

UDC 54.128.13:541.

EFFECT OF PREPARATION METHOD OF IRON-, COPPER- CONTAINING OXIDE CATALYSTS ON THEIR ACTIVITY IN THE REACTION OF OXIDATION OF CARBON MONOXIDE TO CARBON DIOXIDE**¹S.M. Zulfugarova, ¹G.R. Azimova, ¹Z.F. Aleskerova, ²R.J. Qasimov, ²M.A. Bayramov, ¹E.H. Ismailov, ¹D.B. Tagiyev**¹*Institute of Catalysis and Inorganic Chemistry, Azerbaijan National Academy of Sciences, AZ 1143, Baku, H.Javid ave., 113; e-mail: zsm07@mail.ru; ezimova2015@gmail.com*²*Institute of Radiation Problems Azerbaijan National Academy of Sciences, AZ 1143, Baku, H.Javid ave. 31A**Received 14.01.2022**Accepted 16.03.2022*

Abstract: Iron- and copper-containing oxide catalysts have been synthesized by sol-gel technology with autocombustion using organic reagents - citric acid, glycine, urea as a complexing agent and "fuel"; studied their activity in the oxidation of carbon monoxide to dioxide. The obtained samples were characterized by the methods of X-ray powder diffraction, infrared spectroscopy and electronic paramagnetic resonance, the texture characteristics of these samples was determined by measuring the specific surface area. It is shown that, regardless of the preparation method, all synthesized samples are mixtures of iron oxides Fe_2O_3 , copper CuO , and copper ferrite $CuFe_2O_4$. It was found that the nature of the organic reagent affects the catalytic activity of the synthesized catalysts. On a catalyst with a Cu:Fe=1:1 ratio, prepared by the sol-gel method with autocombustion using urea, the complete conversion of CO is achieved at 130°C. The same catalyst, synthesized with citric acid, is active at 250°C and on a catalyst prepared using glycine, complete conversion of CO occurs at a higher temperature of 350°C. It is assumed that the different nature of combustion leads to the formation of different surface morphology and texture, which ultimately determines the catalytic activity. Thus, the most catalytically active sample was obtained using urea as a "fuel" has a higher specific surface area (25 m² / g) than the other two samples (for the samples obtained with citric acid and glycine, the specific surface area is 9 m² / g and 5.8 m² / g, respectively).

Keywords: Iron; copper oxides; copper ferrite; sol-gel synthesis method; citric acid; glycine; urea; carbon monoxide; oxidation; catalytic activity.

DOI: 10.32737/2221-8688-2022-1-82-94

1. Introduction

The increasement of carbon monoxide in the atmosphere continues to pose a serious problem for health and the environment, so the problem of its disposal remains relevant. One of the most effective methods for removing carbon monoxide is catalytic oxidation. The catalysts containing manganese, copper-chromium and platinum group metals are used for the oxidation of carbon monoxide into carbon dioxide [1-4]. The development of active catalysts without noble metals for low-temperature oxidation of carbon monoxide is an important problem. Among the oxides, metal oxides Fe, Ni, Mn, Cu, Co, Cr, Ni and ferrites, perovskites based on

them are distinguished by a noticeable activity in the oxidation of CO to CO₂ [5-8].

Currently, among the methods of obtaining highly dispersed materials, a special place is occupied by the sol-gel method, which the main advantage is the high homogenization of the initial components with the preparation of a sol and its transformation into a gel due to the processes of hydrolysis and condensation, followed by aging, drying and heat treatment [9-10]. In this case, the processes of removing the solvent from the gel play an important role in the sol-gel process, i.e. drying of the gel and its heat treatment.

A type of the sol-gel method, in which the process of drying and heat treatment occurs in one stage, is a sol-gel with autocombustion with the participation of organic reagents that act as a complexing agent in the sol-gel process and as a "fuel" in the combustion reaction. For this, water-soluble amines, acids, amino acids are used. These substances have different values of the heat of combustion, which affect the nature of their combustion, texture and catalytic activity of the synthesized samples. There are not so many works in the literature, which the effect of organic compounds on the texture and

catalytic activity of the synthesized samples has been studied, although their number has noticeably increased over the past 10 years. The mechanism of the effect of organic compounds on the structural features of the synthesized samples is still a subject of discussion [11-22].

This work presents the results of a study of the effect of organic compounds - citric acid, glycine and urea, used as modifiers of the composition and structure of synthesized iron-, copper containing oxide composites on their texture and catalytic activity in the oxidation of carbon monoxide to dioxide.

2. Experimental part

2.1. Materials and methods for preparing catalysts

The salts $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ are precursors for the synthesis of iron-copper-containing oxide systems by the sol-gel method with combustion. Citric acid ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$), glycine ($\text{NH}_2\text{CH}_2\text{COOH}$), urea ($\text{CO}(\text{NH}_2)_2$) were chosen as organic reagents. For the synthesis of catalysts with a molar ratio of the Cu: Fe = 1: 1 components, 2.4 g $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 4 g $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were taken. The amount of organic reagent using citric acid was 4.2 g, glycine - 3.8 g, and urea 2.7 g. For the synthesis of catalysts with a molar ratio of the Cu: Fe = 1: 2 components, 2.4 g $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 8.0 g $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were taken. The amount of organic reagent when citric acid was used was 6.3 g, glycine - 6.0 g, and urea - 4.0 g. For the synthesis of catalysts with a molar ratio of Cu: Fe = 2:1 components, 4.8 g $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 4.0 g $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were taken. The amount of organic reagent when citric acid was used was 6.3 g, glycine - 5.3 g, and urea- 4.0 g. The precursors were dissolved in 10 ml of distilled water. Aqueous solutions of the calculated amounts of salts and organic reagents were stirred on a magnetic stirrer at the 80°C temperature until the formation of a gel. The resulting gel was placed in a drying oven heated to 175-190°C, in which it completely dried and then ignited. At the same time, the so-called "dry" method was also used, i.e. metal salts and organic reagents in the above proportions were mixed, without transferring them into solution, but by grinding in a mortar. Water of

crystallization in the composition of metal salts at the same time contributed to wet grinding and obtaining a homogeneous mass, then heating was carried out in an oven followed by ignition.

2.2. Analysis methods

X-ray powder diffraction of the catalytic systems was carried out on a Bruker D 2Phazer automatic diffractometer with a $\text{CuK}\alpha$ radiation source. The software packages TOPAS and EVA were used. Phase identification was done using PDF cards (ICDD). The quantitative analysis of the phases was done by the method of corundum numbers (RIR).

IR and EPR spectra were recorded on FTIR Alfa and EMXmicro spectrometers from Bruker, respectively.

The size of nanoparticles of synthesized samples in dispersions of isopropyl alcohol was determined by dynamic light scattering on a Horiba LB-550 instrument under ultrasonic treatment.

The specific surface area of the samples was determined by low-temperature nitrogen adsorption by the multipoint BET method on a SORBI-MS device (Russia).

To carry out catalytic experiments, the obtained powders of iron-copper-containing oxide systems in an amount of 1g were mixed with a binder - alumogel, molded into granules, air dried, further heat treatment was carried out in a drying cabinet and a muffle furnace at temperatures of 135 and 500°C, respectively. CO oxidation was carried out by the flow method at a CO: air ratio = 1: (3-5), a space velocity of 6000-12000 h^{-1} . The analysis was

carried out on a JIXM gas chromatograph (Russia), in two columns with CaA sorbents (analysis of oxygen, nitrogen, and carbon monoxide) and poropak Q (analysis of CO₂).

2.3. Catalytic test

The obtained powders of iron-copper-containing oxide systems in an amount of 1g were mixed with a binder - alumogel, molded into granules, air dried, further heat treatment

was carried out in a drying cabinet and a muffle furnace at temperatures of 135 and 500°C, respectively.

CO oxidation was carried out by the flow method at a CO: air ratio = 1: (3-5), a space velocity of 6000-12000 h⁻¹. The analysis could be expanded on a JIXM chromatograph, in two columns with CaA and poropak Q sorbents.

3. Results and discussion

3.1. Catalytic activity of the synthesized iron-copper-containing oxide systems in the oxidation of carbon monoxide to dioxide.

The results of studying the catalytic activity of iron-copper-containing oxide systems with different ratios of metals prepared by the sol-gel method using organic reagents - citric acid, glycine and urea, showed that the nature of the organic reagent in all the studied examples affects to the activity of the catalyst. Fig. 1 shows the dependences of the oxidation of CO to CO₂ on samples of iron-, copper-containing oxides with different ratios of metals and organic reagents. The comparison of the Fig.1

data shows that the complete conversion of CO over these catalysts is observed at different temperatures. From the general picture of the activity of the studied samples, it can be seen that, using various organic reagents, one can noticeably change their catalytic properties.

On a catalyst with 1:1 ratio prepared by the sol-gel method with autocombustion using urea, the complete conversion of CO is achieved at 130°C (Fig. 1, a). The same catalyst synthesized with citric acid, is active at 250°C, and on a catalyst prepared using glycine, complete conversion of CO occurs at a higher temperature of 350°C.

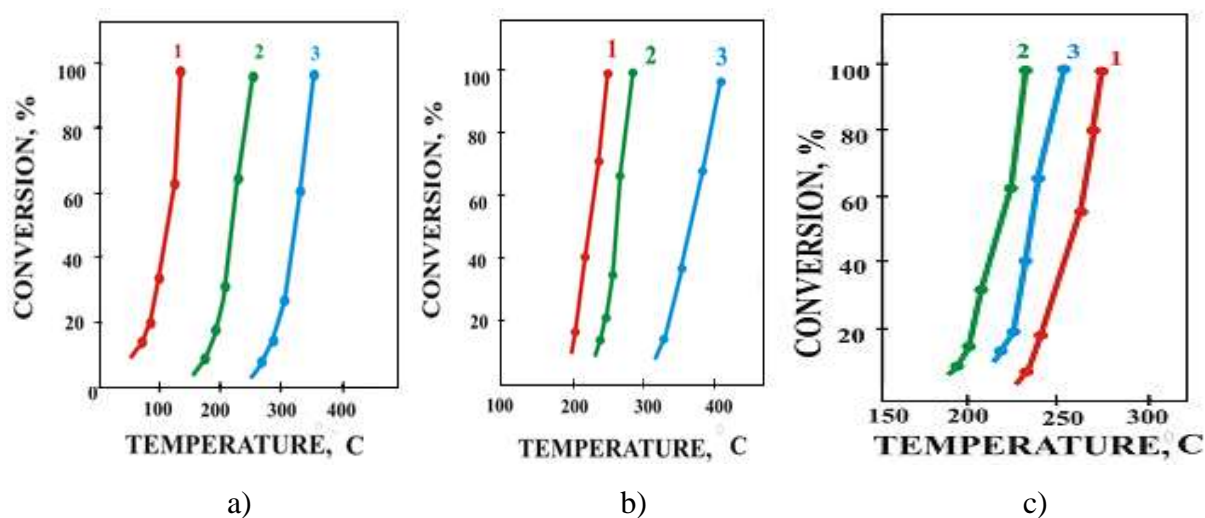


Fig. 1. Temperature dependence of the conversion of carbon monoxide on iron-copper-containing oxide samples with the ratio Cu:Fe = 1:1 (a), 1:2 (b), 2:1 (c), prepared by the sol-gel method with auto-combustion with the participation of urea (1), citric acid (2) and glycine (3). V.s 10000 h⁻¹

A similar dependence is observed for the samples synthesized by the “dry” method (a kind of self-propagating high-temperature synthesis) using the same organic reagents. A slight difference is only at the temperatures at

which the maximum conversion of carbon monoxide is observed - on the samples prepared by the dry method, the corresponding temperatures are 136, 255 and 360°C (Table 1).

It can also be seen from the data in Table 1 that at the ratio of precursors (Cu: Fe = 1: 1 and 2: 1), on the samples obtained with different organic reagents, the complete

conversion of CO is carried out at lower temperatures than on samples with the ratio Cu: Fe = 1: 2.

Table 1. Comparison of the temperature conditions for the complete conversion of CO on iron-copper-containing oxide samples with different ratios of Cu:Fe, obtained by the sol-gel method with autocombustion (s.g) and "dry" methods (d.m) when using various organic reagents. V.s 10000 h⁻¹.

Organic reagent	Ratio Cu:Fe=1:1		Ratio Cu:Fe=1:2		Ratio Cu:Fe=2:1	
	S.g.	D.m.	S.g.	D.m.	S.g.	D.m.
Citric acid	250 ⁰ C	260 ⁰ C	270 ⁰ C	300 ⁰ C	230 ⁰ C	300 ⁰ C
Glycine	350 ⁰ C	360 ⁰ C	400 ⁰ C	420 ⁰ C	250 ⁰ C	330 ⁰ C
Urea	130 ⁰ C	135 ⁰ C	250 ⁰ C	280 ⁰ C	230 ⁰ C	280 ⁰ C

The specific surface area of the synthesized samples using various organic reagents is also different (Table 2). Samples obtained using urea as "fuel" have a higher specific surface area. For them, it fluctuates in

the range 20.9-45 m² / g, depending on the Cu: Fe ratio, while for the samples prepared with citric acid and glycine, the specific surface area is 9-23 m² / g and 2.7-5.8 m² / g, respectively.

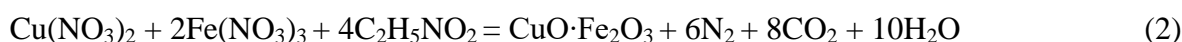
Table 2. Specific surface area of iron-copper-containing oxide samples synthesized by sol-gel with autocombustion and "dry" methods using various organic components.

Ratio Cu:Fe	Specific surface area, m ² /g					
	Citric acid		Glycine		Urea	
	Sol-gel autocombustion	Dry method	Sol-gel autocombustion	Dry method	Sol-gel autocombustion	Dry method
1:1	9	19.3	5.8	5.7	25	43
1:2	18	23	4	5.4	45	26
2:1	15.4	9.5	3.6	2.7	20.9	16.5

The advantage of the sol-gel method with autocombustion is that the formation of the reaction product occurs at low temperatures, relatively. In addition, due to the release of gaseous products because of the combustion of the organic reagent, a large amount of gaseous products is released. These two factors play an important role in the formation of the texture of

the synthesized compound due to some decrease in the aggregation of particles and their "loosening", which ultimately can affect the catalytic activity.

The reaction equations for the formation of the oxide composition CuO · Fe₂O₃ with the participation of the studied organic reagents can be written as follows:



It can be seen from the equations that the largest amount of gaseous products is formed in

the combustion reaction with urea, followed by citric acid and glycine. The specific surface are

of the samples synthesized by us also decreases in the same sequence. Moreover, the samples

3.2. X-ray phase analysis of synthesized samples.

X-ray powder diffraction of the synthesized samples indicates the formation of at least three phases. In addition to copper ferrite, combustion also produces copper oxide (tenorite) and iron oxide (hematite). Their content in the sample depends on the initial ratio of the metals. It is also necessary to consider that organic reagents used as a "fuel" have different values of the calorific value, for instance, for urea this value is 632.2 kJ / mol, for glycine - 973.1 kJ / mol, which also affects the nature of combustion and formation phases.

Figure 2 shows the diffraction patterns of the samples with the ratio Cu:Fe = 1:1, obtained by the sol-gel method with combustion

synthesized using glycine have the least catalytic activity.

with the participation of urea, citric acid, and glycine. The diffraction patterns show reflections of CuFe_2O_4 (PDF 01-074-8585), copper oxide CuO (PDF 00-048-1548), and iron oxide Fe_2O_3 (PDF 01-071-5088). The content of copper ferrite and copper oxide is approximately 90%, but in all samples, the content of ferrite is higher than that of copper oxide. In the sample obtained by combustion with urea, the lowest content of iron oxide is observed; in the other two samples, the corresponding reflections appear quite clearly and in the sample with the combustion of glycine, they are more intense. The content of iron oxide in the sample obtained by combustion with glycine is 9.5%, in the sample with citric acid it is 7.2%.

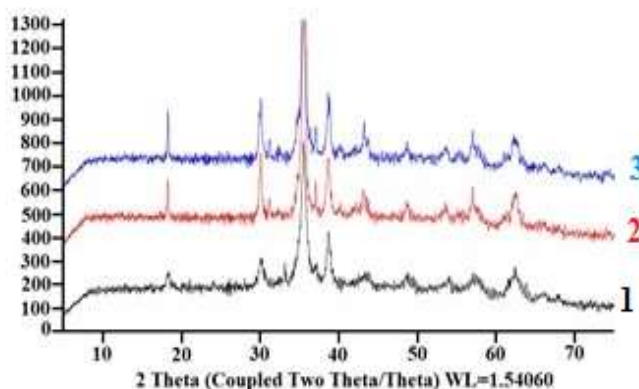


Fig. 2. Diffraction patterns of the sample with the ratio Cu: Fe = 1:1, obtained by the sol-gel method with combustion with the participation of urea (1), citric acid (2) and glycine (3).

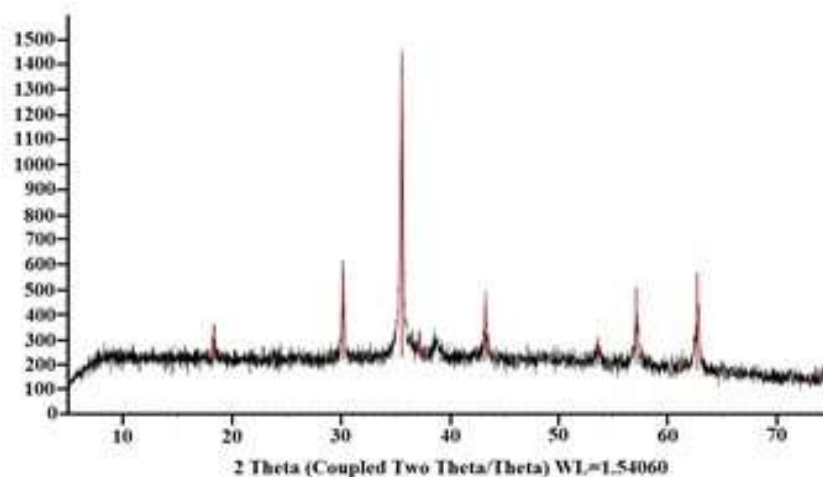
The samples also differ in crystallinity, which is 29.9% for the most catalytically active sample obtained with urea, 36% for the sample synthesized using citric acid, and 39.4% for the sample obtained with glycine. The observed broad diffraction peaks indicate a small particle size. From the above X-ray powder diffraction patterns based on the Scherrer equation, the average particle size (d) was estimated:

$$d = \frac{k\lambda}{\beta \cdot \cos \theta} \quad (4)$$

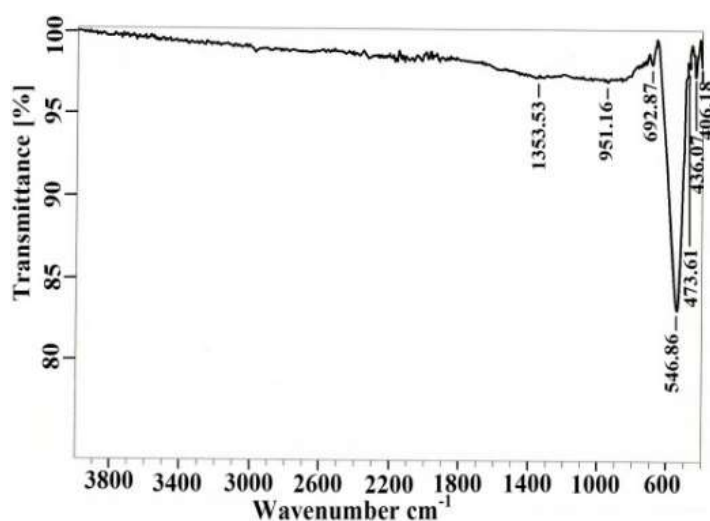
where k is the Scherrer constant equal to 0.9, λ is the wavelength equal to 1.5406 Å, β is

the integral breadth, θ is the reflection angle. The average particle size of samples obtained using urea is in the range of 15-19 nm, with citric acid - 20-23 nm, and with glycine - 29-32 nm.

The diffraction patterns of the sample with the ratio Cu: Fe = 1:2 show reflections of CuFe_2O_4 , hematite and traces of copper oxide (Fig. 3, a). The IR spectrum in the range from 400 to 1100 cm^{-1} contains absorption bands at 436.07; 473.61; 546.86; 692.87; 951.16 cm^{-1} , caused by the lattice vibrations of the M – O and M – OH – bonds [23] (Fig. 3, b).



a)



b)

Fig. 3. Diffraction pattern (a) and IR spectrum (b) of the sample with the ratio Cu: Fe = 1: 2, obtained by the sol-gel method with combustion with the participation of citric acid.

3.3. Determination of the particle size of synthesized catalysts by DLS (dynamic light scattering).

Below are the results of DLS measurements of isopropyl dispersions synthesized using citric acid, glycine, and urea for samples with the Cu:Fe = 1:1 ratio. To control repeatability, at least three repeated measurements were performed on each sample. Before the DLS measurements, the dispersions with the test samples were subjected to ultrasonic (US) treatment. Ultrasonic treatment was carried out for 10, 20, and 60 minutes. The results showed that the spectral pattern significantly depends on the processing time of the dispersions. Figure 3 shows the DLS

histograms of the exposed to ultrasound for 20 min.

It can be seen from the data in Fig. 4 that the average particle size of the synthesized samples in isopropyl alcohol dispersions subjected to ultrasonic treatment for 20 minutes ranges from 381 to 447 nm. For each of the samples, a mono-modal distribution with high values of the polydispersity index (2.607, 2.731 and 2.597, respectively) is found. Large values of the distribution width indicate that the dispersion contains aggregates of particles of various sizes. These values are much larger than the average particle size determined by X-ray diffractometry.

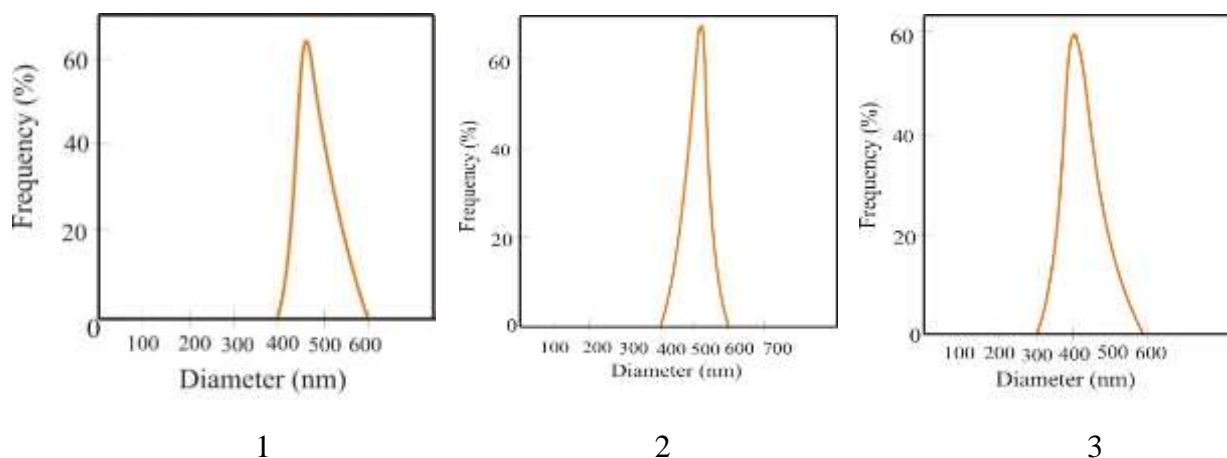


Fig. 4. Particle size distribution in dispersions subjected to ultrasonic treatment for 20 min. 1 - sample with the ratio Cu: Fe = 1:1 synthesized with urea; 2 - citric acid; 3 - glycine.

Most likely, the studied dispersions contained aggregates that were not destroyed by ultrasonic treatment. Figure 4 shows the DLS

histograms of those treated with ultrasound for 60 min. isopropyl dispersions of powders of synthesized samples.

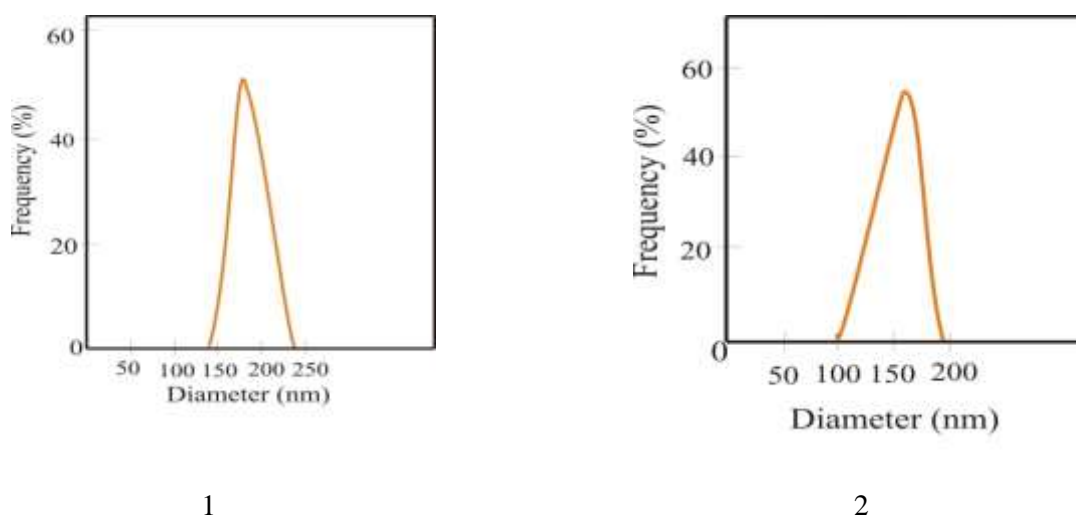


Fig. 5. Particle size distribution in samples with the ratio Cu: Fe = 1:1, synthesized with urea (1) and glycine (2), subjected to ultrasonic treatment for 60 min.

Comparison in this case of the results of DLS measurements with the data of X-ray powder diffraction of the microstructure, namely, with the average size of the coherent scattering regions (CSR), also shows that the average CSR size is significantly less than the average particle size dispersed in isopropyl alcohol. In X-ray powder diffraction, CSR is a region of a crystal that scatters X-ray radiation coherently and independently of other similar regions [11]. Note that the CSR size determined from X-ray diffraction patterns is usually

smaller than the particle (grain) size measured by electron microscopy.

Fig. 1 and tab. 1 that, in the samples with the Cu: Fe = 1:2 ratio, the conversion of CO into CO₂ proceeds at a higher temperature than in the samples with the 1:1 ratio, but a similar dependence of the conversion on the nature of the organic reagent is retained, i.e. on the sample obtained with the participation of urea, the complete conversion of CO proceeds at a lower temperature (250°C) than the other two samples obtained with the participation of

citric acid (270°C) and glycine (400°C) by the sol-gel method, as well as by the dry method. After 60 minutes of sonication, the particle size decreases and fluctuates in the range 123 - 153 nm (Fig. 5).

3.4. EPR studies of synthesized systems

Figure 6 shows the EPR spectra of iron-copper-containing oxide systems with a ratio of Cu:Fe = 1:2 prepared by the sol-gel method using: a) citric acid, b) glycine and c) urea and Table 3 shows the values of magnetic resonance parameters of these samples.

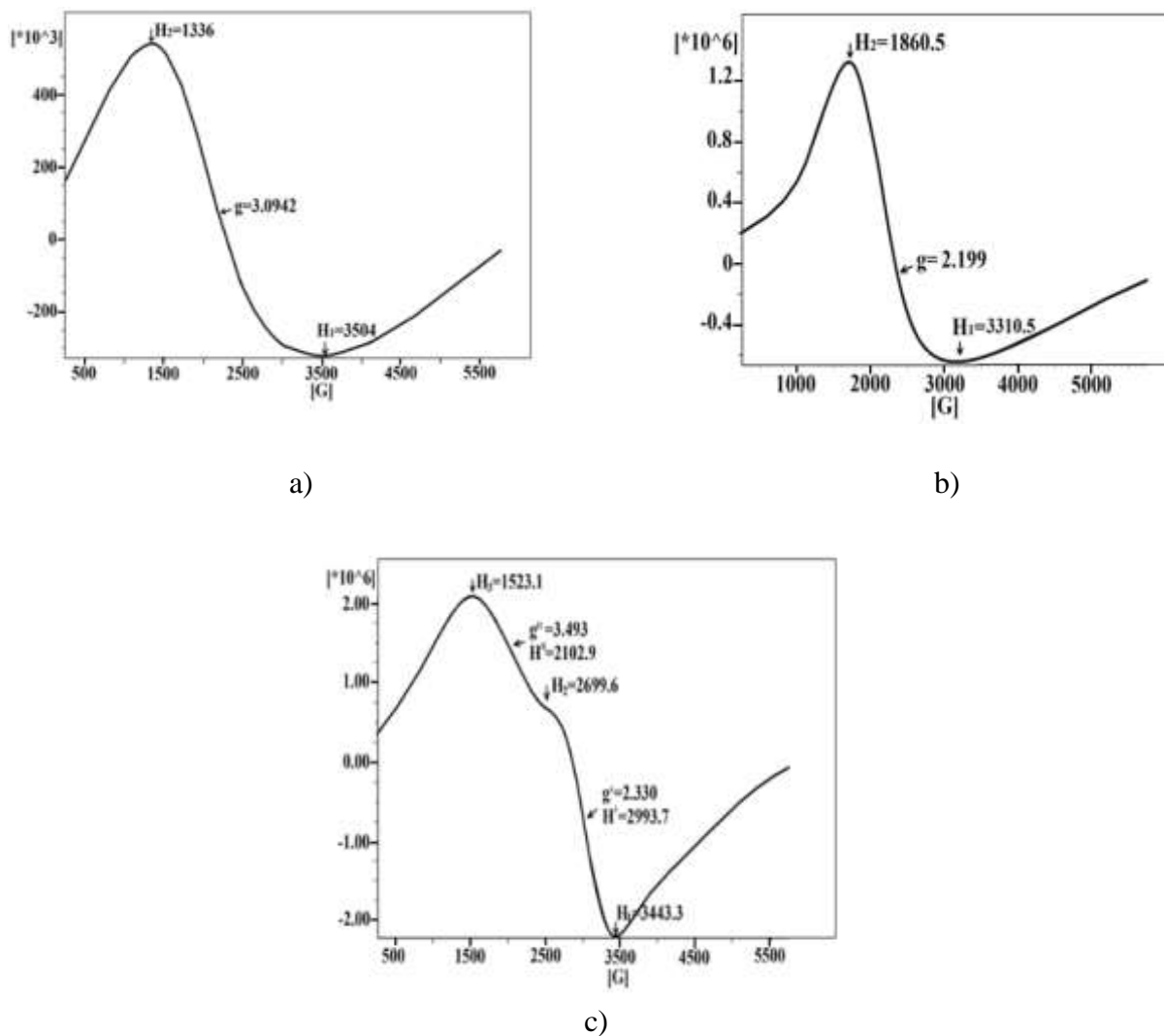


Fig. 6. EPR spectra of iron-copper-containing oxide systems with the ratio Cu:Fe = 1: 2, prepared by the sol-gel method using: a) citric acid, b) glycine, c) urea.

Table 3. The values of the magnetic resonance parameters of the EPR spectra of iron-copper-containing oxide systems with the ratio Cu: Fe = 1:2, prepared by the sol-gel method using: a) citric acid, b) glycine, c) urea.

Sample	g-factor	Signal width, ΔH , G	Signal strength, I	Integrated signal intensity $I(\Delta H)^2$
a	3.094	2168	0.85×10^6	4.0×10^{12}
b	2.199	1450	2×10^6	4.2×10^{12}
c	2.330	744	3×10^6	1.7×10^{12}
	2.912	2998	3×10^6	27×10^{12}

The observed EPR spectra are due to the presence in the samples of ferro / ferromagnetic phases of oxides of iron, copper and copper ferrite. As can be seen from the presented EPR spectra and the data in Table 3, the values of the magnetic resonance parameters the width (ΔH) of the signal and the g-factor, in general, the shape of the signals, differ markedly and this difference is primarily due to the influence of the nature of the organic reagent used in synthesis of these samples. We believe that these organic reagents mainly affect the textural characteristics of these samples, which affects the distribution of magnetic phases relative to each other in the composite and ultimately, the magnetic resonance characteristics of the synthesized samples. Thus, one can notice an interesting feature between the behaviour of the magnetic and catalytic properties, namely, in the change in the magnetic and catalytic properties of the synthesized samples, depending on the content and distribution of the above oxide phases in them.

It is known that copper oxide is very active in the oxidation of CO, and shows the catalytic effect depends on the particle size of the copper oxide. Thus, coarse-crystalline copper oxide exhibits oxidizing properties only at 150-200°C, and nanosized particles even at room temperature¹. It was also found that Fe₂O₃ nanoparticles with a size of ~ 3 nm are more effective as catalysts for carbon monoxide than oxide phases of large sizes and the presence of a hydroxylated phase of iron oxide (FeOOH) [24].

In [25], a series of mesoporous composite oxide catalysts CuO – Fe₂O₃ with different contents of CuO was prepared. They are characterized by a narrow pore size distribution and a large surface area, showing high catalytic activity and stability against low temperature CO oxidation. The content of CuO in the catalyst affects its activity and the authors explain this by the high dispersion and reducibility of CuO, as well as the high concentration of oxygen vacancies in the catalyst.

Taking into account the above, to clarify the effect of oxides present in the synthesized samples on CO oxidation, copper and iron oxides were also obtained by the sol-gel method with combustion. The study of their activity in

the CO oxidation reaction showed that the reaction on iron oxide proceeds at a noticeable rate at temperatures above 400°C.

At the stoichiometric ratio of metals Cu: Fe = 1: 2, as shown above, the diffractograms exhibit reflections of CuFe₂O₄ (spinel) and hematite (Fig. 3, a) Here, the role of the spinel phase in the catalytic activity of the catalyst is obvious. In the samples with the ratio Cu: Fe = 1:1 and 2:1, the oxide phase of copper is present in a noticeable amount.

In the presence of the synergistic effect, one would expect a significantly higher CO conversion on samples with Cu:Fe = 1:1 and 2:1 ratios, but this does not happen. Experiments with individual copper oxide showed that the conversion on copper oxide at 250°C is about 80%; on these samples, even at these temperatures, the conversion reaches 100%.

Different mechanisms have been proposed for the mechanism of CO oxidation on spinel ferrites. In [26] it is noted that the process of CO oxidation on copper ferrite can proceed along one- and two-stage routes. In a one-step scheme, CO reacts directly with the bridging oxygen of octahedral Cu and Fe to form a CO₂ molecule without a barrier. In a two-stage scheme, CO is first adsorbed on the surface and then reacts with oxygen bound to octahedral Cu and Fe, generating CO₂.

The sol-gel combustion method can be considered as a type of self-propagating high-temperature synthesis method, but proceeding at lower temperatures. Combustion occurs when a short-term thermal effect on the system is initiated, in which an exothermic reaction is initiated, due to which further combustion occurs due to its own heat release. In this case, various physical and chemical transformations occur - melting, chemical reaction, diffusion, which affect the formation of the structure.

In the self-propagating high-temperature synthesis method boundary layer combustion and combustion in the thermal explosion mode are distinguished, differing in how initiation occurs - from the surface or throughout the entire volume. In the sol-gel combustion method, it is possible to influence the combustion process using organic reagents with different physicochemical properties - melting point, heat of combustion.

You can also vary their ratio to the precursors of the reaction. Combustion occurs in different ways depending on these factors (Photo. 1).



1)

2)

3)

Photo 1. Images of copper ferrite samples obtained by the sol-gel combustion method using citric acid (1), glycine (2), and urea (3).

When burning with citric acid, the final product turns out to be more voluminous and branched, the process does not last long. With glycine, combustion occurs in a flash and rapid combustion. With urea, the process takes longer with the release of a large amount of gaseous

substances. The different nature of combustion affects the formation of phases, leads to the formation of different surface morphology, texture, which ultimately determines the catalytic activity.

4. Conclusion

Thus, it can be concluded that the use of organic reagents of different nature in the synthesis of an iron-copper oxide catalysts by the sol-gel method with combustion significantly affects its phase composition, magnetic properties, texture and catalytic activity in the oxidation of CO to CO₂.

The low temperatures of the formation of the catalytic system and the release of gaseous products during the combustion of the organic reagent, as a result of which the combustion products are "loosened", leads to a decrease in the aggregation of the formed catalyst particles. The largest amount of gaseous products is formed in the combustion reaction with urea, followed by citric acid and glycine. In the same

sequence, decreases the specific surface area of the synthesized samples and their catalytic activity. The largest surface is formed when using urea (25 m² / g), and the smallest - glycine (5.8 m² / g). The catalytic activity of the samples in the oxidation of CO in CO₂ in the temperature range from 135 to 450^oC was determined. It is shown that, under the conditions of the experiments carried out, the most active catalysts are the samples obtained using urea as an organic reagent. On a catalyst with a Cu: Fe=1:1 ratio, prepared by the sol-gel method with autocombustion using urea, the complete conversion of CO is achieved at 130^oC.

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ВЛИЯНИЕ СПОСОБА ПРИГОТОВЛЕНИЯ ЖЕЛЕЗО-, МЕДЬСОДЕРЖАЩИХ ОКСИДНЫХ КАТАЛИЗАТОРОВ НА ИХ АКТИВНОСТЬ В РЕАКЦИИ ОКИСЛЕНИЯ МОНООКСИДА УГЛЕРОДА В ДИОКСИД

¹С.М. Зульфугарова, ¹Г.Р. Азимова, ¹З.Ф.Алескерова, ²Р.Дж. Гасымов, ²М.А. Байрамов, ¹Е.Г.Исмаилов, ¹Д.Б. Тагиев

¹Институт катализа и неорганической химии им. акад. М.Нагиева
Национальной АН Азербайджана

AZ 1143 Баку, пр.Г.Джавида, 113; e-mail: zsm07@mail.ru; ezimova2015@gmail.com

²Институт радиационных проблем Национальной АН Азербайджана
AZ 1143, Баку, пр. Г.Джавида, 31А; e-mail:nukl@box.az

Аннотация: Синтезированы железо-, медьсодержащие оксидные катализаторы по золь-гель технологии с автогорением с использованием органических соединений - лимонной кислоты, глицина, карбамида в качестве комплексообразователя и «горючего»; изучена их активность в реакции окисления монооксида углерода в диоксид. Полученные образцы охарактеризованы методами рентгенофазового анализа, инфракрасной спектроскопии, электронного магнитного резонанса, определены текстурные характеристики этих образцов путем измерения удельной поверхности. Показано, что независимо от способа приготовления все синтезированные образцы представляют собой смеси феррита меди CuFe₂O₄, оксида меди SiO и железа Fe₂O₃. Установлено, что природа используемого органического компонента влияет на каталитическую активность синтезированных катализаторов. На катализаторе с соотношением Си:Fe=1:1, приготовленным золь-гель методом с автогорением с использованием карбамида, полная конверсия СО достигается при 130°С. Этот же катализатор, синтезированный с лимонной кислотой, активен при 250°С, а на катализаторе, приготовленном с использованием глицина, полная конверсия СО происходит при более высокой температуре 350°С. Сделано предположение, что разный характер горения приводит к формированию различной морфологии поверхности, текстуры, что, в конечном счете, определяет

каталитическую активность. Так, наиболее каталитически активный образец, полученный с использованием карбамида в качестве «горючего», обладает более высоким значением удельной поверхности ($25 \text{ м}^2/\text{г}$), чем остальные два образца (для образцов, полученного с лимонной кислотой и глицином, удельная поверхность составляет $9 \text{ м}^2/\text{г}$ и $5.8 \text{ м}^2/\text{г}$ соответственно).

Ключевые слова: оксиды железа, меди, феррит меди, золь-гель метод синтеза, лимонная кислота, глицин, карбамид, монооксид углерода, окисление, каталитическая активность

KARBON MONOOKSIDİN OKSIDLƏŞMƏ REAKSİYASINDA DƏMİR,- MİS TƏRKİBLİ OKSİD KATALİZATORLARININ HAZIRLANMA ÜSULUNUN ONLARIN AKTİVLİYİNƏ TƏSİRİ

¹S.M. Zülfiqarova, ¹G.R. Əzimova, ¹Z.F. Ələskərova, ²R.C. Qasimov, ²M.A. Bayramov, ¹E.H. Ismailov, ¹D.B. Tağıyev

¹AMEA-nın akad. M.Nağıyev adına Kataliz və Qeyri-üzvi Kimya İnstitutu
AZ 1143, Bakı, H.Cavid pr., 113; e-mail: zsm07@mail.ru; ezimova2015@gmail.com

²AMEA-nın Radiasiya Problemləri İnstitutu
AZ 1143, Bakı, H. Cavid pr., 31A; e-mail:nukl@box.az

Xülasə: Dəmir,- mis tərkibli oksid katalizatorları zol-gel yanma metodu ilə, üzvi birləşmələrdən - limon turşusu, qlisin, sidik cövhəri kompleks əmələgətirici maddə və "yanacaq" kimi istifadə olunmaqla sintez edilmiş və dəm qazının dioksida oksidləşməsi reaksiyasında onların aktivliyi öyrənilmişdir. Alınan nümunələr rentgen faza, infraqırmızı spektroskopiya və elektron maqnit rezonansı metodları ilə xarakterizə edilmiş, eləcə də nümunələrin xüsusi səthi BET usulu ilə müəyyən edilmişdir. Göstərilmişdir ki, hazırlanma üsulundan asılı olmayaraq bütün sintez edilmiş nümunələrin tərkibini mis ferrit, mis və dəmir oksid təşkil edir. Müəyyən edilmişdir ki, istifadə olunan üzvi komponentin təbiəti sintez edilmiş katalizatorların katalitik aktivliyinə təsir göstərir. Karbamiddən istifadə etməklə hazırlanmış və daha yüksək xüsusi səth sahəsinə ($25 \text{ m}^2/\text{g}$) malik olan Cu:Fe=1:1 katalizatoru CO-nun tam çevrilməsini 130°C -də aparırsa, limon turşusu ilə sintez edilən və səthi $9 \text{ m}^2/\text{g}$ olan eyni katalizatorunda CO-nun tam çevrilməsi 250°C -də, qlisinlə hazırlanan və səthi $5.8 \text{ m}^2/\text{g}$ olan katalizatorunda isə 350°C temperaturda baş verir. Eyni nümunənin fərqli katalitik aktivliyi sintez zamanı yanmanın təbiətindən asılı olaraq səthin fərqli morfolojiya və teksturasının formalaşması ilə əlaqədardır.

Açar sözlər: dəmir oksid, mis oksid, mis ferrit, sol-gel sintez üsulu, limon turşusu, qlisin, karbamid, karbon monooksid, oksidləşmə.