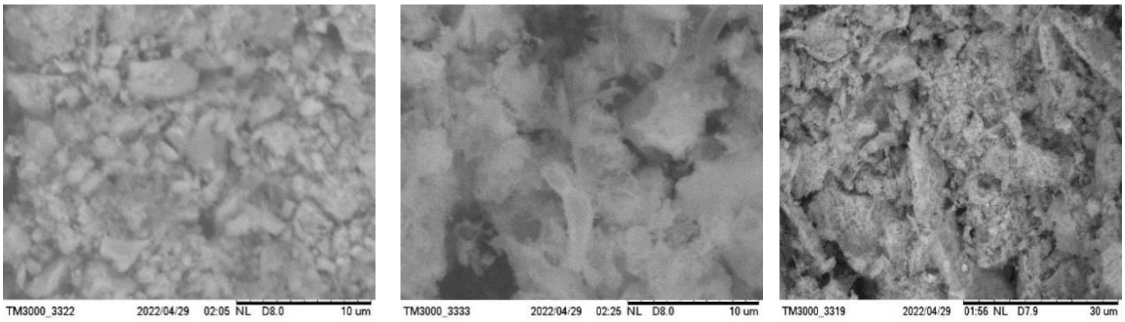
4. DISCUSSION

As is known, solids with a defective surface have a higher catalytic and adsorption activity as compared to the structure of the perfect crystal. Therefore, using various synthesis methods, it is possible to increase the defectiveness of the outer surface of crystals. From this point of view, the sol-gel method with combustion is the most suitable. It can be seen as a variation of the SHS (Self-Propagating High Temperature Synthesis) method but at lower temperatures. Combustion occurs with a short-term thermal effect on the system, in which an exothermic reaction is initiated and further combustion occurs due to its own heat release. In this case, various physicochemical transformations occur: melting (due to crystallization water of salts), chemical reaction (decomposition of salts with the formation of the appropriate oxides and further interaction of oxides due to mutual diffusion). All these processes occur within a very short time, which affects the formation of the composition and structure, textural parameters of the system. It should be noted that in most works devoted to the synthesis of complex oxide systems, including ferrites of transition metals, for example, cobalt, nickel, by the sol-gel method with combustion, additional heat treatment is carried out at a temperature of 600-700 °C of the powder obtained after combustion. This is due to the requirements of their area of application. These compounds are used as fuel cell electrodes, oxygen membranes, sensitive components of gas sensors, in microelectronics, where the high purity and crystallinity of the resulting compound plays an important role. In catalysis, a similar picture is not always observed. For example, in (53), we synthesized cobalt, nickel, and copper ferrites from oxides of these metals by microwave treatment. Prolonged microwave processing led to a decrease in the content of individual oxides and an increase in the corresponding ferrite, which occurs due to an increase in the degree of conversion of the initial oxides. An increase in the degree of crystallinity was also observed. However, these samples, when tested in the CO oxidation reaction, showed low catalytic activity. Conversely, two- and three-component systems obtained by the sol-gel method with auto-combustion without additional heat treatment showed high activity in low-temperature CO oxidation.

As follows from Table 1, the specific surface area of systems obtained by this method is significantly higher than similar samples obtained using long-term microwave irradiation, measured in minutes, at which a powerful temperature rise occurs throughout the entire volume, leading to intense aggregation of particles of the resulting substances. However, as noted above, if microwave irradiation is used only to “ignite” the gel, then systems with a similar catalytic activity are obtained as the samples obtained with conventional combustion. Incidentally, the authors of (54) also note that the catalyst synthesized at 550 °C with the Cu/Mn = 1/2 ratio in the precursor exhibits the highest catalytic activity with respect to CO oxidation due to the formation of the $CuMn_2O_4$ phase with poor crystallinity.

As noted above, the catalytic systems obtained by us through the use of the sol–gel method with auto-combustion are mainly a combination of simple oxides and spinels. They can be considered as solid solutions, and as the composition becomes more complex, various combinations of mixed oxides are possible. During a very short combustion, crystallites of various sizes are formed in the systems, and along with nanosized agglomerates, there are also larger agglomerates, as can be seen from Fig. 11, which shows micrographs of two and three-component cobalt-containing catalytic systems.

The binary and ternary catalysts synthesized by us are multiphase oxide systems of variable composition; therefore, they may have all types of defects in solids, including point defects, extended defects (dislocations), electronic defects representing local disturbances in the charge distribution (38). On the one hand, the presence of defects that can potentially be considered as catalytically active centers, on the other hand, the presence of oxide and spinel phases in the composition of the synthesized catalysts favors the coordination of surface oxygen with different metal atoms of the structure, thereby exhibiting different reactivity. Spinels in an ideal structure are crystallized in the cubic space group Fd-3m. In a close-packed lattice, two types of voids are distinguished: tetrahedral, limited by four oxygen anions, and octahedral, limited by six oxygen anions. The unit cell of spinel contains 32 oxygen anions, forming 64 tetrahedral positions (8 are occupied by metal cations) and 32 octahedral positions (16 are occupied by metal cations). In spinels, transition metals can be placed in tetrahedral and octahedral positions. Based on a large number of theoretical and experimental works, cations are arranged in the following row according to their tendency to occupy octa-pores (at T = 0): Cr^{3+}, Ni^{2+}, Mn^{3+}, Cu^{2+}, Al^{3+}, Cu^{+}, Fe^{2+}, Co^{2+}, Fe^{3+}, Mn^{2+}. The cations on the left up to Al^{3+} are more inclined to occupy octahedral pores, while the cations from Al^{3+} to Fe^{2+} can occupy both tetra- and octa-pores (55). The placement of transition metal ions in octahedral vacancies leads to a decrease in the Me–O bond energy, which contributes to an easier electronic transition and thereby an increase in the rate of the oxidation reaction, which, apparently, can also be associated with a higher activity of the synthesized double and ternary systems as compared to individual oxides.



1 2 3

Figure 11: Micrographs of cobalt-containing oxide systems obtained by the sol-gel method with combustion: 1-Co-Mn; 2 - Co-Mn-Fe; 3-Co-Cu-Fe

The mutual influence of the oxide and spinel phases on the catalytic activity was established in (38). The authors synthesized the sol-gel method using citric acid copper-manganese oxide catalyst with different initial ratios of metals. One of the components of the resulting catalyst was spinel $Cu_{1.5}Mn_{1.5}O_4$; the other component, depending on the ratio, was either copper oxide CuO or Mn_3O_4. The study of the catalytic activity of the obtained systems showed that the CuO-$Cu_{1.5}Mn_{1.5}O_4$ system manifested the best performance in the temperature range of 80-170 °C than the $Cu_{1.5}Mn_{1.5}O_4$ and Mn_3O_4-$Cu_{1.5}Mn_{1.5}O_4$ systems. The authors opine that there is a synergistic effect between CuO and $Cu_{1.5}Mn_{1.5}O_4$, since individual copper and manganese oxides exhibit low activity in low-temperature CO oxidation, and only the presence of copper oxide in the system (the authors call this modification) makes it active.

The systems synthesized by us also contain spinel phases and oxides. But not all of these systems can demonstrate the effect of mutual influence. Individual oxides Co_3O_4 and Mn_3O_4, obtained by us by means of the sol-gel method with combustion, as well as two-component systems based on them containing spinel (cobalt manganite), are active in the oxidation of CO in the temperature range of 180-190 °C, i.e. in this case, there is no synergistic effect. However, the Co-Cr=2:1 system, which, along with chromite, also contains cobalt oxide, is active already at a much lower temperature – 145 °C, than systems with a ratio of Co-Cr=1:1 and 1:2 (Table 3). A similar dependence was obtained in the Co-Fe=2:1 system, i.e. in a sample that, along with cobalt ferrite, also contains cobalt oxide. On this catalyst, 100% conversion of CO to CO_2 occurs at a temperature of 200 °C. A Co-Fe=1:2 sample with a stoichiometric ratio of metals, in which the ferritization reaction almost completely occurs, as experiments have shown, are active only at temperatures above 300 °C. Only Co_3O_4, CuO and a small amount of Cu_2O were found in the Co-Cu=1:1 system, but it is active at 150 °C (Table 3). That is, in these two systems, there is an intensifying effect of the influence of the components on its activity The effect of synergy can also be observed in the obtained three-component systems, on which the complete conversion of CO occurs at a temperature of 145-160 °C. In these systems, along with spinels - ferrites of cobalt, copper, there are oxides of copper, cobalt, and iron.

The authors of (41) also associated the high catalytic activity in low-temperature CO oxidation of the Cu-Mn-O catalyst with a synergistic effect. They found that the Cu-Mn-O spinel has a higher catalytic activity as compared to the activity of pure copper or manganese CO. The Cu1Mn2-550 sample (550 - catalyst synthesis temperature) not only provides more defects and vacancies to create more active sites, but also generates more highly active Cu (II), which promotes CO oxidation. On the contrary, a decrease in the amount of Cu(II) and a higher degree of crystallinity as a result of a higher synthesis temperature lead to a deterioration in catalytic activity.

In the catalysts under study, both lattice oxygen and oxygen adsorbed on the surface of a metal or oxide in atomic or molecular form can serve as the so-called active oxo center. Depending on this, the reaction can proceed both in one stage (the Langmuir-Hinshelwood mechanism) and in two stages (the Mars-van-Krevelen mechanism) (33). In the first case, carbon monoxide adsorbed on the catalyst reacts with adsorbed oxygen (fusion mechanism). According to the Mars–van Crevelen mechanism, CO is initially oxidized by the oxygen of the catalyst outer lattice, resulting in the formation of an oxygen vacancy; then, the spinel is re-oxidized by oxygen from the gas phase; the active form of oxygen is lattice oxygen, and during the reaction, alternating reduction and oxidation of the catalyst occurs.

To clarify this issue, special experiments were carried out on Co-Mn and Co-Mn-Fe catalysts. First, the oxidation reaction of CO on the catalyst was carried out in the absence of air; then, the surface of the catalyst was preliminarily cleaned with an inert gas at the reaction temperature, after which the reaction was carried out without access to air. In the third version of the experiments, after cleaning the catalyst surface with an inert gas, the reaction was carried out in an inert gas atmosphere by adding carbon monoxide to the reaction medium. The results showed that in all experiments there was a slight conversion of carbon monoxide, as evidenced by the increase in the reaction temperature by 12-15 °C during the first 3 minutes. The temperature then drops very slowly to the initial temperature, indicating the termination of the reaction. Only when air is introduced into the reaction medium, the reaction begins to proceed intensively, and within a few minutes the monoxide conversion reaches 100%. These experiments confirm the assumption that the reaction proceeds according to the Langmuir-Hinshelwood mechanism.

Summarizing the above, we can say that the use of a technologically simple sol-gel method with auto-combustion in the synthesis of active multicomponent oxide catalysts based on transition metals is promising.

The formation of multiphase systems, including oxide and spinel phases during gel combustion without additional heat treatment, is a proven advantage of this method in the synthesis of active catalysts for the low-temperature oxidation of carbon monoxide to dioxide.

5. CONCLUSION

1. Two- and three-component cobalt-containing oxide catalytic systems were synthesized by the sol-gel method with auto-combustion.

2. It found that the synthesized cobalt-containing oxide systems are active in the low-temperature oxidation of carbon monoxide in the temperature range of 145-180 °C.

3. The synthesized binary and three-component catalysts are multiphase oxide systems of variable composition. X-ray phase analysis established that they contain ferrites, manganites and individual oxides of cobalt, copper, manganese and iron.

4. The use of a technologically simple sol-gel method with auto-combustion for the synthesis of oxide cobalt-containing catalysts based on transition metals contributes to the formation of multiphase systems during gel combustion, including oxide and spinel phases, which provide catalytic activity. Needlessness for additional thermal treatment of the synthesized catalysts is an advantage of this method for the synthesis of active catalysts in terms of the low-temperature oxidation of carbon monoxide to dioxide.

6. CONFLICT OF INTEREST

The authors confirm that this article's content has no conflict of interest.

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