BINARY AND TERNARY COPPER FERRITES IN THE OXIDATION OF CARBON MONOXIDE

S.M. Zulfugarova*, G.R. Azimova, Z.F. Aleskerova, D.B. Tagiyev

Institute of Catalysis and Inorganic Chemistry named after acad. M. Nagiyev
Ministry of Education and Science of Azerbaijan, Baku, Azerbaijan
**e-mail: zsm07@mail.ru*

Received 08.10.2024
Accepted 13.12.2024

***Abstract**: The replacement of noble metal-based catalytic systems with oxide catalysts based on transition metals of variable valency for the oxidation of carbon monoxide, the reduction of catalyst production costs, and simultaneously the reduction of energy costs for carrying out the reaction is a pressing issue. In this work, binary copper ferrites and ternary copper-manganese-iron oxide systems were synthesized for low-temperature carbon monoxide oxidation using the sol-gel method with self-combustion, as well as using microwave technology. The samples were characterized using X-ray diffraction technique, infrared spectroscopy, and thermogravimetric differential thermal analysis methods, their specific surface area was measured by the BET method, and microphotographs were taken using a scanning electron microscope. The adsorption of carbon monoxide on catalysts has also been studied. It has been found that the resulting binary and ternary copper-containing oxide systems are multiphase systems containing ferrites, manganites, and oxides of copper, manganese and iron. The resulting catalysts are active in the low-temperature carbon monoxide oxidation in the temperature range of 145-180°C. In the systems, an enhancing effect of the influence of its components - oxide and spinel (ferrite) phases - on the catalytic activity is observed. Due to thermal desorption data, for the studied catalysts on which the oxidation of carbon monoxide occurs at sufficiently low temperatures, carbon monoxide adsorption is observed approximately in the same range. The appearance of various structural defects during short-term combustion of the gel without additional heat treatment, which can be considered as catalytically active centers, on the one hand, and the presence of oxide and spinel phases in the catalyst composition, which exhibit a mutually reinforcing effect, on the other hand, are the advantages of this synthesis method active catalysts for low temperature oxidation of carbon monoxide to carbon dioxide.*
***Key words**: copper-containing ferrite catalysts, sol-gel method with auto-combustion, oxidation of carbon monoxide.*
DOI: 10.32737/2221-8688-2025-3-329-342

Introduction

The study of the reaction of low-temperature oxidation of CO is of practical interest since CO is one of the dangerous toxicants that enter the air in the form of gas emissions from industrial enterprises and motor vehicles. Currently, catalysts used in transport and industry for the neutralization of carbon monoxide emissions based on noble metals have high catalytic activity at relatively low temperatures and at the same time are expensive, which stimulates the search for new catalytic systems without the use of noble metals.

Replacing catalytic systems based on noble metals with oxide catalysts based on transition metals of variable valence for the oxidation of carbon monoxide, reducing the cost of producing catalysts and at the same time reducing energy costs for the reaction is an actual issue. For the synthesis of active catalyst for the oxidation of carbon monoxide to carbon dioxide without the traditional use of noble metals, metal oxides Fe, Ni, Mn, Cu, Co, Cr, Ni [1-10] and complex systems based on mixed oxides [11-13, 5-9] are used. In recent years, many works in the literature have been dedicated to the oxidation of CO on spinel-structured catalysts, including ferrites [14-28].

Spinel ferrites are interesting for catalysis in terms of their structure, into which cations with different sizes and charges can be

introduced to vary their catalytic activity in oxidative reactions.

Thus, in [17] it was shown that samples of ferrospinel catalysts containing nickel, cobalt, and copper are effective for the oxidative removal of carbon monoxide from automobile exhaust gases. A study of the catalytic activity of CO oxidation using ferrospinel samples in the temperature range of 80 to 140°C showed an increase in activity with temperature. The two best catalyst samples in terms of specific activity are mixed copper, cobalt, nickel containing ferrite samples. It is believed relatively higher CO conversion for copper-rich mixed ferrite samples is due to the influence of copper ions in lowering the temperature of reduction of hematite to magnetite. It is more catalytically active than hematite. The presence of cobalt can stabilize the ferrite structure even at high temperatures. The inclusion of nickel helps protect the surface of ferrite samples even after high temperature processing, also these systems suitable for high temperature applications.

Cobalt ferrite nanoparticles synthesized by hydrothermal method using glucose showed high catalytic activity in the conversion of CO to CO_2 within 30 hours at 250°C [20].

In [22], a solid solution containing $CuFe_2O_4$ was synthesized by the sol-gel method with self-combustion, and the conversion of CO to CO_2 was studied in its presence. The amount of CuO in the solid solution was 5, 10, 15, 25, 30, and 40%. According to the results, the activity of all samples exceeds the activity of Fe_2O_3. So, if 100% conversion of CO for Fe_2O_3 occurs at a temperature of 480-500 °C, then in the presence of CuO, complete oxidation of carbon monoxide occurs at 180-300°C. The catalyst containing 15% CuO shows the best result.

In [24], the catalytic properties of nickel ferrite obtained by precipitation from a mixture of iron and nickel hydrosulfates were studied in the temperature range of 500-1200°C. It has been determined that the conversion of CO to CO_2 in the presence of samples calcined at 500 and 700 °C is 44% at 300°C. The crystallite size of these samples is 2-8 nm, and the specific surface area is 26-56 m^2/g. The sample thermally treated at 1200°C shows lower catalytic activity under reaction conditions. The authors attribute that the sample crystallite size (240 nm) is large, and the specific surface area (1.6 m^2/g) is very small.

In [26], a series of cobalt ferrites with large surface area were synthesized by deposition method. Cobalt ferrites with crystalline and nanocrystalline contents and a large surface area were prepared without the use of surfactants. The authors determined that the activity of ferrite depends on the amount of nanocrystalline phase. Thus, with increasing nanocrystallinity, the catalytic activity of cobalt ferrite in the conversion of CO to CO_2 also increases. The best result is observed for cobalt ferrite obtained at pH=9 and with high nanocrystallinity. In this example, 50% conversion of CO to CO_2 occurs at 155°C and 100% conversion occurs at 220°C. In comparison, in a sample taken at pH=11, 100% conversion was obtained at 296°C.

Since the CO oxidation reaction is exothermic and is accompanied by a temperature rise of 150-200°C, lower "ignition" temperatures for CO oxidation catalysts are a significant technical and financial benefit. The sol-gel approach with auto-combustion is interesting from this perspective. The method involves 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 "fuel". 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, the combustion of the organic component produces a large amount of gaseous products, which prevents the crystallites of the solid phase from sintering - it is obtained in the form of ashes or fine powder. The reaction occurs quickly and at a fairly low temperature. The method is simple enough for practical implementation and economical in terms of time and energy. In recent years, the use of microwave radiation to create environmentally friendly technologies that save raw materials and energy is also considered one of the promising directions.

Microwave heating is characterized by high speed and efficiency. In terms of low energy consumption and environmental safety, which are common advantages of the sol-gel combustion method and microwave technology, their combined use seems promising. In this regard, the development of effective catalytic systems for low-temperature oxidation of carbon

monoxide using a combined sol-gel combustion method and microwave technology is also of interest.

This paper presents the results of a study of the oxidation reaction of carbon monoxide on copper-containing binary (Cu-Fe) and ternary (Cu-Mn-Fe) ferrite catalysts obtained both by the sol-gel method with combustion and by microwave treatment. It was assumed that by introducing manganese into the composition of copper ferrite through joint synthesis it is possible to obtain compositions with improved oxidizing properties. In addition, during the synthesis of multicomponent systems by the sol-gel method with combustion, combinations of different metals lead to different states of oxygen in the structure, which affects the oxidation process.

Experimental part

The salts $Fe(NO_3)_3$•$9H_2O$ (CAS NO:7782-61-8 98% purity, CDH), $Cu(NO_3)_2$•$3H_2O$ (CAS NO: 10031-43-3 Merch Darmstadt), $Mn(NO_3)_2$•$4H_2O$ (CAS NO: 20694-39-7, 97% purity, CDH) and citric acid were used as precursors for the synthesis of catalysts. Aqueous solutions of the calculated amounts of salts and citric acid at a rate of 1 mol acid to 1 mol metal were stirred on a magnetic stirrer with heating for 1 hour. Then it was heated in a drying oven, at a temperature of 175-200°C, combustion occurred with the formation of ash, after grinding which a fine powder was obtained. Glycine and urea were also used as organic components.

Microwave technology was also used in the synthesis of catalytic systems.

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

- the gel was subjected to microwave treatment until combustion ceased completely to form a powder within a few minutes.
- microwave treatment of the gel was stopped at the moment of its ignition, i.e. microwave energy was used to ignite the gel without further prolonged irradiation.

In the microwave synthesis of ferrites, a microwave oven EM-G5593V (Panasonic) with a resonator volume of 25 L, varying the magnetron power of 160-900 W with an operating frequency of 2450 MHz was used to burn the gel. Microwave treatment of dried gels was carried out at low and medium magnetron modes corresponding to powers of 150 W and 450 W.

X-ray diffraction technique (XRD) of the products was carried out on "D2 Phaser" diffractometer system from Bruker with a source of CuKα radiation. IR spectra were recorded on FTIR Alfa spectrometers from Bruker. The specific surface area of the samples was determined by low-temperature nitrogen adsorption using the multipoint BET method.

The obtained ferrite powders in the amount of 1 gr were mixed with an aluminum gel binder, molded into granules, dried in air, and further heat treatment was carried out in a drying cabinet and a muffle furnace at temperatures of 175 and 500°C, respectively.

CO oxidation was carried out by flow method at a CO:air ratio of 1:(3-5), space velocity of 6000-12000 h^{-1}. The analysis was carried out on JIXM-80 gas chromatograph, in two columns with sorbents CaA and Poropak Q.

Results and Discussions

Synthesis and study of copper ferrite. In the synthesis of copper ferrite, glycine and urea were used as an organic reagent, acting as a complexing agent and fuel, in addition to citric acid. Fig. 1 shows a diffraction pattern of copper ferrite obtained using citric acid, and Table 1 shows data on the composition of ferrite and the use of various "combustibles".

The diffraction patterns of the obtained ferrite samples showed maxima (111), (220), (311), (222), (400), (422), (511) and (440), characteristic of the cubic spinel structure. Table 1 makes it clear that copper ferrite is always produced during the synthesis of metals in stoichiometric ratios. When glycine is used, partial reduction of copper and formation of iron oxide (hematite) occurs, but with further microwave treatment of the obtained powder, the copper and hematite reflexex disappear and a

delafossite reflex appears. When burning with urea, in addition to copper ferrite and delafossite, hematite is also present.

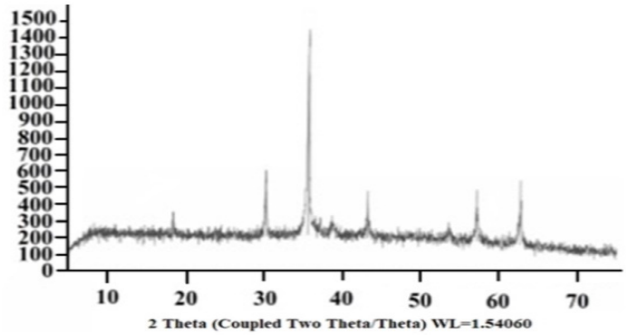


Fig. 1. X-ray diffraction pattern of copper ferrite

Table 1. Composition of synthesized copper ferrite samples according to XRD analysis

Sample	Organic reagent	Method of preparation	Phase composition
Cu:Fe=1:2	Citric acid	Sol-gel combustion	$CuFe_2O_4$
Cu:Fe=1:2	Glycine	Sol-gel combustion	$CuFe_2O_4$, Fe_2O_3, Cu
Cu:Fe=1:2	Glycine	Microwave thermal treatment after sol-gel combustion	$CuFe_2O_4$, $CuFeO_2$
Cu:Fe=1:2	Urea	Sol-gel combustion	$CuFe_2O_4$, $CuFeO_2$, Fe_2O_3

At the ratio of metals Cu:Fe= 2:1, copper oxide and a small amount of magnetite are formed along with copper ferrite in sol-gel synthesis with combustion involving citric acid (Fig. 2).

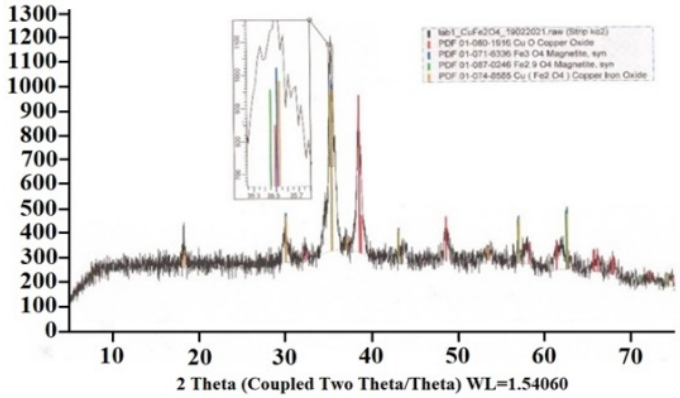
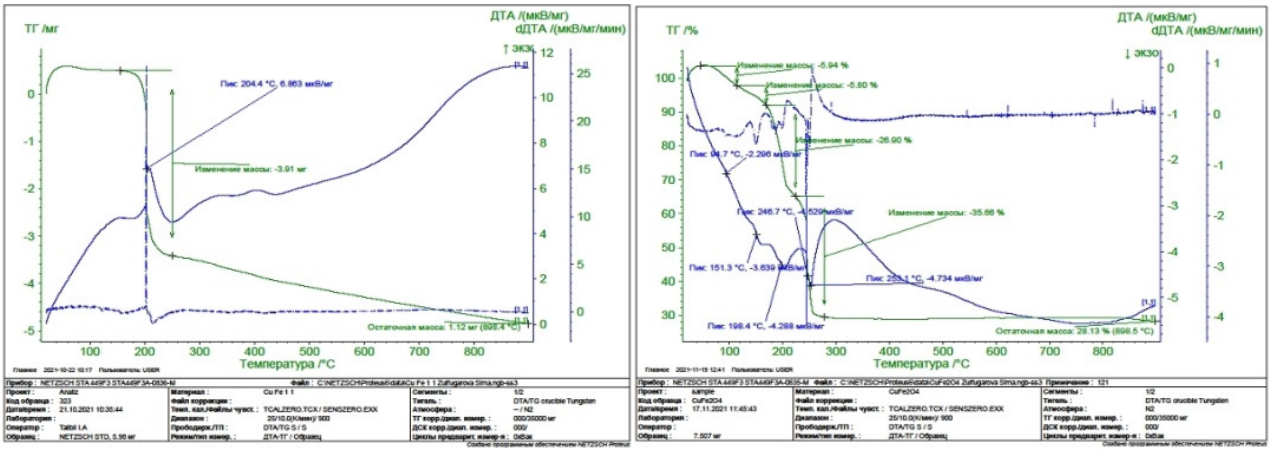


Fig. 2. X-ray diffraction pattern of a sample with a metal ratio of Cu:Fe=2:1, prepared by the sol-gel method with combustion with citric acid

Derivatographic studies are of particular interest in our case because the gel obtained from metal nitrates and complexing agent is subjected to thermal treatment. In this case, the derivatographic study can be considered an in situ study, since the formation of ferrite actually occurs during gel combustion under the conditions of derivatogram taking. Fig. (3 a, b) shows the derivatograms of gel combustion using citric acid and urea. The combustion thermogram of the gel containing copper and iron nitrates and citric acid shows a pronounced exothermic peak

at 204°C and two smaller ones at 320 and 400°C (Fig. 3a). At 204°C there is a sharp loss of mass - about 65%. Then, there is a gradual decrease in weight and in the range from 250-420° C weight loss is 9% and above 420 about 15%.

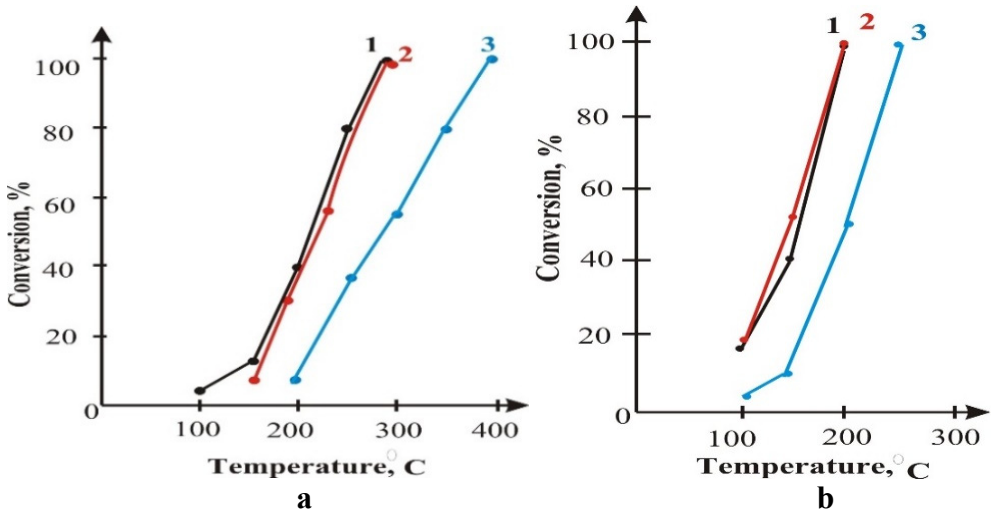


a **b**

Fig. 3. Derivatograms of the [$Cu(NO_3)_2$ +$Fe(NO_3)_3$+ $C_6H_8O_7$] (**a**) and [$Cu(NO_3)_2$ +$Fe(NO_3)_3$+ $CO(NH_2)_2$] (**b**) systems

Fig. 3b shows the derivatogram obtained during the combustion of the gel containing copper and iron nitrates and urea as a "fuel". The thermogram shows two small peaks at 151°C and 198°C and a slightly larger peak at 253°C. Up to 300 °C, there is a stepwise mass loss: 5.94%, 5.8%, 26.9% and 35.66%. A sharp decrease in mass occurs starting at 1800°C - 26.9% and then at 230°C - 35.6% to 300°C. Above this temperature mass loss is almost not observed.

The presented derivatograms show that all transformations during the combustion of gels (melting, evaporation, ferritization) occur up to 500°C; above this temperature, the mass decrease is insignificant and is apparently associated with the burnout of residues of the organic component.



a **b**

Fig. 4. Dependence of CO conversion on temperature on catalysts Cu:Fe=1:2 (**a**) and Cu:Fe=2:1 (**b**), obtained by microwave "ignition" of the gel method (1), sol-gel method with combustion (2), and long-term microwave treatment of the gel (3). GHSV=12000 h^{-1}, CO:air=1:3

Copper ferrite samples synthesized in different initial ratios of copper and iron completely convert CO to CO_2. The difference is in the temperature at which complete conversion of CO occurs. The complete conversion of carbon monoxide on copper ferrite with Cu:Fe=1:2 ratio occurs at 280 °C. On the catalyst with metal ratio Cu:Fe=2:1 the reaction proceeds

at a lower temperature of 230°C. The higher activity of this sample in the conversion of carbon monoxide at a relatively low temperature in comparison with the sample Cu:Fe = 1:2 can be associated with the content of copper oxide phase in this sample. Fig. 4a and 4b shows the temperature dependence of CO conversion on copper ferrite samples synthesized by different methods. The most active in the oxidation of CO are samples of copper ferrite prepared by the sol-gel method with combustion both in the traditional way and by "igniting" in a microwave oven. On these samples, complete conversion of CO to CO_2 occurs at 180-230°C, while samples with prolonged microwave treatment completely convert CO at 250-325°C.

The specific surface area of ferrites obtained by the sol-gel method with conventional combustion and microwave "ignition" are quite close (Table 2).

Table 2. Specific surface area of copper ferrite samples synthesized by the sol- gel method with conventional and microwave combustion.

Catalyst	Citric acid		Glycine		Urea	
	z.g.	z.g.-m.d.	z.g.	z.g.-m.d.	z.g.	z.g.-m.d.
Cu:Fe=1:2	18	14.8	4	5.4	25.5	22.6
Cu:Fe=2:1	15.4	10.5	3.6	2.8	20.9	18.7

At the same time, during long-term microwave treatment of the gel, the specific surface area of ferrite is very small and amounts to 1-2.1 m^2/g, which is associated with the aggregation of ferrite particles.

Cu-Mn-Fe oxide catalytic systems. In contrast to other binary oxide systems, structural changes in spinels can occur more easily and their structure contains defects, mobile oxygen, and oxygen vacancies. They act as activation centers for oxygen from the gas phase and ensure the activity of the catalyst in the oxidation reaction [29-30].

In [31], the authors note that with an increase in the amount of different metals in spinel, its catalytic activity also increases, and in addition, their surface can be improved by using it on a large support.

The results of X-ray diffraction analysis showed that Cu-Mn-Fe oxide catalysts have a complex phase composition. In addition to the double oxides of manganese and iron (Mn_3O_4 and Fe_3O_4), manganese $Mn_{0.98}Fe_{2.02}O_4$ and copper $CuFe_2O_4$ ferrites, copper $CuMn_2O_4$ manganite, and manganese substituted copper ferrites ($Cu_{0.5}Mn_{0.5}Fe_2O_4$, $Cu_{1.2}Mn_{1.8}O_4$, $Mn_{0.43}Fe_{2.57}O_4$) are formed.

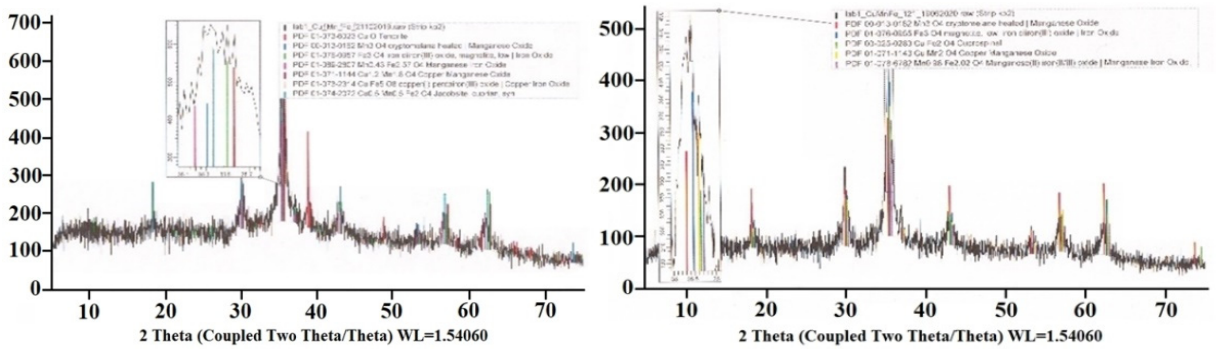
Table 3. Phase composition of synthesized Cu-Mn-Fe oxide system

Sample	**Phase composition**
Cu:Mn:Fe=1:1:1	CuO, Mn_3O_4, Fe_3O_4, $CuFe_2O_4$, $Mn_{0.43}Fe_{2.57}O_4$ $Cu_{1.2}Mn_{1.8}O_4$, $CuFe_5O_8$, $Cu_{0.5}Mn_{0.5}Fe_2O_4$
Cu:Mn:Fe=1:1:2	Mn_3O_4, Fe_3O_4, $CuFe_2O_4$ $CuMn_2O_4$, $Mn_{0.98}Fe_{2.02}O_4$
Cu:Mn:Fe=2:1:1	Mn_3O_4, Fe_3O_4, $CuFe_2O_4$, $CuMn_2O_4$, $Mn_{0.98}Fe_{2.02}O_4$
Cu:Mn:Fe=1:2:1	Mn_3O_4, Fe_3O_4, $CuFe_2O_4$ $CuMn_2O_4$, $Mn_{0.98}Fe_{2.02}O_4$

As an example, diffraction patterns of samples Cu:Mn:Fe = 1:2:1 and 2:1:1 are represented in Fig. 5a and 5b. The phase compositions of the obtained samples are listed in Table 3.

There are many works in the literature on the synthesis of these phases, the study of their structure, and their use as catalysts and adsorbents. For example, in [32], Cu 0.5 $Mn_{0.5}Fe_2O_4$ was synthesized and characterized

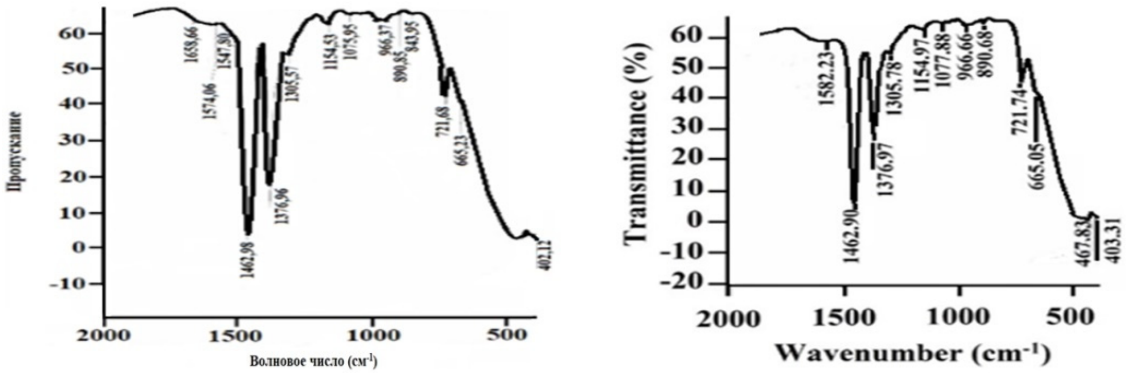
by IR, XRD and SEM methods. In [33], a compound of the formula $Cu_{1.2}Mn_{1.8}O_4$ was synthesized and the distribution of valence of cations at room temperature was studied. It was shown that all copper in the compound is in the form of Cu^{2+}, and Mn is in the form of a multivalent composition with valency fractions: 55% Mn^{4+}, 37% Mn^{3+} and 8% Mn^{2+}. Manganese ferrite $Mn_{0.98}Fe_{2.02}O_4$ was studied in [34]. In [35], $CuMn_2O_4$ was obtained and studied during the oxidation of CO.



a **b**

Fig. 5. X-ray diffraction patterns of samples Cu:Mn:Fe=1:2:1 (a) and Cu:Mn:Fe=2:1:1 (b)

IR spectra of some synthesized systems are shown in Figure 6a and 6b.



a **b**

Fig. 6. IR spectra of samples Cu:Mn:Fe=1:1:1 (a) and Cu:Mn:Fe=1:1:2 (b)

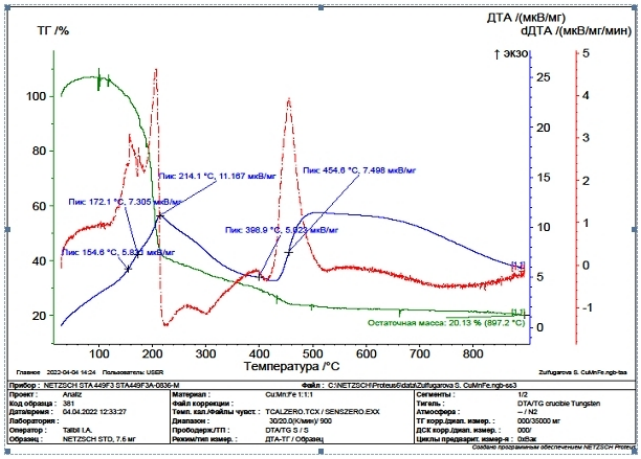


Fig. 7. Derivatogram of the $[Cu(NO_3)_2 + Fe(NO_3)_3 + Mn(NO_3)_2 + C_6H_8O_7]$ system

The absorption bands from 800 to 400 cm^{-1} in the IR spectra characterize the Me-O bonds for tetrahedrally coordinated ions [36-37]. In the spectrum, these are bands corresponding to 625 and 721 cm^{-1}. The absorption bands between 900 and 1400 cm^{-1} (966.66, 1077.88, 1154.97,

1376.97, 1462.90) belong to the Me-OH bond. The bands in the range 900–1100 cm^{-1} are attributed by the authors of [38] to the bands characterizing the ferrite system.

Derivatographic analysis of the Cu:Mn:Fe=1:1:1 system was carried out (Fig. 7).

The DTA curve has three exothermic peaks: one very clear at 214°C, and the other two very weak at 399 and 454°C. At 209°C, there is a sharp mass loss due to the ignition and combustion of the nitrate-citrate gel in the region of the first exothermic peak. At this time, the weight loss is about 66%. Then, in the range of 350-500°C, combustion of the residual amount of the organic component occurs, corresponding to a mass loss of about 14%, and the residual mass is about 20%.

The time dependence of CO conversion is shown in Fig. 8a and 8b. As can be seen from the figure, with increasing temperature, the complete conversion of carbon monoxide is achieved in less time. Thus, in the catalyst with the ratio of metals Cu:Mn:Fe = 1:1:1, the complete conversion of carbon monoxide to carbon dioxide at 170°C is achieved in 9 min, and at 200°C - in 3-4 min (Fig. 8a). In the catalyst Cu:Mn:Fe=2:1:1, the time of complete conversion of carbon monoxide to carbon dioxide is 10 min at 145°C and 6 min at 170 °C (Fig. 8b).

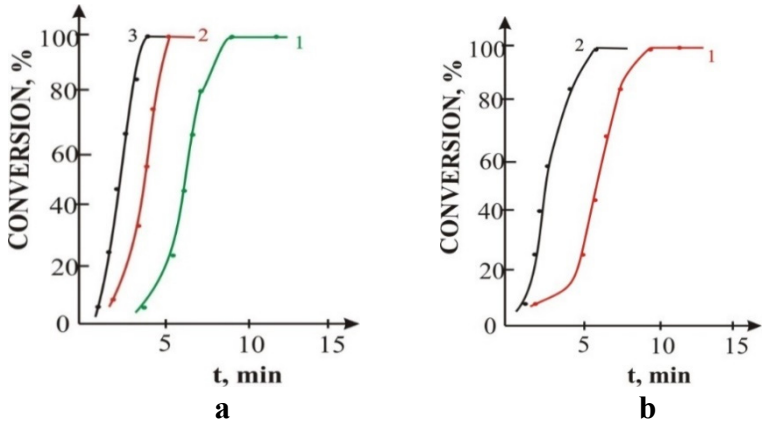


Fig. 8. Carbon monoxide conversion as a function of time:
a) Cu:Mn:Fe=1:1:1 (1-T=170 °C, 2-T=180 °C, 3 – T=200 °C).
b) Cu:Mn:Fe=2:1:1 (1 - T=145 °C; 2 – T=170 °C).

Similar to the binary systems, these ternary catalytic systems were prepared by sol-gel with microwave combustion. The samples obtained by this method showed higher catalytic activity. Thus, while the temperature of complete conversion of carbon monoxide on the samples obtained by sol-gel combustion method was 140-170°C, on the same samples synthesized with microwave ignition, complete conversion of CO occurred in the temperature range of 130-150°C.

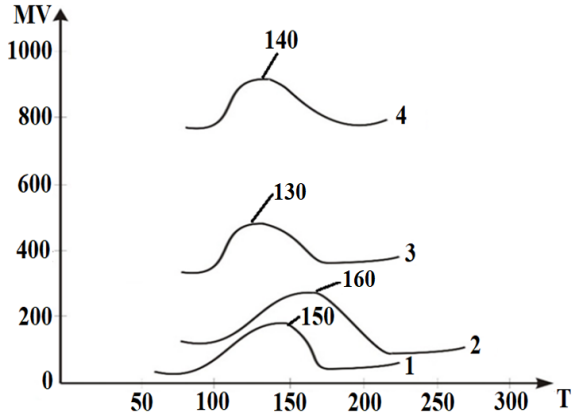


Fig. 9. Thermal desorption of carbon monoxide from the surface of Cu-Mn-Fe catalytic systems:
1 - 1:2:1; **2** – 1:1:1; **3** – 1:1:2; **4** – 2:1:1.

Thermal desorption of CO from the surface of synthesized catalysts. In CO oxidation, the stage of adsorption of gas molecules on the catalyst surface is of great importance, since the efficiency of the catalyst depends on the number of adsorbed gas molecules on its surface. For this reason, the thermodesorption of carbon monoxide from the surface of the synthesized catalysts was studied (Fig. 9).

The interaction of CO with catalysts was studied at a linear heating rate of 20 deg/min in the temperature range of 20-300°C. The presented images show that in the temperature range up to 200°C only one form of adsorbed carbon monoxide is present on the surface of the studied catalysts. At relatively high temperatures, the thermodesorption curves do not have pronounced peaks. This is true for catalysts active at higher temperatures, such as cobalt and copper ferrites. For them, deviations from the main line are observed as the desorption temperature increases.

Discussion. The ferrite catalysts synthesized by us are multiphase oxide systems of variable composition, which are mainly a combination of simple oxides and spinels, therefore, all types of solid defects are possible for them: a) point defects, extended defects (dislocations), electronic defects representing local charge distribution disorders [39]. These systems can be considered as solid solutions. When ferrite catalysts are synthesized by sol-gel method with combustion, crystallites of various sizes, including nanoscale crystallites, are formed in a very short combustion time. As can be seen from micrographs of binary copper ferrite and ternary system, larger agglomerates are formed along with nanosized compounds (Fig. 10).

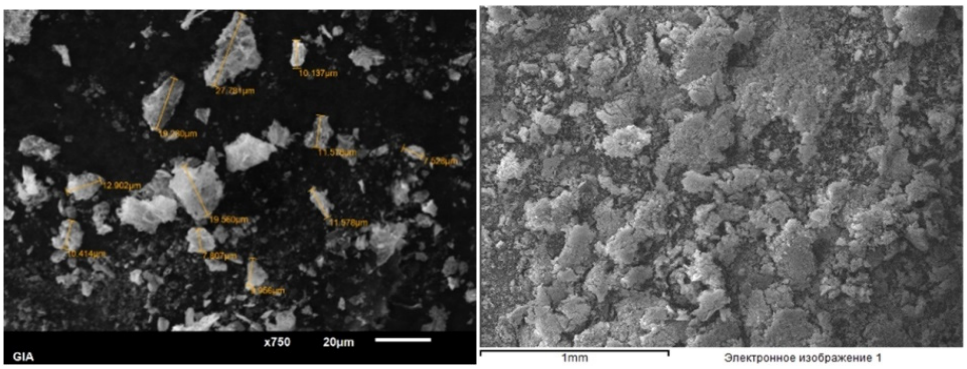


Fig. 10. Microphotographs of ferrite samples

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, thus exhibiting different reactivity, which can in some cases be observed in the synergism effect.

In spinels, transition metals can be located in tetrahedral and octahedral positions [39]. The placement of transition metal ions in octahedral vacancies leads to the fact that the Me-O bond energy decreases, which facilitates easier electron transfer and thereby increases the rate of the oxidation reaction. For example, in [28], the authors suggest that $CuFe_2O_4$ spinel is an oxygen carrier due to its synergistic enhanced characteristics. The reaction mechanism of $CuFe_2O_4$ spinel with CO during chemical combustion was studied by the authors based on thermogravimetric analyzes (TGA) and density functional analysis. The increased oxygen release activity of $CuFe_2O_4$ at low temperatures was confirmed by both experimental and theoretical methods. The authors identified three types of surface oxygen, respectively, with different metal atoms, which exhibit different reactivity. Two types of reactions are involved in the oxidation of CO. In the one-step reaction pathway, CO directly reacts with the oxygen bond of two octahedral Cu and one octahedral Fe atom to form a CO_2 molecule without an energy barrier, which is consistent with the surface oxygen consumption observed in TGA experiments. In a possible two-step reaction pathway, CO is first adsorbed on the surface and then reacts with oxygen bound to one octahedral

Cu and two octahedral Fe atoms, generating CO_2, overcoming the energy barrier of 10.84 kJ/mol, which is kinetically and thermodynamically the most favorable pathway.

The mutual influence of oxide and spinel phases on the catalytic activity was established in [40]. The authors synthesized by sol-gel method using citric acid copper-manganese-containing oxide catalyst with different initial ratio of metals. The study of catalytic activity of the obtained systems showed that the CuO-$Cu_{1.5}Mn_{1.5}O_4$ system demonstrated 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 believe 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 it modification) makes it active.

We observe the same picture for copper ferrite. At superstoichiometric copper content in ferrite (Cu:Fe=2:1), the sample is active in CO conversion at lower temperature than the sample with Cu:Fe=1:2 ratio, which is probably due to the higher content of oxide phase in the sample.

Opinions of different authors differ as to which oxygen participates in CO oxidation-oxygen adsorbed on the metal surface or catalyst oxygen. The reaction can proceed both in one stage (Langmuir-Hinshelwood mechanism) and in two stages (Mars-van Krevelen mechanism). In the first case, carbon monoxide adsorbed on the catalyst reacts with adsorbed oxygen (fusion mechanism). According to the 2-stage Mars-Krevelen mechanism, at the first stage, carbon monoxide from the gas phase reacts with oxygen of the catalyst lattice, as a result of which the catalyst is reduced. In the second stage, the reduced catalyst is oxidized at the expense of oxygen from the gas phase. In other words, the active form of oxygen is the lattice oxygen of the catalyst and during the reaction, alternate reduction and oxidation of the catalyst takes place. For example, in [17] it is assumed that oxidation on mixed metal oxides (ferrospinels) occurs by a redox mechanism, in which the metal ion changes the degree of oxidation while absorbing lattice oxygen to form CO_2. Gaseous oxygen apparently, oxidizes the catalyst surface at the octahedral sites and enhances the oxidation of adsorbed CO. The validity of these assumptions was verified by us on Cu-Mn-Fe catalysts by the results of special experiments on the conversion of carbon monoxide. First, the reaction on the catalyst was carried out in the absence of air; then the surface of the catalyst was first cleaned with inert gas at the reaction temperature, and then the experiment was carried out without access to air. In the third version of the experiments, after cleaning the catalyst with inert gas, the reaction was carried out in an atmosphere of inert gas by adding carbon monoxide to the reaction medium. The results showed that a slight conversion of carbon monoxide was observed in all experiments, as evidenced by the increase in the reaction temperature of 12-18 °C during the first 3 min (Fig. 11).

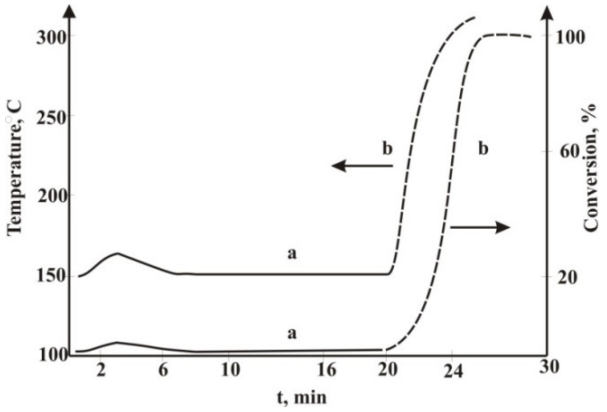


Fig. 11. Dependence of the conversion of CO into CO_2 and the rise in reaction temperature on time in an oxygen-free (a) and oxygen (b) atmosphere on catalyst Cu-Mn-Fe=1:1:1

Then temperature drops very slowly to the initial temperature, indicating that the reaction has stopped after about 20 min. Only when air is introduced into the reaction medium the reaction starts to proceed intensively, and within 5-7 min the conversion of carbon monoxide reaches 100%. Interestingly, if CO oxidation in an inert medium is carried out for a longer time (40 min) followed by the introduction of air, the reaction proceeds somewhat more slowly in the first minutes, as can be seen from the slower increase in temperature. It can be assumed that part of the oxygen supplied to the reaction is consumed for oxidation of the catalyst surface. It can be assumed that the conversion of carbon monoxide in the synthesized ferrite-containing catalysts is possible by both mechanisms. However, given that the reaction "ignition" period is very short, preference can be given to the Langmuir-Hinshelwood mechanism. Carbon monoxide and oxygen are adsorbed on the surface of the catalyst and react with each other.

As for the use of microwave technology in the synthesis of active ferrite catalysts, here we have established how the time of exposure to microwave radiation affects the catalytic activity. The use of microwave energy to "ignite" the gel even at low magnetron powers for several seconds, without further prolonged irradiation, leads to the production of ferrites with smaller crystallite sizes and higher specific surface area. And the catalytic activity in the oxidative conversion of carbon monoxide of ferrites obtained by this method is comparable to the activity of ferrites obtained by conventional combustion. The formation of multiphase systems, including oxide and ferrite phases during gel combustion without additional thermal treatment, is an advantage of this method for the synthesis of active catalysts for the low-temperature oxidation of carbon monoxide into dioxide.

Conclusion

Binary and ternary copper ferrites were prepared by sol-gel method with conventional combustion and in microwave oven and their catalytic activity in the oxidation of carbon monoxide into carbon dioxide was investigated. It is shown that the time of microwave treatment of the gel affects the catalytic activity of the obtained catalysts. The highest catalytic activity in low-temperature oxidation of carbon monoxide showed by ternary ferrite catalysts obtained by sol-gel method with combustion, as well as microwave ignition of the gel. On these catalysts, the complete conversion of carbon monoxide occurs in the temperature range of 130-170°C.

References

1. Royer S., Duprez D. Catalytic oxidation of carbon monoxide over transition metal oxides. *ChemCatChem.* 2008, **Vol. 3(1)**, p. 24-65. https://doi.org/10.1002/cctc.201000378
2. Xanthopouloua G.G., Novikova V.A., Knysha Yu.A., Amosova A.P. Nanocatalysts for Low-Temperature Oxidation of CO: Review. *Eurasian Chemico-Technological Journal.* 2015, **Vol. 17**, p. 17-32.
3. Soliman N.K. Factors affecting CO oxidation reaction over nanosized materials: A review. *Journal of Materials Research and Technology.* 2019, **Vol. 8(2),** p. 2395-2407. https://doi.org/10.1016/j.jmrt.2018.12.012
4. Gómez-Cuaspud J.A., Schmal M. Nanostructured metal oxides obtained by means polymerization-combustion at low temperature for CO selective oxidation. *International Journal of Hydrogen Energy,* 2013, **Vol. 38(18)**, p. 7458-7468. https://doi.org/10.1016/j.ijhydene.2013.04.024
5. Mahammadunnisa S., Reddy M.K., Lingaiah N. $NiO/Ce_{1-x}Ni_xO^{2-\delta}$ as an alternative to noble metal catalysts for CO oxidation. *Catalysis Science & Technology.* 2013, **no. 3**, p. 730-736.
6. Dey S., Dhal G.C., Mohan D., Prasad R. Copper based mixed oxide catalysts (CuMnCe, CuMnCo and CuCeZr) for the oxidation of CO at low temperature. *Mater. Discovery.* 2017, Vol. 10, p. 1–14. DOI:10.1016/J.MD.2018.02.001

7. Dey S., Dhal G.C., Mohan D., Prasad R. Low-temperature complete oxidation of CO over various manganese oxide catalysts. *Atmos. Pollut. Res.* 2018, **Vol. 9(4)**, p. 755-763. https://doi.org/10.1016/j.apr.2018.01.020
8. Zulfugarova S.M., Azimova G.R., Aleskerova Z.F., Qasimov R.J., Bayramov M.A., Ismailov E.H., Tagiev D.B. Effect of preparation method of iron, copper-containing oxide catalysts on their activity in the reaction of oxidation of carbon monoxide to carbon dioxide. *Chemical Problems*, 2022, **Vol. 20(1)**, p.82-94. https://doi.org/10.32737/2221-8688-2022-1-82-94.
9. Dasireddy V.D.B.C., Bharuth-Ram K., Hanzel D., Likozar B. Heterogeneous Cu–Fe oxide catalysts for preferential CO oxidation (PROX) in H_2-rich process streams. *RSC Adv.* 2020, **Vol. 59(10)**, p. 35792–35802. https://doi.org/10.1039/d0ra06969h
10. Zulfugarova S.M., Azimova G.R., Aleskerova Z.F., Tagiev D.B. 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, **Vol. 10(3)**, p. 577-788. https://doi.org/10.18596/jotcsa.1261839
11. Dey S., Mehta N.S. Selection of Manganese oxide catalysts for catalytic oxidation of Carbon monoxide at ambient conditions. *Resources, Environment and Sustainability.* 2020, 1: 100003. https://doi.org/10.1016/j.resenv.2020.100003
12. Al Soubaihi R.M., Saoud Kh.M., Dutta J. Critical Review of Low-Temperature CO Oxidation and Hysteresis Phenomenon on Heterogeneous Catalysts. *Catalysts,* 2018, **Vol. 8(12)**, 660. https://doi.org/10.3390/catal8120660
13. Li X.-N., Wang L.-N., Mou L.-H., He Sh.-G. Catalytic CO Oxidation by Gas-Phase Metal Oxide Clusters. *J. Phys. Chem. A.* 2019, **Vol. 123(43)**, p. 9257–9267. https://doi.org/10.1021/acs.jpca.9b05185
14. Zulfugarova S.M., Azimova G.R., Aleskerova Z.F., Litvishkov Yu.N., Tagiyev D.B. Synthesis of Transition Metal Ferrites (Co, Cu, Ni, Mn) by the Sol-Gel Method with Combustion and the Use of Microwave Processing. *Bulleten of the Karaganda University,* 2022, **Vol. 4(108)**, p. 118-135.
15. Dey S., Dhal G.Ch. Catalytic conversion of carbon monoxide into carbon dioxide over spinel catalysts: An overview. *Materials Science for Energy Technologies,* 2019, **Vol. 2(3)**, p. 575–588. https://doi.org/10.1016/j.mset.2019.06.003
16. Prasad R., Singh P. A Review on CO Oxidation Over Copper Chromite Catalyst. *Catalysis Rewiews: Science and Engineering.* 2012, **Vol. 54**, p. 224-279. https://doi.org/1080/01614940.2012.648494.
17. Aniz C.U., Nair T.D.R. A study on catalysis by ferrospinels for preventing atmospheric pollution from carbon monoxide. *Open J. Phys. Chem.,* 2011, **Vol. 22 - 1 (3)**, p. 124–130.
18. Kharisov B.I., Rasika Dias H.V., Kharissova O.V. Mini-review: Ferrite nanoparticles in the catalysis. *Arabian Journal of Chemistry,* 2014, **Vol. 12(7)**, p. 1234-1246.
19. Santos P.T.A., Lira H.L., Gama1 L., Argolo F., Andrade H.M.C., Costa A.C.F.M. Evaluation of $NiFe_2O_4$ spinel, synthesized by combustion reaction, as a catalyst for selective CO oxidation. *Seventh International Latin American Conference on Powder Technology, November 08-10, Atibaia, SP, Brazil. Materials Science Forum* . 2010, Vol. 660-661, p. 771-776. https://doi.org/10.4028/www.scientific.net/MSF.660-661.771
20. Chagas C.A., de Souza E.F., de Carvalho M.C.N.A., Martins R.L., Schmal M. Cobalt ferrite nanoparticles for the preferential oxidation of CO. *Applied Catalysis A, General.* 2016, **Vol. 519(5)**, p. 139-145. http://dx.doi.org/10.1016/j.apcata.2016.03.024
21. Lou J.-Ch., Chang Ch.-K. Catalytic Oxidation of CO Over a Catalyst Produced in the Ferrite Process. *Environmental Engineering Science.* 2006, **Vol. 23(6)**, p. 1024-1032. https://doi.org/10.1089/ees.2006.23.1024
22. Amini E., Rezaei M., Sadeghinia M. Low temperature CO oxidation over mesoporous $CuFe_2O_4$ nanopowders synthesized by a novel sol-gel method. *Chinese Journal of Catalysis.* 2013, **Vol. 34(9)**, p. 1762-1767.

https://doi.org/10.1016/S1872-2067(12)60653-6
23. Béjaoui M., Elmhamdi A., Pascual L., Pérez-Bailac P., Nahdi K., Martínez-Arias A. Preferential Oxidation of CO over $CoFe_2O_4$ and M/$CoFe_2O_4$ (M = Ce, Co, Cu or Zr) Catalysts. *Catalysts,* 2021, **Vol. 11**, 15. https://dx.doi.org/10.3390/catal 11010015
24. Fouad O. A., Abdel Halim K.S., Rashad E.M.M. Catalytic Oxidation of CO Over Synthesized Nickel Ferrite Nanoparticles from Fly Ash. *Top Catal.,* 2008, **Vol. 47**, p. 61–65. https://doi.org/10.1007/s11244-007-9034-3
25. Konichenko T.S., Liberman E.Yu., Nefedova N.V., Mikhailichenko A.I., Petrov A.Yu. CO oxidation catalysts based on ferrites. *Advances in chemistry and chemical technology*. 2015, **Vol. 29(3)**, p. 125-127. (In Russian).
26. Thomas J., Thomas N., Girgsdies F., Beherns M., Huang X., Sudheeshe V.D., Sebastiane V. Synthesis of Cobalt Ferrite Nanoparticles by Constant pH Coprecipitation and their High Catalytic Activity in CO Oxidation. *New Journal of Chemistry.* 2017, **Vol. 15***,* p. 7356-7363.
27. Zulfugarova S.M., Azimova G.R., Aleskerova Z.F., Ismailov E.H., Litvishkov Yu.N., Tagiyev D.B. Microwave Sol-Gel Synthesis of Co, Ni, Cu, Mn Ferrites And The Investigation of Their Activity In The Oxidation Reaction of Carbon Monoxide. *Current Microwave Chemistry.* 2022, **Vol. 9(1)**, p. 37-46. https://doi.org/10.2174/2213335609666220303105233
28. Liu F., Liu J., Yang Y., Wang Z., Zheng Ch. Reaction mechanism of spinel $CuFe_2O_4$ with CO during chemical-looping combustion: An experimental and theoretical study. *Proceedings of the Combustion Institute.* 2019, **Vol. 37(4)***,* p. 4399-4408. https://doi.org/10.1016/j.proci.2018.06.222
29. Margolis L.Ya., Krylov O.V. *Some features of catalysts for deep oxidation – Problems of kinetics and catalysis. Deep catalytic oxidation of hydrocarbons*. Moscow: Nauka. 1981. 120–124 p. (In Russian).
30. Trusova E.A., Tsodikov M.V., Slivinsky E.V., Marin V.P. State and prospects of catalytic purification of gas emissions (review). *Petrochemistry.* 1995, **Vol. 35**, p. 3-23. (In Russian).
31. Jacobs J.P., Maltha L., Reintfes J.G., Drimal J., Ponec V., Brongersma H.H. The surface of catalytically active spinels. *J.Catal.* 1994, **Vol. 147**, p. 294-300.
32. Hashemian S., Dehghanpor A., Moghahed M. $Cu_{0.5}Mn_{0.5}Fe_2O_4$ nano spinels as potential sorbent for adsorption of brilliant green. *Journal of Industrial and Engineering Chemistry,* 2015, **Vol. 24**, p. 308-314. DOI: 10.1016/j.jiec.2014.10.001
33. Maunders Ch., Martin B.E., Wei P., Petric A., Botton G. Investigation of the electronic structure of the cubic spinel $Cu_{1.2}Mn_{1.8}O_4$ using electron energy loss spectroscopy. *Solid State Ionics.* 2008, **Vol. 179**, p. 718–724.
34. Angotzi M.S., Mameli V., Cara C., Peddis D., Xin H.L., Sangregorio C., Mercuria M.L., Cannas C. On the synthesis of bi-magnetic manganese ferrite based core–shell nanoparticles. *Nanoscale Adv.,* 2021, **Vol. 3**, p. 1612–1623. https://doi.org/10.1039/d0na00967a
35. Tang Z.-R., Kondrat S.A., Dickinson C., Bartley J. K., Carley A.F., Taylor S.H., Davies T. E., Allix M., Rosseinsky M.J., Claridge J.B., Xu Z., Romani S., Crudace M.J., Hutchings G.J. Synthesis of high surface area $CuMn_2O_4$ by supercritical anti-solvent precipitation for the oxidation of CO at ambient temperature. *Catalysis Science & Technology.* 2011, **no. 5**, 740-746.
36. Rana S., Philip J., Raj B. Micelle based synthesis of cobalt ferrite nanoparticles and its characterization using Fourier Transform Infrared Transmission Spectrometry and Thermogravimetry. *Materials Chemistry and Physics.*, 2010, **Vol. 124(1)**, p. 264-269. https://doi.org/10.1016/j.matchemphys.2010.06.029
37. Srinivasan T.T., Srivastava C.M., Venkataramani N., Patni M.J. Infrared absorption in spinel ferrites. *Bull. Mater. Sci.,* 1984, **Vol. 6(6)**, p. 1063-1067.
38. Sagayaraj R., Jude Leonard Hilary H., Xavier S., Praveen P., Elayakumar K., Yogambal C. Structural, Vibrational, Morphological and Magnetic Properties of Copper Ferrite Nano Particles ($Cu_{0.4}MFe_{2.96}MO_4$) by Co-

precipitation Method. *Journal of Humanities and Science.* 2019, **Vol. 6(1)**, p. 58-62.
39. Brusentsov Yu.A. *Fundamentals of physics and technology of oxide semiconductors*. Tambov. 2002. 80 p. (In Russian).
40. Sun R., Zhang S., An K., Song P., Liu Y. $Cu_{1.5}Mn_{1.5}O_4$ spinel type composite oxide modified with CuO for synergistic catalysis of CO oxidation. *Journal of fuel chemistry and technology.* 2021, Vol. 49(6), p. 799-808. https://doi.org/10.1016/S1872-5813(21)60032-4