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ABSTRACT

of the dissertation for the degree of Doctor of Science

DEVELOPMENT OF INORGANIC NANOCOMPOSITE MATERIALS FOR THE MAIN STAGES OF THE PROCESS OF OBTAINING HYDROGEN FROM METHANE-CONTAINING GASES

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Field of science:	Chemistry
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The work was performed at Institute of Catalysis and Inorganic Chemistry named after Academician M.Nagiyev of the Ministry of Science and Education of the Republic of Azerbaijan in the laboratory "Processing of mineral raw materials containing non-ferrous metals".

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GENERAL CHARACTERIZATION OF THE WORK

The actuality and degree of development of the thesis theme. Currently, active research is being conducted to develop composite materials containing nano-sized metal particles and/or their oxides. This is mainly due to their catalysts, adsorbents, semiconductors, magnetic materials, etc., it is related to the fact that they have a wide range of applications as functional materials.

The main reason for intensive research in the direction of creating catalytically active materials is that traditional catalysts of many processes do not meet modern requirements, although in most cases they have reached the maximum limit of their functional properties. The production requirements include minimizing the harmful impact on the environment, reducing raw material and energy costs, and transportation expenses, and maximizing raw material potential. Failure to comply with these requirements also applies to composite systems used in hydrogen production[1]. For this reason, a significant part of scientific publications on the creation of next-generation composite materials is devoted to the development of catalytic systems for the processes underlying hydrogen production from methane.

The focus of researchers on this process is due to the fact that hydrogen is an indispensable raw material for the production of many products and is seen as a universal energy carrier that enables the use of renewable and alternative energy sources in the future.

The availability of a cheap source of raw materials with high methane content (bio or natural gas) for the main stages of the hydrogen production process, the reduction of the harmful impact on the environment (fulfillment of the UN Convention obligations) and the increased use of biogas, the possibility of economic development of rural areas, make the development of new composite materials necessary and research is timely and promising.

It is known that a typical scheme for obtaining hydrogen from methane-containing gases includes several main stages: purification of primary raw materials from sulfur-containing compounds, obtaining

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[1] Крылов, О.В. Катализ в 2004 г. к итогам XIII Международного конгресса по катализу, Париж, 10-15 июля, 2004// Кинет. и катал. N 3,–2005. т.46, –с.474-480.

hydrogen-containing gas (synthesis gas) and purification from carbon monoxide[2]. Analysis of the scientific literature reveals a significant focus on developing new composite systems containing precious (noble and rare) metals, which increases the cost of hydrogen and limits its widespread use[3]. The dominant concept of recent publications is the creation of catalytically active materials in which the active component is highly dispersed and/or in the nano-range in order to improve the functional properties of composite materials. In this context, the creation of composite systems that meet the necessary requirements at minimum cost is still very topical and necessary.

In terms of the discussed problem, using multicomponent mineral man-made or natural raw materials, or "soft" (for example, in hydrothermal conditions) synthesis methods, etc. composite materials obtained by applying it seem to be very promising but little studied. Developing the scientific basis of such composites and determining the relationships between their target properties and their composition, structure and physico-chemical properties is undoubtedly one of the key issues.

An integrated approach involving the development of an effective composite material with specific functional properties, as well as the identification of the most important physicochemical properties that drive their activity, will contribute significantly to the theory and practice of creating new, effective composite systems for the mentioned reactions.

The relevance of the conducted (conducted, seen) studies in their Institute of Catalysis and Inorganic Chemistry named after Academician M.Nagiyev of the Ministry of Science and Education of the Republic of Azerbaijan No. 0106 AZ00420 (2007-2010); 0111 AZ2094, 2095 (2014-2016) inclusion in the development plans are approved with the financial support of grant No. 07 under the project "Synthesis of catalysts for the obtaining and purification of hydrogen for fuel cells".

The topic of the research is "The Scientific Research Program of

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[2] Справочное руководство по катализаторам для производства аммиака и водорода /Под ред. В.П.Семенова, ГИАП, Ленинград: Химия, −1973, −248 с.

[3] Centeno, M.Á., Reina, T.R., Ivanova, S. [et al.] Au/CeO_2 Catalysts: Structure and CO Oxidation Activity: [Electronic resourse] /Catalysts, 6(10), 158, −2016. URL: https://doi.org/10.3390/catal6100158

the Azerbaijan Academy of Sciences for 2014-2020", "The National Program on the Use of Alternative and Renewable Energy Sources" (Decree dated 21.10.2004), "The 2009-2013 Program of the Regions of the Republic of Azerbaijan corresponds to the State Program on socio-economic development.

Object and subject of the study. The main **object** of the research is inorganic composite materials based on oxides of metals of variable valence (Fe, Co, Mn, Cu, Ni, etc.) and zeolites (NaX, NaY, clinoptilolite, etc.) for the main stages of the process of obtaining hydrogen from methane. The **subject** of the research was the development of a method for obtaining composite materials with a certain structure and properties; and identification of factors that ensure the efficiency of the developed systems.

The purpose and objectives of the work. The aim of the work was to develop the scientific foundations for the production of new inorganic nanocomposite materials with the required functional properties for the main stages of the process of producing hydrogen from methane-containing gases; to determine the complex of the most important physico-chemical properties that ensure the functioning of materials.

To achieve this goal, the following tasks have been solved:

– compositions and the optimal mode of obtaining composite materials have been developed, taking into account the target characteristics;

– the main indicators of the effectiveness of the obtained systems are established: the influence of phase, structural and chemical factors on activity; the patterns of phase transitions depending on the composition and conditions of synthesis are determined;

– the properties (physicochemical, catalytic, acid-base) of the obtained materials are investigated; optimal parameters (temperature, ratio of reagents, volumetric feed rate of gas raw materials) of processes with their application are determined;

– quantitative correlations between the physicochemical characteristics and catalytic properties of composite materials have been determined;

– the prospects of using the results of the dissertation research in other applications are evaluated.

Research methods. To solve these tasks, the following instrumental research methods were used: X-ray phase (XRF), derivatographic (DTA, DTG, TG), Mossbauer spectroscopy (MS), scanning electron microscopy (SEM), energy dispersion analysis (EMF), X-ray fluorescence spectroscopy (XFS), spectroscopy in the ultraviolet (UV) and infrared regions (X). Gas chromatography (GC) and analytical methods were used to determine the composition of gases, the geometric characteristics of the samples were determined by the BET method, the physicochemical properties of the surface of materials were studied by thermoprogrammed surface reactions (TPPR), the method of processing and analyzing experimental data was mathematical, including statistical.

Basic provisions for protection:

–optimal composition and basic techniques for obtaining a new composite material based on inorganic substances (iron, aluminum and titanium oxides), the source of which was man-made oxide mineral raw materials (slurries); their functional properties; the influence of the genesis of raw materials, phase changes and structure of iron oxides on functional properties; the relationship of activity with surface properties;

–preparation and characterization of a nanocomposite based on natural zeolite (clinoptilolite); the influence of the type of structure (for example, some synthetic NaY, NaX, CaX, CaA, NZSM-5, etc.) of zeolites, the composition of the matrix, the composition of the mother liquor in the synthesis of zeolites, as well as the nature of the intercalated metal on their functional properties in the process of obtaining synthesis- gas; determination of the quantitative correlation between composition, structure, acid-base and catalytic properties;

–optimal composition and conditions for the synthesis of compositions with the spinel structure Co-Mn-O; Co-Mn-Fe-O with the required functional properties in the reactions of deep oxidation of methane and CO; their characteristics;

–method of obtaining Cu-Me-O (Me-Co, Zn, Ni); Co-Mn-O; Cu-Me-Al-O (Me-Co, Zn) systems by hydrothermal method in an ethylene glycol or glycerin medium and their characteristics; regularities of the process; the relationship between composition, structure and activity in the oxidation reaction of CO in a hydrogen-containing medium; production of hydrothermal redox synthesis of Li-Me-O (Me-Co, Ni, Mn; Co-Ni) powders with a pronounced nanostructure.

Scientific novelty. For the first time, rational methods have been developed for obtaining functional materials with the required characteristics in the process of gas purification from sulfur compounds from slurries, the macrocomponent composition of which is represented by iron, aluminium and titanium oxides.

The possibility of regulating the structural, mechanical and coagulation properties by introducing montmorillonite into the composition has been established. The functional features of the resulting material ensure a high degree of extraction of sulfur dioxide from primary raw materials without sulfation of the aluminium oxide component.

The method of preparation is characterized by ease, the absence of stages of modification with transition and alkali metals and dangerous reagents during preparation, which determines its advantages over the described in the literature and commercial analogue (based on Al2O3). The "protective" role of iron oxides in sludge has been established, providing high activity rates for a long time, and it has been shown that an increase in the defectiveness of its structure increases the activity of the composite material. The evaluation of the quantitative correlation "activity - acid-base properties" allowed us to establish a high correspondence and recommend this criterion for expanding the range of catalytically active composites obtained for this process.

The scientific novelty of the research presented below is included in the list of the most important scientific results of ANAS in 2009- in the field of inorganic chemistry[4].

A nanocomposite with optimal functional properties has been developed based on the expansion of the functions of the components of natural zeolites by using the latter as matrices to stabilize the particles of the active phase obtained by chemical modification of an intercalated metal-containing precursor.

The functional properties of a nickel-zeolite composite system have been theoretically and experimentally substantiated that the carrier has a unique structure and composition (optimal concentration of alkali

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[4] AMEA-nın 2009-cu ildəki fəaliyyəti və respublikanın digər elm təhsil müəssisələrində yerinə yetirilmiş elmi tədqiqat işlərinin əsas nəticələri haqqında hesabat./ - Bakı: Elm nəşriyyatı, - 2010. – 294s.

and alkaline earth metals) that contributes to high dispersion of nickel, its high degree of metan processing into hydrogen-containing gas In addition, resistance to carbon deposition, significant reduction of nickel concentration, absence of the stage of inclusion of oxides of alkaline and alkaline earth metals into the composition of the carrier determines its advantages over those described in the literature and industrial analogue (GIAP).

Methodological techniques for obtaining these systems, which differ from traditional ones, are justified by determining the quantitative relationship between the "matrix structure – composition – physicochemical properties – catalytic properties", as well as the nature and activity of active centres, and were proposed as a criterion for creating new highly efficient systems.

The influence of the nature and concentration of alkali metal cations in the mother liquor during the synthesis of zeolites on the functional properties of nickel systems has been established. The influence of the matrix structure, composition, and the nature of the introduced metals on the properties of composite systems has been revealed. The effect of the size of the matrix input window on the selectivity of hydrogen formation is shown.

The composition and conditions for obtaining cobalt-manganese spinel with a certain degree of distortion of the crystal structure, providing deep oxidation of methane at a lower temperature, have been experimentally substantiated.

A technique has been developed for the production of highly dispersed Mn-Fe-Co-O compositions (ferrospinels and cobaltites) with a certain structure, giving the material the necessary functional properties. The features of the composition and structure of these spindles, which perform the function of a reversible oxygen source, ensure high efficiency in CO oxidation reactions in a hydrogen-containing medium and are thermally stable at high temperatures. The method of producing ferropinel is characterized by lightness, absence of noble and rare earth metals, and environmental safety compared to those described in the literature and the traditional industrial analogue (Fe-Cr-O).

A method of hydrothermal redox synthesis of systems (Cu-Me-O (Me -Co, Zn, Ni); Co-Mn-O; Cu-Me-Al-O (Me-Co, Zn); Li-Me-O (Me

- Co, Ni, Mn, Co-Ni)) in an organic medium (ethylene glycol or glycerin) from nitrates, which makes it possible to obtain nanodisperse particles of metal-metal oxide compositions. The influence of the physicochemical parameters of synthesis on the evolution of the formation of nanodispersed particles, surface morphology and dispersion is shown. The scheme of formation of nanoparticles is substantiated based on a complex of physicochemical research methods. The conditions for the production of nano oxides with certain characteristics have been established, which make it possible to reduce the temperature of the CO oxidation process in a hydrogen-containing medium.

The work was supported **by grant No. 07 of 15.10.2014 for the project "Synthesis of catalysts for obtaining and purifying hydrogen for fuel cells" (2014-2016).**

Theoretical and practical significance of the work. The theoretical significance lies in the scientific substantiation of the composition and basic techniques for obtaining new composite materials based on affordable and cheap inorganic substances with the required functional properties for the main stages of the process of obtaining hydrogen from methane.

The interrelationships "composition-structure-functional properties" were established, which made it possible to determine the complex influence of these factors, and determining the strength of this relationship will allow predicting the functional properties of raw materials with similar physicochemical characteristics to the studied systems.

Prepared composite materials can be of interest to enterprises in terms of cleaning gases released into the atmosphere from inorganic sulfur compounds, processing bio-, and natural gas into synthesis gas, as well as implementing processes required for refined gas purification.

Determining the main technological parameters that affect the size and composition of nanoparticles of oxide systems obtained with the presence of polyols in hydrothermal conditions opens the way to directed synthesis. Synthesized nanoparticles can find various applications in the fields of modern science and technology.

The use of composite systems based on slurries will ensure the complete purification of primary raw materials from sulfur at a minimum cost, expand the range of used sorbents, and also allow obtaining a valuable product - sulfur, which is used in various fields of the national economy and the chemical industry. Determining the temperature range in which these systems retain their functional properties allows recommending them for use in catalysis and sorption processes at high temperatures, as well as in the frontal layer in an environment with a significant concentration of oxygen.

The proposed new solutions for the purchase of composite systems for hydrogen production processes allow to ensure a significant economic effect and high competitiveness.

The results can be used in the design work of scientific-research institutes, some of them are currently used in the teaching process at ADPU. The completeness of the research was developed to obtain other nanooxide systems (Li-Me-O (Me-Co, Ni, Mn)) in laboratory conditions that can be used as electrodes in fuel cells, contained by the successful application of iron-containing slurries and natural zeolite-based systems (No.i20040160) in other catalytic processes

The degree of reliability of the results and conclusions. The use of standard experimental and computational methods, a large scale of experimental data, and modern complex physicochemical analysis methods ensure the necessary reliability of the results. The interpretation of the experimental results does not contradict the fundamental scientific ideas in this field, and it is consistent with the results of the studies of other authors in the part of the studies where comparison is possible. Additional confirmation of the validity of the results can be the expert opinion of the results during the examination of publications in journals, approval at conferences, scientific examination of the grant application, grant and scientific reports of planned works.

Approbation of the work. The main provisions and results of the work were reported and discussed at various conferences, congresses, and symposia listed below: "Cooperation to solve the problem of waste" IV international conference (Kharkov (Ukraine, 2007); «Catalysis: Fundametals and Application» III International Conference (Novosibirsk (Russia), 2007); XVIII Mendeleev Congress on General and Applied Chemistry (Moscow (Russia), 2007); «Zeolites and Mesoporous Materials: Achievements and Prospects» V All-Russian Conference

(Zvenigorod (Russia), 2008); Scientific conference dedicated to Academician M.F. Nagiyev's 100th anniversary (Baku, 2008); Scientific conference of postgraduate students of ANAS (Baku, 2009); "Problems of Theoretical and Experimental Chemistry" XIX, XXVI Scientific Conference (Yekaterinburg (Russia), 2009, 2016); international scientific-practical conference “Modern energy and resource saving technologies. Problems and Prospects» (Odessa (Russia), 2009, 2012); dedicated to the 95th anniversary of professor A.A. Verdizade "Organic reagents in analytical chemistry" konfransı (ADPU, Bakı, 2009); 50th International Symposium "Actual problems of strength" (Vitebsk (Belarus), 2010); «Functional materials and nanotechnologies-2011» international conference (Riga (Latvia), 2011); "Perspectives of using alternative and renewable energy sources" (Baku, 2011); «Euro-ecohannover-2012» international symposium (Hannover (Germany), 2012); International conference "The role of multidisciplinary approach in solving current problems of fundamental and applied sciences (earth, technical and chemical sciences)" (Baku, 2014); «International Congresson Chemical, Biological and Enviromental Sciences» (Kyoto (Japan), 2015); «Modern science technologies» international conference (Tenerife (Spain), 2015); "Successes in synthesis and complex formation" (Moscow (Russia), 2016); "XX Mendeleev Congress on General and Applied Chemistry" conference (Volgograd (Russia), 2016); "Actual problems of adsorption and catalysis" scientific conference (Plyos (Russia); «Technical chemistry. From theory to practice" V International Conference (Perm (Russia), 2016); "Actual issues of chemical technology and environmental protection" VI All-Russian Conference with international participation (Cheboksary (Russia), 2016); «2nd IWA Regional Symposiumon Water, Wastewater and Environment» symposium (Çeşme-İzmir, (Turkey), 2017); "Nagiev Readings" Scientific conference dedicated to the 110th anniversary of Acad. M. Nagiyev (Baku, 2018); "Actual problems of chemistry" XII international scientific conference (Baku, 2018); "Chemistry and Modernity" (Cheboksary (Russia), 2019); XXI Mendeleev Congress on General and Applied Chemistry" (St. Petersburg (Russia), 2019); "New materials and promising technologies" scientific forum with international participation (Moscow (Russia), 2019).

60 scientific papers have been published on the topic of the

dissertation, including 27 articles in peer-reviewed leading domestic and foreign journals, and 1 patent.

Contributed by the author. Formulation of the main idea, setting of the problem and selection of the research direction, development of goals and objectives, approaches to achieve them, systematization, and discussion of the results were carried out by the author personally.

Also, the author directly participated in the organization and conduct of the laboratory research done together with the participants of the grant work within the framework of the dissertation work of the two graduate students, whom he was the scientific supervisor of, to receive the degree of Doctor of Philosophy in Chemistry. The author's contribution was crucial in defining the objectives and interpreting the results of the study while working with the co-authors.

The name of the institution where the dissertation work was performed. Institute of Catalysis and Inorganic Chemistry named after Academician M.Nagiyev of the Ministry of Science and Education of the Republic of Azerbaijan.

Structure and scope of the dissertation. The dissertation consists of an introduction, 6 chapters, a conclusion, a bibliography including 579 cited sources. Dissertation work is presented on page 423 with 123 pictures and 38 tables.

The total number of characters in the thesis is 447057 (without spaces), including: introduction - 18654; chapter I - 123326; II - 32588; III - 81445; IV - 104599; V - 62722; VI- 17284; conclusions - 6439 characters.

MAIN CONTENTS OF THE WORK

In the introduction, the relevance of the problem is substantiated, the purpose and tasks for its solution are formulated, and the scientific novelty, practical significance and degree of approbation of the work are shown.

The first chapter highlights the factors determining the relevance of research, substantiates the prospects of searching for composite materials (CM) for the main stages of the process of producing hydrogen from methane, and collects basic knowledge on the effective development of catalytically active composites.

The advantages and disadvantages of CM used in the reactions underlying these stages are considered, various synthesis methods are described and compared, and the features of compositions, structures and their effect on target characteristics are discussed in detail. Special attention is paid to the synthesis of CM based on oxides and the criteria for their selection. An analytical review of the features of CM concludes with a statement of the fact of the high cost and low availability of the catalytically active phase of most of the studied systems, which limits their application, and many studies remain at the level of academic development.

The first chapter concludes with the formulation of the problem and the designation of new promising directions in the field of CM creation, the formulation of tasks and ways to solve them.

In the second chapter, the characteristics of the materials used are given and the choice of research objects is justified; methods for studying the structural and physico-chemical properties of the obtained systems are described; schemes of laboratory installations used to study their functional properties are given and the research methodology is described [10].

X-ray phase analysis was performed on a diffractometer "PANalytical Empyrian-2" (Netherlands), "D2 Phaser" and "D8 ADVANCE" (Germany); DRONE-2, DRONE-4-07 (FeK$_a$ radiation). The derivatographic studies were carried out on a NETZSCH derivatograph of the brand "STA 449 F3 Jupiter" (Germany), "Paulik-Paulik-Erdey" (Hungary). Studies of samples in the IR region of the spectrum were carried out on the Nicoletti S10 spectrometer, SPECORD-80, and the spectra of reaction solutions in UV were carried out on the Evolution 60S (USA). The Mossbauer spectra were obtained using a spectrometer operating in the constant acceleration mode. 57Co in a Sg matrix with an activity of 50 mCi was used as a resonant source of gamma quanta. The computer processing of the spectra was performed using the “Univvem-2" program. X-ray fluorescence analysis was performed on the "Innov XSystems" spectrometer. The images from the SEM were obtained using a Sigma VP scanning microscope (Germany, Carl Zeiss). The elemental composition of micro inclusions or microparticles (EDS or EDX spectra) was determined using an energy-dispersive spectrometer detector.

Thus, the research methods were determined based on the provision of the required level of experience and processing of the obtained results.

The third chapter presents the results of the development of functional materials based on inorganic material, the main component of which is represented by iron, aluminum and titanium oxides, for the process of purification of primary raw materials from impurities of inorganic sulfur compounds.

Based on the literary analysis of the composition and features of the functional materials of this process, a hypothesis has been put forward about the possibility of obtaining CM with the required qualities using non-standard raw materials - iron-containing sludge.

The reliability of the hypothesis put forward was verified using two types of iron-containing waste as an object of research: a factory sample of RS formed during the processing of bauxite, and a sample obtained in laboratory conditions during the processing of sulfide ore (SS).

The macro component composition of RS is presented (mass. %): Fe_2O_3–45,8; Al_2O_3–24,6; TiO_2–4,8; Na_2O and K_2O–3,1; SiO_2–5,8, PPP-16.6. The dispersion of raw materials is 0.2~3 microns. The composition of the SS is as follows: Fe_2O_3 – 66,2; Fe $((Fe_{1.616}Ti_{0.354}Al_{0.03})\ O_4)$– 14,3; $PbSO_4$ – 8,5; SiO_2 – 11 wt.%.

Studies of the composition and behavior of sludge samples during heating have shown the possibility of their use as raw materials for the creation of KM.

Initially, the task was to obtain CM with the required texture and mechanical properties. The regulation of structural and mechanical characteristics was carried out by introducing various types of binders (synthetic and montmorillonite), varying the ratio of sludge to binder, modes and temperature of heat treatment. CM granules with the necessary structural and mechanical properties were obtained by mechanical mixing when using montmorillonite as a plasticizing component of the charge. To increase the strength characteristics, the granules were subjected to heat treatment in slow heating mode with exposure at a final temperature (600^0C) for four hours [1, 33,40, 45]. The high dispersibility between sludge particles and the unique structure of montmorillonite, which acts as a barrier for volatile products (for example, water vapor), determined the advantages of its use and allowed to obtain granules of various sizes (rings, tubes, cylinders, block structures).

Thus, the use of montmorillonite made it possible to increase the operational and strength characteristics of the granules (almost three times) and their thermal stability. The CM had a multi-dispersed texture with sufficient mechanical strength.

To study the functional properties, a sample with characteristics (total pore volume-0,40±0.01 cm^3/g, mechanical strength~23±1MPa, Ssp-79±0,1 m^2/g, density 1,1±0,02g/cm^3) comparable to an industrial (aluminium oxide) catalyst of the Klaus process [41,45] was used.

The results of the study of the sample activity in the Claus process in the temperature range 220-300^0C, the volumetric velocity (W) 500-2000ч$^{-1}$, the ratio of the initial reagents N ((H_2S+COS)/SO_2) = 1,7-3,5, showed that the optimal condition for the process is T= 250±15^0 C, W=500-1000h^{-1}, N=2 ± 0,1 (fig.1,2).

The activity was estimated by the yield of elemental sulfur and at T= 250^0C and W=500 h^{-1} is 96,8 vol.%

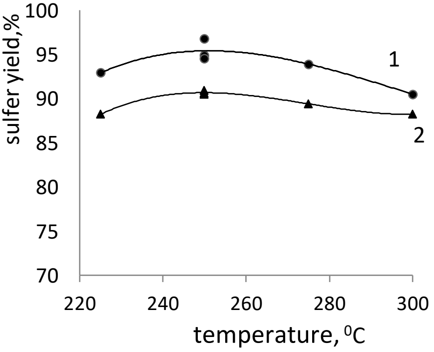

Fig. 1. Dependence of sulfur yield on temperature at volumetric velocity: 1- 500; 2-1000 h^{-1} (N=2; C_{H2S}=13,16± 0,64vol.%).

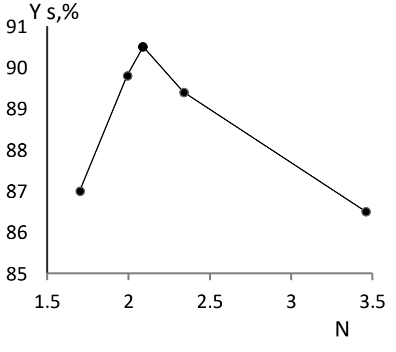

Fig. 2. Dependence of sulfur yield on the N ratio at T=250^0C, W=1000h^{-1}.

Based on the literature data, the inclusion of some transition metals (Cu, Cr, Ni, Co) and an additional amount of $Al(OH)_3$ in the composition of CM on the basis of Red Sludge, which usually increases the yield of sulfur, increases the composition of the components and the concentrations of the added metals changes did not significantly affect the yield of sulfur [30]. This determines the advantage of the developed CM, since it eliminates harmful emissions into the atmosphere.

Experimental verification of additive catalytic properties confirmed that the catalytic role is mainly performed by components of Red Sludge. The formation of defects in the crystal lattice of hematite, consisting of the formation of iron (II, III) oxide during the reduction treatment of the sample, led to an increase in the degree of sulfur extraction by 3 ± 1vol.%.

The quantitative composition of the macro component segment of the factory sample of sludge, as is known, can fluctuate, and foreign impurities can also get into the process of its formation. Thus, it has been experimentally established that fluctuations in the quantitative content of macrocomponents (aluminium, iron and titanium oxides) in sludge samples taken in different years, as well as the presence (according to XRD results) of extraneous phases ($Al(OH,F)_3$) practically do not affect the conversion rates of CM [45, 42].

The effect of the genesis of the cuttings on the properties of CM was studied using the SS. On this sample conversion to sulfur was 91,3 vol.% (at $T=250^0C$, $W=1000\ h^{-1}$), on the same sample reduced in a hydrogen flow – 96,0 vol. % The comparability of the properties of slurries of various genesis is of great practical importance since it creates prerequisites for the use of materials with a similar composition and physico-chemical properties as raw materials.

The study of the effect of artificial hydrothermal aging ($T=810^0C$; $C_{SO2}=24\pm1$ vol.%; $C_{H2O}=24{,}5\pm1$,vol.% in nitrogen flow; the rest is air; $\tau=5h.$) on the structure of the samples showed that these changes are not more than those in industrial CM.

The study of the dynamics of long-term activity at constant indicators ($T=250^0C$, $W=1000s^{-1}$) showed its persistence for more than 400 hours (with a spread of data of $92{,}42\pm2{,}46$ vol.%, the average indicator of sulfur removal is 95,06 v.%).

To clarify the causes of prolonged activity, solid-phase transformations in samples during catalysis were studied [44].

The interpretation of the XRD results of the sample for the main components before and after the Claus conversion is summarized in Table 1.

Table 1

Interpretation of XRD spectra for the main components of CM [44]

File number	Chemical formula	Connection name
before the process		
96-900-9783	$Fe_{12.00}\,O_{18.00}$	hematite
96-901-2276	$Al_{4.00}O_{8.00}$	boehmite
96-900-8217	$Ti_{4.00}\,O_{8.00}$	anatase
96-900-2780	$Al_{4.00}Si_{8.00}O_{24}$	montmorillonite
96-900-5563	$Al_{14.00}Fe_{5.20}\,Ti0$	ferrogombehmite 2N2S
96-900-8136	$Al_{4.00}O_{12.00}H_{12.00}$	bayerite
after the process		
00-024-0072	Fe_2O_3	iron oxide
96-901-2252	$Al_{4.00}O_{8.00}$	boehmite
96-720-6076	$Ti_{4.00}O_{8.00}$	anatase
96-900-9371	$Fe_{4.00}S_{4.00}O_{20.0}$	somolnokit
96-901-2334	$S_{72.00}$	sulfur
96-200-2080	$S_{32.00}$	γ- sulfer
96-901-0916	$Fe_{6.00}Ti_{6.00}O_{18.00}$	ilmenite

As can be seen from the data in the table, it is characterized by iron sulfates after sample catalysis, and the presence of free sulfur presumably condensed on the internal (channel) surface of the sample when the process was stopped. According to the EDS spectra, the amount of sulfur element on the sample surface (1,6 wt.%) did not exceed those in industrial [45]. The SS sample after the process also indicated the presence of sulfite-sulfate iron compounds.

The results of the derivatography and İR confirmed the results of the X-ray phase analysis and provided valuable additions to the conducted research methods [44].

Thus, it has been reliably proven that phase transformations occur in the sample with the formation of sulfur-containing iron compounds, while aluminium and titanium compounds remain unchanged, which ensures high activity of the samples during the catalysis process. Consequently, iron oxides perform a "protective function", the long-term preservation of which is ensured by a balance between the formation of sulfite-sulfate compounds and their reduction with hydrogen sulfide to form elemental sulfur and water [45]. This circumstance allows us to recommend them for use as a pre-contact.

It is known that an important property of functional materials is their versatility, i.e. they can have several applications.

The analysis of scientific literature showed that the adsorption method is used for the purification of primary raw materials when H_2S and SO_2 (200 to 500 ppm) are in low density. When H_2S is removed by combustion, gas purification is reduced to SO_2 purification [34,36,38].

Determination of the adsorption capacity by SO_2 of the proposed sample, as well as its modified (Cu, Cr, dolomite, P_2O_5) forms, depending on the component composition, calcination temperature and H_2 treatment (at 500^0C, 5h.) showed that CM with P_2O_5 has the highest adsorption capacity (0.23 ± 0.003 mmol/g). The adsorption capacity of SO_2 and H_2S of CM proposed for Klaus conversion was 0,214 and 0,47 mmol/g, respectively. Here, the developed systems act as a chemisorbent. The mathematical processing of data on the identification of the "conversion to sulfur - adsorption capacity by SO_2" relationship showed a moderate correlation ($r=+0,6$).

Thus, sludge-based CM are effective functional materials that are used both as catalysts and adsorbents [42, 46, 47, 50-52].

To identify the strength of the connection between acid-base and functional properties, the nature of active centres on the surface of the CM was studied.

A comparative study of the active centres on the surface of the samples showed that the RS-based sample is characterized by electron-acceptor centres of moderate strength (271^0C) and strong (437^0C) centres that distinguish it from others, as well as the presence of strong main centres (only at 480^0C), which creates an optimal combination of acid-base properties for the manifestation of the greatest activity in the Klaus process.

Strong basic centers with clear peaks at 360°C and 440°C with desorption energy of 43,84 µVs/mg on the surface of CM with P_2O_5, absent in other samples, and acid centers are present which are not seen as distinct peaks, so that which creates an optimal combination of acid-base properties for the manifestation of the highest adsorption capacity for SO_2.

Based on the calculated values of the concentration of active centers per surface unit, their correlation relationship with the degree of conversion of sulfur dioxide to Klaus conversion was determined (Table 2).

Table 2

Determination of the quantitative relationship between the nature of the centers on the surface of the samples and the activity

Sludge type and modifier in the example	Character of the centers	Density of centers, mmol/g	Correlation with SO_2 conversion
RS RS withP_2O_5 SS	electron-akseptor	0,088 1,3505 0,842	1
RS RS with P_2O_5 SS	protonodonor	0,094 0,65 1,547	0,769
RS RS with P_2O_5 SS SS (reduced)	alkali	0,119 0,0371 0,6485 1,544	0,91

Analysis of the data in the table 2 shows that high activity is most provided by the presence of electron acceptor centers on the surface (r=+1) and slightly less by basic centers (r=+0,91).

Manifestation of the highest basicity by the CM sample with SS after the reduction treatment indicates the formation of oxygen vacancies in the crystal lattice of hematite, increasing the conversion to sulfur.

Thus, the composition and basic techniques for obtaining functional materials based on man-made raw materials have been developed, the main component of which is represented by Al, Fe and Ti oxides for the process of purification of gas raw materials from sulfur compounds. Techniques have been established to adjust the functional characteristics depending on the application.

The fourth chapter presents the results of developments on the production of zeolite-based CM with functional properties in the process of synthesis gas production by carbon dioxide conversion of methane (CCM).

The criterion for selecting zeolites as a matrix for CM synthesis was their composition and unique structure, which allows increasing dispersibility by isolating metal particles or the possibility of reducing the degree of their aggregation. [6].

The initial task was to investigate the influence of the zeolite structure on the characteristics of the obtained systems and to determine the quantitative correlations.

It is known that nickel is a generally recognized active component of this process, both in terms of cost and performance. In this regard, the functional properties of nickel zeolite-containing materials (NiZCM) were initially obtained and studied.

To study the effect of the matrix type on the functional properties of synthesized NiZCM using granular zeolites of industrial production of various structural types: NaX, CaX, CaA, NaY.

The activities of the samples are in the temperature range of 500-800°C when the volume ratio of the components included in the reaction is CH_4/CO_2=1:1, p=1atm., W=500h^{-1}, in the hydrogen flow (45 ml/min) with a loading of 7 cm^3 into the reactor (5 hours) studied after activation at 400^0C.

NiZCMs were obtained by impregnating zeolites with nickel nitrate with the calculation of obtaining 10 wt.% (in terms of oxide).

Studies of the activity of NaX, CaX, NaY zeolites without an active component under the above conditions showed their inability to catalyze the reaction of the interaction of the initial gas components, while partial methane conversion of 11,46 ± 0,74 vol was observed on CaA zeolite in the temperature range of $600-800^0$C. %, CO_2 – 10,53 ± 2,06 vol.%, the yield of H_2 and CO each separately was 5,5 ± 0,7 vol.%. This is explained by the relatively low SiO_2/Al_2O_3 ratio in the CaA zeolite, which probably ensures the activation of the reacting molecules due to the relatively greater adsorption of one of the components.

On nickel-containing CMs' based on NaY, NaX, CaX, complete conversion of methane was observed at T=800^0C, while on CMs' based on CaA at 750^0C. Statistical processing of the results on the study of the influence of the structure of zeolites on activity is presented in Table 5.

Table 3

Influence of the structure of synthetic industrial zeolites on the activity of nickel CMs in the CCM

Nickel based KM	SiO_2/Al_2O_3 ratio	X_{CH4}, (vol.%) at 700^0C	$T_{80\%}$ CH_4.^{0}C	H_2 yield (vol.%) at 700^0C.	Residual amount of CO_2 at 7000C, vol.%
CaA	1,9	93	590	49,9	4,4
CaX	2,9	95,6	605	46,3	6,2
NaY	5,6	96,4	615	41,4	8,7
NaX	2,75	95,6	622	45,0	7,8
Correlation		0,765	0,52	-0,92	0,815

An analysis of the data in the table shows that with an increase in the SiO_2/Al_2O_3 ratio, the methane conversion increases from 93 to 96,4%, and the highest H_2 yield is observed on the CaA-based CM, which has the smallest diameter of the inlet windows. It is noteworthy that calcium ion zeolites have a lower $T_{80\%}$ than sodium zeolites. This is explained by the greater adsorption of CO_2 on the surface of CaA, leading to a partial conversion of methane.

The quantitative correlation between X_{CH4} and the type of zeolite structure is above average and is 0,765, and the relationship with the residual amount of CO_2 is 0,815.

The results of quantitative correlation between acid-base surface properties and structure of NiZCM zeolites are summarized in Table 4 [7,9, 14,15].

An analysis of the data in the table shows that in zeolites of various types, with an increase in the ratio of silicon and aluminum oxides, the concentration of acidic and basic centers decreases, and the zeolite with small entrance windows has the highest concentration. The high degree of correlation indicates that the acid-base properties of the surface are determined by the structure of the zeolite.

Table 4

Correlation between the concentration of active sites (a, mmol/g) and the structure of zeolites

The nature of the sites	NiZCM based	a, mmol/g	Correlation
electron-acseptor acidic	NaX	0,370	-0,999
	CaX	0,123	
	CaA	1,539	
proton-donor acidic	NaX	0,734	-0,974
	CaX	0,098	
	CaA	1,859	
basic	NaX	0,207	-0,999
	CaX	0,041	
	CaA	1,370	

It is of interest to determine the quantitative relationship between the nature of the surface and activity in the MCC process.

The determination of such a bond is quite appropriate, since the determination of the concentration of active centers was carried out using molecular probes, which behave in relation to the surface of the CM in the same way as the reacting molecules.

The calculated values of the quantitative relationship between the acid-base properties of the surface and the main indicators of activity are given in Table. 5.

Table. 5

Correlation values between the nature of the centers and the activity indices of NiZCMs based on synthetic zeolites

The nature of the centers	Correlation			
	yield of H_2	S_{H2}	$T_{80\%\ CH4}$	The residual amount of CO_2
electron-acseptor	0,91	0,935	-0,75	-0,79
proton-donor	0,81	0,85	-0,60	-0,65
basic	0,93	0,95	-0,78	-0,82

An analysis of the data in the table shows that the highest correlation is observed with the selectivity of hydrogen formation (S_{H2}), and with $T_{80\%}$ the relationship is above average and negative, which indicates that with an increase in the concentration of centers, the activity increases, since $T_{80\%}$ decreases.

The greatest relationship between activity indicators is observed with the concentration of the main centers.

The binding strength of the main centers with the residual amount of CO_2 is higher than with the conversion of methane, and is also negative, that is, with an increase in the number of centers, the amount of unreacted CO_2 decreases, which indicates an increase in the activity of CM.

Thus, the highest correlation of activity is observed with the basic and electron-acseptor acid sites of the surface.

The influence of the structural type of zeolite resistant to high temperatures on the activity is shown in Figure 3.

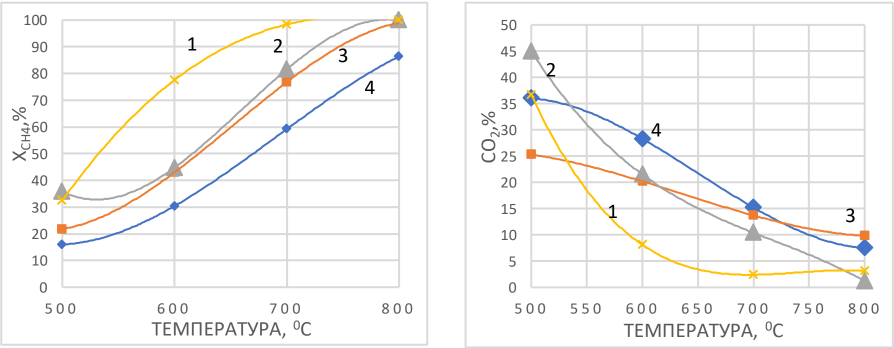

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Fig.3. Comparative temperature dependences of the degree of methane conversion (X_{CH4}, %) (a) and the residual content of CO_2 (%) (b) on

NiZCM samples based on: 1-HZSM-5, 2-natural mordenite, 3-analcime, 4- mordenite type.

Comparative testing of CM activities showed that samples based on HZSM and natural mordenite have the highest activity[12,13,53].

At 700^{0}C, CH_4 on CM based on HZSM reached 98,4%, and on natural mordenite 81,6%.The residual amount of CO_2 on CM samples based on HZSM and natural mordenite at 800°C was 3,1 and 1,2%, respectively. This is due to the presence in natural mordenite of associated minerals containing oxides of alkaline earth metals (calcium or magnesium), which promote CO_2 adsorption and accelerate the MCC process.

Further, the influence of the nature and concentration of alkaline cations in the mother liquor during the synthesis of zeolite of the chabazite type on the activity of NiZCM was investigated [18].

Figure 4 shows the results of a study of the activity of samples depending on the nature of the zeolite cation.

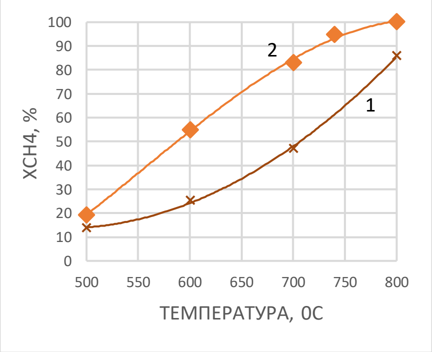

Fig. 4. Temperature dependences of methane conversion on the nature of the zeolite cation: 1 – K^+; 2 – Na^+ on NiZCM.

Comparison of the dependence curves in Fig. 4 shows that the nature of the zeolite cation has a significant effect on activity: complete conversion is observed on the sodium form of the support, while on the potassium form the maximum conversion is 85,8 vol.%.

This circumstance correlates with the relative value of the oxygen-catalyst bond energy, experimentally determined by the TPHR (thermoprogrammed hydrogen reduction) method, according to which the recovery rate of the sodium form of the sample is higher (T_b-375^{0}C) than the potassium form (T_b -395^{0}C).

The study of the effect of the amount of sodium ions (N_{Na+}) (0,9-2,1×10^{22}) in the mother liquor during the synthesis of zeolite on the conversion of CH_4 shows (see Table 6) high activity of samples ($T_{100\%}$ =800^{0}C) with N_{Na+} = 0,9 × 10^{22} and 1,2×10^{22}, whereas on a sample with a maximum amount of Na^+, complete conversion in the studied temperature range is not achieved, which is probably due to the interaction of excess alkaline ions with CO_2 to form stable low-activity surface carbonates.

It was found that there is a correlation between Na^+ and $T_{80\%}$ above the average value of r=+0,689.

In the table 6 Data on the amount of deposited carbon on the surface of the samples are also provided.

Table 6

Activity indicators and the amount of carbon deposited on the surface, depend on the amount of sodium ions (Na^+)

Index	Na^+ ion concentration (×10^{22})		
	0,9	1,2	2,1
Max. X_{CH4}, (%)	100	100	86,8
X_{CH4}, at 700^{0}C, %	79,2	83	71,8
Residual CO_2 content at 800^{0}C, %	14,6	7,7	8,9
S_{CO}, at a temperature of 800^{0}C, %	45,43	45,17	42,48
Coke, q/q cat	0,058	0,009	0,011

An analysis of the data in the table shows that the largest amount of coke is formed at the lowest C_{Na+}, which is probably explained by the relatively high rate of coke formation compared to the rate of its gasification with CO_2.

This assumption is confirmed by the highest residual CO_2 content in the reaction products of this sample.

A slightly larger amount of formed coke on the surface of the sample with the maximum amount of sodium, compared with the sample with N_{Na+}=1,2×10^{22}, indicates the existence of an efficiency limit for the included alkali metals, the effect of which is to increase the effective concentration of the oxidizer on the active surface and accelerate the carbon gasification reaction [54].

It was found that there is a strong correlation between the amount of deposited coke and the concentration of strong acid centres (r=+0,999), whereas with weak and moderate acid centres it is less than the average (-0,468)

After determining the dependence of functional properties on the structure and composition of the matrix, the cationic composition of the mother liquor in the synthesis of zeolites, and the influence of the nature of the introduced d-metals is of interest.

To do this, based on clinoptilolite (from the domestic Ai-Dag deposit), CM samples were prepared by the impregnation method, including Ni, Co, Fe, and Cr- and Mo for comparative analysis [6,8].

Testing of the activity of samples with Cr or Mo showed, as expected, that they do not catalyze the process of processing CH_4 into synthesis gas.

The activity of Fe-containing CM was low (even at T=800^{0}C, X_{CH4}=24v.%) and quickly deactivated. The results of testing nickel, cobalt-containing CM are shown in Fig.5.

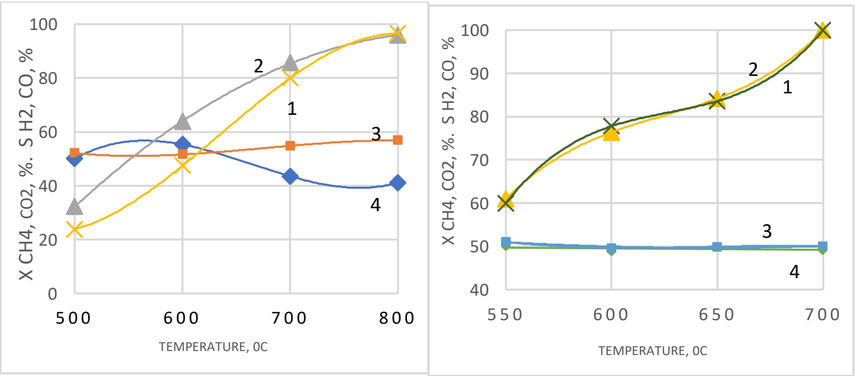

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Fig. 5. Dependence of the conversion ($X_{CH4, CO2}$, %) of CH_4 (1) and CO_2 (2) and the selectivity of formation ($S_{H2, CO}$, %) of CO (3) and H_2 (4) on temperature at CH_4/CO_2 = 1 on CM samples containing : a-Co, b-Ni.

Analysis of the dependences obtained shows Fiq.5 that the highest activity and selectivity is observed on a nickel sample.

The temperature for achieving full conversion on this sample is 700^0C, while on the Co sample at 800^0C the maximum conversion of methane is 96,48 vol.%.

A comparative analysis of the activity of NiZCM based on natural clinoptilolite and mordenite showed that $T_{80\%}$ in the first case is 615^0C, in the second - 695^0C [53]. This indicator is in accordance with the proportion of free volume in dehydrated zeolites, which in the first case is 0,34, and in the second 0,28

In addition, it is known that in clinoptilolite, Na^+ and K^+ ions are predominantly located near the entrance windows, while in mordenite, Na^+ and larger ions are Ca^{2+}, which can make the mordenite 8-membered channels completely inaccessible to reacting molecules.

Thus, the role of the structure of natural zeolites in the manifestation of activity is clearly shown.

The question of the influence of the nature of active centres on the CM surface on the activation of methane to produce synthesis gas is still controversial.

A comparative study of the acidic properties of the surface of the samples showed that the surface of the nickel-containing sample is characterized by weak electron-withdrawing centers (at 220^0C with a concentration of 0,431 mmol/g) capable of ionizing the molecule with a force of 9,69 ± 0,01 eV and the absence of strong centers, while there are also strong centers on inactive Cr and Mo-containing samples.

Comparative evaluation of acid centers of another type showed that on the surface of active CM's, there are moderately strong proton-donor centers with an ionizing capacity of 10,59 ± 0,01 eV, and the particle interacting with these centers on a nickel sample was desorbed at temperatures of 340 and 420^0C, on cobalt, it is slightly higher - 360 and 480^0C, and on inactive samples, acid centers of medium strength were absent.

A comparative evaluation of the main centers on the surface of the samples showed that on a nickel sample the number of main centers capable of ionizing a particle with a dissociation constant of 9,89±0,01 is the smallest, and there are weak basic centers on the surface from which the adsorbed particles are desorbed at 220^{0}C, while these centers are absent on other CM samples.

Thus, the nickel sample, which exhibits the highest activity and selectivity in the process of processing bio- and natural gas into synthesis gas, is characterized by the presence of weak electron-withdrawing centers with an ionizing power of 9,69±0,01 eV, moderately strong acidic (proton-donor) centers with ionizing power of 10,59±0,01 eV, and weak basic centers capable of ionizing a particle with a dissociation constant of 9,89 ± 0,01, which distinguish it from other samples [15, 56].

Thus, it has been experimentally established that the structure and optimal combination of acid-base properties of the NiCM surface based on natural clinoptilolite ensures its high activity.

With the participation of nickel CM based on natural clinoptilolite (NiPCM), the optimal mode of the process was determined, for which the effect on the activity of the main indicators was studied: the volume velocity of the gas mixture and the volume ratio of the reacting components (Fig.6 and 7) [16].

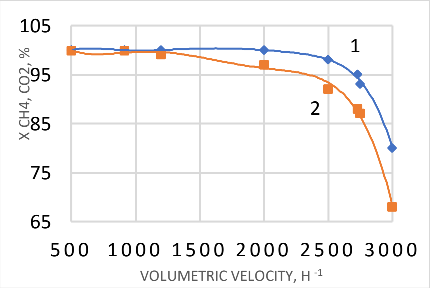


Fig.6. Dependence of the degree of conversion ($X_{CH4,\ CO2}$, %) of CH_4 (1) and CO_2 (2) on the volumetric velocity of the gas mixture on NiPCM (T=700^{0}C, CH_4/CO_2= 1).

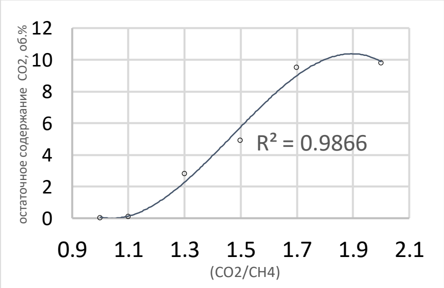


Fig.7. Residual content of CO_2 (%) in the reaction products depending on the ratio of CO_2/CH_4 on NiPCM (T=700^{0}C; W=500h^{-1}).

The analysis of the regularities obtained shows that the optimal condition for the process is the ratio $CO_2/CH_4=1-1,1$ and $W=500-1200\ h^{-1}$, taking into account the complete conversion of the initial products.

It is important to determine the optimal nickel concentration and the method of obtaining NiCM.

The results of studying the effect of nickel concentration (from 0,5-15 wt.%) on the activity showed that the concentration within about 5 wt.% can be considered optimal, since with such a minimum content a high conversion of CH_4 and CO_2 is achieved, which is probably due to with a high nickel content.

It should be noted that the concentration of nickel in traditional industrial catalysts can reach 20-40 wt.%. The reduction in the cost of the active component in our case, apparently, is achieved by using a zeolite, which can provide a high dispersion of nickel due to pores of a molecular size.

It has been experimentally established that the activity remains at the same level regardless of the method of introducing the active component into the carrier (template, exchange, mechanical mixing, hydrothermal reduction).

To optimize the chemical composition and properties of CM, it is necessary to study the relationship between the acidity of the carrier and the functional properties.

For this, samples were prepared containing a carrier activated with hydrochloric acid at various concentrations [11,17].

The results of studying changes in the porous structure of the carrier during acid activation, as well as the effect on the properties of NiCM based on them, are shown in Table 7. The acidic properties of the surface of the samples were studied by the thermo-programmed ammonia desorption method.

Table 7

Influence of the concentration of an activating acid on the physicochemical properties of the support and the properties of nickel systems based on them

№	Acid concentration,	Mole ratio SiO_2/Al_2O_3	The value of the	Maximum volume of	NiPCM properties

	n		limiting adsorption of water, mmol/g	sorption space, cm^3 /g	$T_{80\%}$, ^{0}C	X_{CH4}, (%) at 700^{0}C	∑K NH_3, mmol/g
1	-	8,6	6,81	0,124	610	100	0.08
2	0,5	10,1	6,65	0,121	680	84	-
3	1	10,4	8,61	0,153	665	93	0.34
4	2	11,7	8,90	0,161	540	100	0.12
5	10	42,3	7,15	0,125	650	99	0.10

Analysis of the data in the table shows that among the acid-activated samples, the highest conversion is observed on No. 4, which correlates with the largest volume of the sorption space.

Acid activation had a certain effect on the activity and contributed to a change in the selectivity for hydrogen ($H_2/CO \approx 2,2$), while for No. 1 $H_2/CO=1$.

Compared to sample No. 4, the decrease in the volume of the sorption space and the total concentration of acid sites in sample No. 5 is due to the partial destruction of the zeolite crystal lattice due to a significant decrease in aluminum oxide, which is confirmed by an increase in the SiO_2/Al_2O_3 molar ratio.

The correlation coefficient between the degree of methane conversion at 700^{0}C and the total acidity of the surface is K = -0,96, moderate (K = 0,50) with the volume of the sorption space, and barely reaches the average value (K = 0,47) with the molar ratio SiO_2 / Al_2O_3.

These samples were studied by the THR method and it was found that the NiCM sample (No. 1) is characterized by a low temperature of the beginning of reduction (T_b = 247^{0}C) and maxima in the spectra at relatively low temperatures (485 and 513^{0}C), while the spectra of the remaining samples are shifted to the high temperature region .

The low T_b of reduction and the largest area under the spectra of THR of sample No. 1 indicate the occurrence of the reduction reaction on the centers of metallic nickel, the sizes of which are in the range of 1-5 nm.

One of the important characteristics of the catalysts used is their resistance to carbon deposition.

One of the important characteristics of the catalysts used is their resistance to carbon deposition. An analysis of the literature data shows that not all types of carbon deposits lead to decontamination. On the surface of catalytic systems in a real process, atomic, amorphous and graphitized coke can form, the latter of which is the most dangerous. The type and structure of the coke formed on the surface of the catalytic systems during the process was characterized by its reactivity.

The studies were carried out by the method of thermoprogrammed oxygen oxidation and derivatography. It has been established that the number of carbonaceous formations on the surface of a unit mass of CM based on clinoptilolite for an hour on a sample with a carrier without acid activation is 0,0066 g/g CM, with activation – 0,008 g/g CM. The maximum temperature required for burning out the precipitated coke for the first sample is up to 700°C, for the second - more than 760°C, for mordenite - 830°C. Consequently, the strength of the carbon-catalyst surface bond is the lowest in the sample with a non-activated support. This indicates the amorphous nature of the deposits.

The effectiveness of the use of NiPCM has been experimentally confirmed by comparing its activity under identical conditions with the activity of an industrial catalyst of the GIAP-16 brand.

The advantage of the proposed KUM is that it contains less active component (5-8,6% by weight) and does not require additional modification by basic oxides such as CaO, etc.. The availability of zeolite-rich rock at a low price will expand the range of competitive materials, reduce their material and energy consumption, improve operational properties, and reduce the cost of the process.

Thus, the basic techniques for obtaining functional materials based on zeolites have been developed, and the influence of the composition, structure of the matrix, conditions for the synthesis of the zeolite matrix and the most active component to obtain the required functional properties have been studied.

In this work, Co-Mn-O systems with functional properties in the deep oxidation reaction of methane have been synthesized and characterized [22,25]. This reaction is the main approach to solving the problem of self-sufficiency of heat in the process of conducting the MCC.

It is synthesized in the system by heat treatment of co-precipitation products from nitrates of β-$Co(OH)_2$ hydroxides and α-$Mn(OH)_2$..

It has been established that the ratios of the resulting compounds (spinels) and, consequently, the degree of tetragonality (c/a) change depending on the synthesis parameters:

–at a Co/Mn ratio of 2:1–1,5:1, Mn-Co spinels with cubic or slightly tetragonal distortion (c/a=1,01–1,05) crystal structures are formed; tetragonal spinels (c/a=1,14–1,15) are formed at a Co/Mn ratio of 1:2–1:1,5;

–during heat treatment at low temperatures (300–500^{0}C), the formation of the $CoMnO_3$ phase with the ilmenite structure in addition to spinel is shown.

The synthesized samples were studied in the process of deep oxidation of methane and information about the samples showing the greatest activity is presented in Table 8.

Table 8

Influence of the ratio Co/Mn and the heat treatment regime on the phase composition of some samples [25]

№	Co/Mn Ratio	T, ^{0}C Time, (c)	Phase composition	Phase designation	Spinel kristal şəbəkəsinin parametrləri, nm		
					a	c	c/a
1	2: 1	500 (2)	$(Co,Mn)(Mn,Co)_2O_4$* $CoMnO_3$	T_2 + $CoMnO_3$	0.7981	0.8101	1.015
2	1: 2	400 (4)	$(Co, Mn) Mn_2O_4$ $CoMnO_3$	T_1 + $CoMnO_3$	0.8089	0.9302	1.15
3	1: 2	600 (4)	$(Co, Mn) Mn_2O_4$	$T_1 + T_2$	0.8092	0.9265	1.145
			$(Co, Mn) (Mn,Co)_2O_4$		0.8191	0.8600	1.05

(*the predominant phase is indicated in the first place)

From the data in the table, it can be seen that the phases based on Co_3O_4 (or phases enriched with $MnCo_2O_4$ and Co_3O_4) are characterized by a cubic (K) or tetragonal phase (T_2) with a low degree of tetragonality with /a = 1.015 (No.1). Mn3O4-based phases (or phases enriched in $CoMn_2O_4$ and Mn_3O_4) are characterized by a tetragonal structure (T_1) with ratios c/a =1.14-1.15 (No. 2).

In Nos.1, 2, in addition to spinel, the presence of a second phase, $CoMnO_3$, with a hexagonal structure of the ilmenite type is fixed. Obviously, some of the Mn^{2+} ions in these samples are oxidized to Mn^{4+}, which leads to the precipitation of the $CoMnO_3$ phase.

The results of testing the samples shown in Table 8 during the deep conversion of methane are shown in Fig.8.

As can be seen from Fig.8, sample No.1, which differs from No. 2 in the degree of tetragonality of the crystal structure, shows great activity. So, at No. 1, complete conversion of methane is ensured at $T=500^0C$, which is 110^0C lower than at No. 6

Thus, the Co_3O_4–$MnCo_2O_4$ system (T_2 phase) has a higher activity. Comparison of activities Nos. 1, 6 and 7 shows a positive contribution of $CoMnO_3$.Thus, No. 3, which is characterized by the absence of this phase, exhibits less activity.

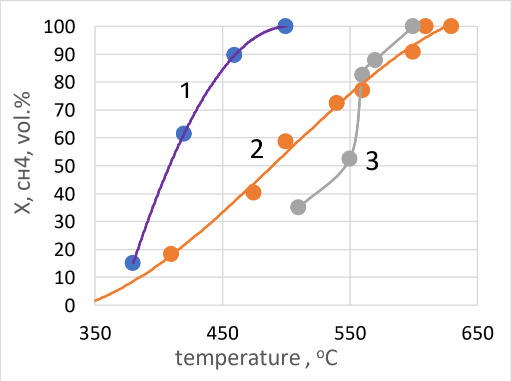


Fig.8. Dependence of methane conversion on temperature on Co-Mn-O samples consisting of phases based on: 1 – Co_3O_4 (T_2+$CoMnO_3$); 2 - Mn_3O_4 (T_1+$CoMnO_3$); 3 – both phases (T_1+T_2). (C_{CH4}=1,6 об.% W=9000s^{-1}).

The high activity of the synthesized spinels is explained by the ease of structure rearrangement, the presence of defects in it, and a special mechanism of electron exchange - "jumping" of electrons between neighboring ions.

The composition and mode of obtaining systems based on hundreds of spinels with functional properties have been developed, and the influence of the crystal lattice structure has been shown. The synthesized spinels are much cheaper than catalysts with noble metals and are more thermally stable

The fifth chapter is devoted to the results of research on the synthesis of nanoxides based on transition metals (Fe, Co, Mn, Cu, etc.), their characteristics and functional properties in the CO oxidation reaction.

Hypothesis: it is possible to create more advanced catalysts by selecting fundamentally new compositions based on iron, cobalt, manganese oxides due to the significant mobility of oxygen ions, as well as by obtaining nanosized compositions due to the structural sensitivity of the CO oxidation reaction.

An analysis of the scientific literature shows that this reaction is a donor reaction; therefore, it is best catalyzed by reverse spinels, in which Fe^{3+} ions located in octahedral positions chemisorb carbon monoxide.

Publications report that the formation of substitutional solid solutions makes it possible to achieve an increase in catalytic activity and, at the same time, thermal stability under reaction conditions. Solid solutions of cobalt and manganese ferrospinels can be attractive for CO steam reforming, which is associated with the electronic structure determined by the tendency of Co^{II}, Mn^{II}, and Fe^{III} ions to occupy certain positions in the spinel structure.

Thus, Co^{II} ions with the $3d^7$ electron shell prefer an octahedral environment of oxygen, which leads to the formation of an inverted structure in $CoFe_2O_4$. Mn^{II} and Fe^{III} ions with a spherically symmetric $3d^5$ shell do not show a certain tendency to tetra- and octahedral coordination, but can be controlled by changing the chemical composition and heat treatment regimes.

For the process of steam conversion of CO, which makes it possible to obtain an additional amount of hydrogen, a ferrospinel of the composition $Mn_{0.5}Co_{0.5}Fe_2O_4$ was synthesized and studied [23, 26].

The spinel precursor was obtained by coprecipitation of α-

$Mn(OH)_2$, α-FeOOH, and β-$Co(OH)_2$ hydroxides from a mixture of nitrates with a NaOH solution at pH=10 (using a reflux condenser) for 4 h. The precipitate was filtered off, washed to the absence of NO_3- ions, and after drying, it was calcined at T=700^{0}C (4 h.).

The synthesized sample was characterized by XRD, derivatographic analysis, MS, SEM and EDS spectra were obtained.

Identification of X-ray reflections showed the presence of spinels: $CoFe_2O_4$ (PDF 01-079-1744) (2Θ = 35.30^0; 56.89^0; 62.47^0); $Mn_{0.98}Fe_{2.02}O_4$ (PDF 01-078-6782) (2Θ = 35.76^0; 62.96^0; 57.65^0); $CoFe_{0.8}Mn_{1.2}O_4$ (PDF 00-055-0682) (2Θ = 35.48^0; 30.12^0; 62.57^0) and Hematite (PDF 01-071-5088) (2Θ = 33.19^0; 35.70^0; 54.10^0). Estimation of particle sizes by half-width of diffraction maxima belonging to each of the phases at 2Θ equal to 33.190; 35.30; 62.960; 35.480 gives values L = 94; 80; 78; 76 nm, respectively[26]. Derivatographic studies showed no significant changes in the interval T= 20-10000C.

In order to quantify the phases and investigate the fine structure of the sample, Mössbauer spectra were taken (Fig.9) and their parameters were calculated [26].

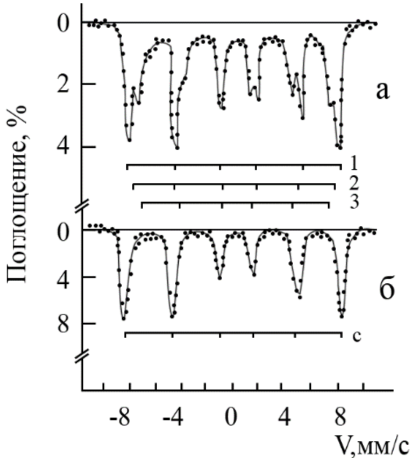


Fig.9. Mössbauer spectra of the sample taken at: a - room temperature; b - liquid nitrogen temperature. (1-hematite; 2-spinel: B-sublattice; 3-spinel: A-sublattice; c- the total of all the components) [26].

The data obtained showed that 33% of Fe^{III} goes to the formation of the α-Fe_2O_3 phase, and 67% - to spinel.

With equal probabilities of the Mössbauer effect on the Fe^{57} nuclei for different crystal chemical positions, the Fe^{III} ions in the spinel are distributed as follows: 45% in A and 55% in B sublattices. On the diffraction pattern of the studied sample, the interplanar distances related to the hematite phase correspond to those of pure α-Fe_2O_3.

Therefore, the cationic distribution in the resulting spinel can be expressed as: $M_{0.40}Fe^{III}_{0.60}[M_{0.60}Fe^{III}_{0.74}]O_{4-\delta}$, where M is Co and Mn.

It can be seen from the formula that the spinel obtained under these conditions is characterized by a mixed structure with an inversion parameter (a parameter that determines the proportion of Fe^{III} ions in A-positions) equal to 0.60. Spinel electroneutrality can be maintained through partial oxidation of Co^{II} and Mn^{II} to Co^{III} and Mn^{III} and/or oxygen vacancies.

The synthesized sample was tested in the process of CO steam reforming in a fixed bed reactor in the range T= 350-600^{0}C, p=1 atm, steam:gas ratio=3.2; the range of W of the wet gas flow was 1800-12735 h^{-1} (Fig. 10).

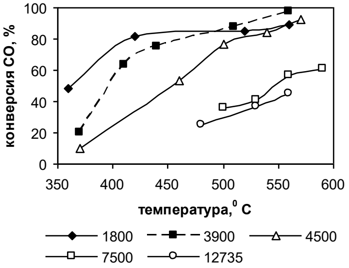


Fig.10. Temperature dependence of CO conversion at different volume rates [26].

As can be seen from Fig.10, on the catalyst under study, the conversion of CO was 82 vol.% at 420^{0}C with W=1800 h^{-1}.

An increase in this indicator by a factor of 2,5 (4500 h^{-1}) or more (up to 12735 h^{-1}) reduces the degree of CO conversion, which is explained by a reduction in the contact time of the reagents.

The subsequent tightening of the reaction conditions, namely, the decrease in the ratio $\alpha=H_2O/CO$ to 1,28 at W=3900 h^{-1} contributes to a decrease in the activity of the catalyst. So, at α = 1,28; 1,65 and 3,2 X_{CO} at T=500^{0}C, respectively, is 69,2; 74,9 and 84,5 vol.%. This dependence is explained by the positive effect of a high concentration of water vapor on the equilibrium. Increasing α>3,2 is impractical, since the degree of CO conversion in this case increases slightly.

The effect of an increase in the concentration of hydrogen in the gas-vapor mixture going for processing on activity at 3900h^{-1} is shown in Fig.11.

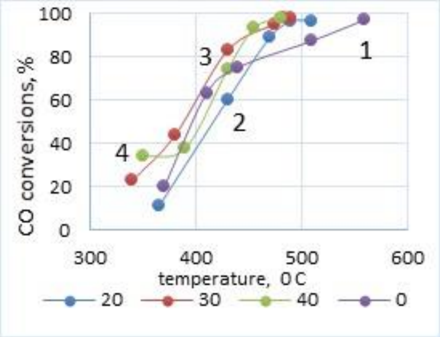


Fig.11. Temperature dependence of CO conversion in the presence of different concentrations of H_2 in the initial gas: 1-0; 2- 20; 3- 30; 4 – 40vol.%.

As can be seen from Fig.11, increasing the hydrogen concentration to 20-40 vol.% contributes to a decrease in the maximum conversion temperature by 80-100^{0}C, which is explained by the catalytic effect of molecular hydrogen on the CO conversion process.

The high activity of the sample is explained as follows. It is known that hematite, under the conditions of the reaction medium, is reduced to magnetite according to the reactions:

$$3\ Fe_2O_3 + H_2 \rightarrow 2\ Fe_3O_4 + H_2O$$

$$3\ Fe_2O_3 + CO \rightarrow 2\ Fe_3O_4 + CO_2$$

Under conditions of oxidative conversion, the high catalytic activity and stability of spinels is associated with the possibility of rearrangement of their surface layer, the presence of structural defects, and electronic exchange between neighboring ions.

These structures are characterized by the formation of defects as a result of electronic disordering by means of electronic exchange (“electron hopping”) between: opposite ions located in the same sublattice; ions of the same name in different sublattices; different ions in different sublattices.

It should be noted that in traditional industrial Fe-Cr catalysts, iron-chromium spinel (Fe_3O_4 Cr_2O_3) is formed before operation during the reduction process, with which residual magnetite forms a solid solution.

The advantage of the proposed sample is to obtain a highly active sample from sulfur-free raw materials, which reduces costs by 30-40% (from the cost of the Fe-Cr catalyst), does not contain toxic chromium, and is also promising for the CO steam reforming reaction with a single-stage organization of the process.

The main problem in the development of catalysts for the deep oxidation of CO is to reduce their operating temperature. An analysis of the literature data shows that this can be achieved by reducing the dimensionality of the systems used.

We have synthesized and characterized copper-containing systems, as the most traditionally used in this process, by hydrothermal redox synthesis from nitrates with ethylene glycol and glycerin [49].

It was of interest to determine the main parameters of synthesis that allow regulating the required properties [35, 28,29,39, 43].

The influence of temperature on the evolution of phase formation during the reduction of individual metal nitrates and their double and triple compositions in the temperature range of 200-350^{0}C using these reducing agents has been studied preliminarily.

Hydrothermal redox synthesis was carried out in a stainless steel autoclave in which a glass ampoule with starting substances was placed. The autoclave was heated in an oven in isothermal mode at a certain temperature for 5 hours. The obtained precipitate was separated from the reaction solution, washed with water and dried at 60-70^{0}C. The reduction reaction was mild relative to the combustion method, the pressure in the system did not rise above 9MPa. The obtained precipitates (powders) and reaction liquid residues were investigated by instrumental methods of analysis.

Initially, ternary compositions of Cu, Co and Al were synthesized in the presence of aqueous solutions of ethylene glycol and glycerol [35, 48, 57, 32]. Interpretation of XRD results of the obtained powders showed that reduction with ethylene glycol at $T=225\pm5^0C$ produced $CuC_2O_4\cdot H_2O$ (№00-048-1054) and $C_2CoO_4\cdot 2H_2O\beta\text{-}C_2CoO_4\cdot 2H_2O$ (№00-025-0250), which transformed into $CoC_2O_4\beta\text{-}C_2O_4Co$ (№00-037-0719) at $T=270\pm10^0C$. At the reduction with glycerol at 270 ± 10^0C 80^0C in the synthesis products are found phases: (№00-004-0836), Al_2O_3 (№01-070-5679) and $CoC_2O_4\cdot 2H_2O$ (№00-048-1068). At 310 ± 15^0C in the reaction products are observed phases of inorganic compounds only: Cu (№00-004-0836) and the corresponding oxides ($Co_{2.88}O_4$ (№01-078-5633)).

Interpretation of the spectra of reactive liquid residues taken in UV (Fig. 12) absorption regions showed the presence of carboxylic (oxalic) acid, as indicated by absorption bands with a maximum in the 260 nm region.

The absorption bands in the region of 200-210 nm correspond to the $n\rightarrow\pi^*$ transition in carboxylic acids, and the absorption bands with a maximum at 280 nm correspond to the excitation of π-electrons of the free electron pair of oxygen of the carbonyl group C=O. These results are confirmed by the results of the IRS.

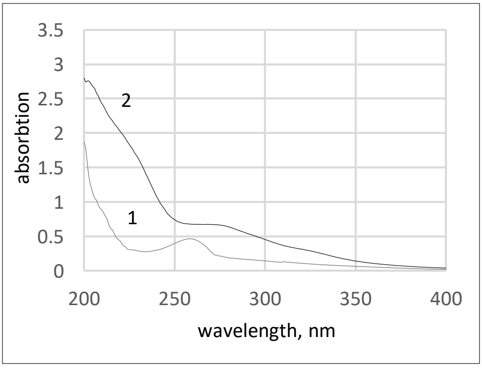


Fig.12. UV spectra of reactive liquid residues of hydrothermal decomposition of Cu, Co, and Al nitrates in the presence of ethylene glycol (1) and glycerol (2) [48].

It is known that ethylene glycol is oxidized to oxalic acid with the release of CO_2. According to experimental data, the further reaction mechanism can be represented as follows. The complex metal cations $[Cu(H_2O)_3]^{2+}$ and $[Co(H_2O)_6]^{2+}$ present in the solution during the dissociation of the corresponding salts interact with the $C_2O_4^{2-}$ dianion formed during the double deprotonation of oxalic acid to form metal oxalate hydrates by reaction:

$$C_2O_4^{2-} + [Me(H_2O)_x]^{2+} \rightarrow MeC_2O_4 \cdot nH_2O + (x-n)H_2O; \ Me – Cu, Co$$

An increase in the reaction temperature first promotes the dehydration of cobalt oxalate hydrate, and a further increase in temperature leads to the decomposition of the resulting oxalate to oxide:

$$CoC_2O_4 \cdot 2H_2O \rightarrow CoC_2O_4 + 2H_2O$$

For CuC_2O_4 H_2O, water is removed simultaneously with the decomposition of oxalate to metal:

$$CuC_2O_4 \cdot H_2O \rightarrow Cu\downarrow + 2CO_2\uparrow + H_2O$$

The reduction of Cu(II) nitrate in general form can be written as follows [28]:

$$5M(NO_3)_2 + 6HOCH_2\text{-}CH_2OH \rightarrow 5M^0 + 12CO_2 + 5N_2 + 18H_2O$$

$$7M(NO_3)_2 + 6HOCH_2CHOHCH_2OH \rightarrow 7M^0 + 18CO_2 + 7N_2 + 24H_2O$$

Thus, it has been experimentally established that the process under study proceeds through the formation of predominantly metal oxalates with their further decomposition. The synthesis products are highly dispersed (from ~240 nm to ~8,5-24,01 μm), after calcination the particle size is up to 27 ± 1,9 nm [31].. EDS spectra of the powder surface showed that it was saturated with more cobalt than copper [48].

An increase in the internal pressure of the system to 9 MPa does not affect the nature of the formation of reaction products.

Further studies are aimed at studying the effect of the Cu/Co metal ratio on the structure and morphology.

It has been established that, regardless of the ratio of metals, oxides of copper (#000050661) and cobalt are formed. At Cu/Co=1, $Co_{2.83}O_4$ (#010785621) is formed; at Cu/Co=1/2, CoO (#030655474(C)) with a tetraganal structure and Co_3O_4 (#010761802(A)) with a cubic structure (a= b=c=8.072Å), at Cu/Co=¼, Co_3O_4 (#000090418(D)) with a cubic structure (a=b=c=8.084 Å) is formed.

The degree of faceting of Co_3O_4, measured as the ratio of (311)/(220) X-ray intensities, was the highest at Cu/Co = 1/2, that is, in this case, more faceted particles were formed.

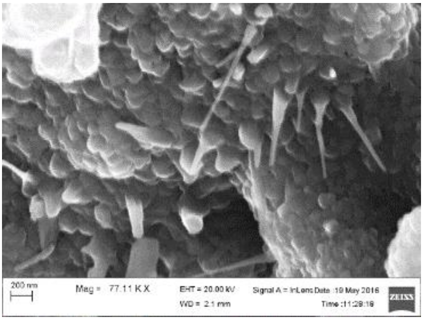
Figure 13 shows SEM images illustrating crystal growth.

Varying the magnification of the scale grid makes it possible to observe the growth pattern as a whole.

Figure 13 (a, c) shows the initial stage of formation of the crystal structure. Then colonies of crystals are formed, which grow up to 30-35nm at Cu/Co=½, and up to >140nm at Cu/Co=1/4.

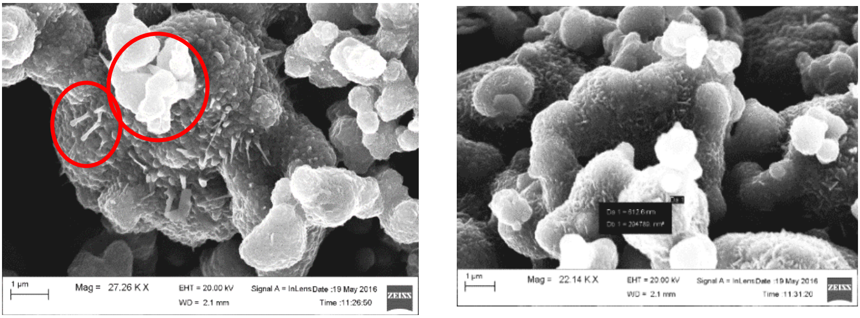
Thus, it is visually confirmed that the defects formed on the surface of the samples in the form of long spike-like growths are additional centers of crystal growth.

EDS of the surface of the samples are shown in Fig.14.

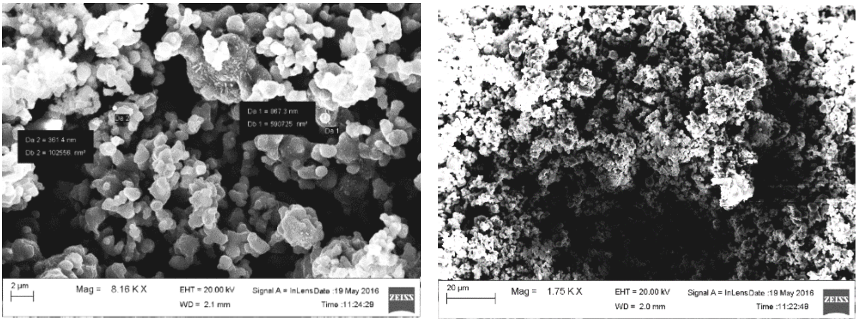


a(200 nm)

b (200nm)

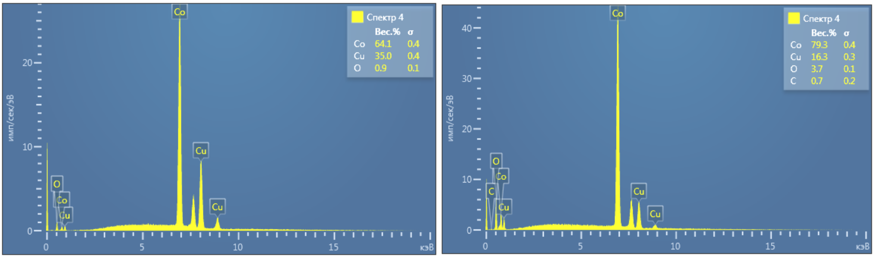


c (1 mkm) d(1 mkm)



e(2 mkm) f (20 mkm)

Fig.13. SEM images of nanoparticles of the Cu/Co oxide system in varying magnification of the scale grid.



a **b**

Fig.14. EDS of the surface of nanoparticles of the Cu-Co-O oxide system depending on Cu/Co: ½ (a) and ¼ (b).

As can be seen from Fig. 14, the surface of both samples is saturated with cobalt.

In the case of Cu/Co=½ (Fig. 14(a)) 64.1 wt.% Co and 35.0 wt.% Cu are observed, with Cu/Co=¼ (Fig. 14(b)) - 79.3 wt. Co and 16.3 wt.% Cu, that is, the ratio of components on the surface corresponds to 0.54 and 0.21, which indicates 100% product yield.

Next, to identify the influence of the nature of the metal, a double oxide composition Cu-Zn (1:1) was synthesized and characterized. Interpretation of XRD results showed the formation of nanosized CuO (#010801916) -20nm and ZnO (#010800075) -12.5nm.

The study of the Cu-Zn-O surface morphology (Fig. 15) showed that there are formations in the form of rods on the surface, which resembles those on the surface of the Cu-Co-O system. However, here they are located randomly, while in the second case they seem to be directed from the center to the surface, that is, they have a direction.

When comparing the surface morphology of the studied systems, it can be assumed that the "hot spots" of the system are copper ions, which contributes to their rapid reduction by polyols, and then other ions are concentrated around them and a complex interaction occurs between them.

Nanooxide systems have been studied in the reaction of selective CO oxidation [57]. Initially, the influence of the nature of the metal on the activity in the range T=50-350^{0}C (Fig. 16) was studied.

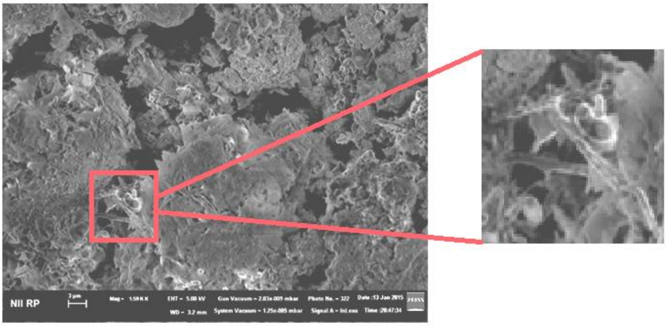


Fig.15. Surface morphology of Cu-Zn-O oxide composition.

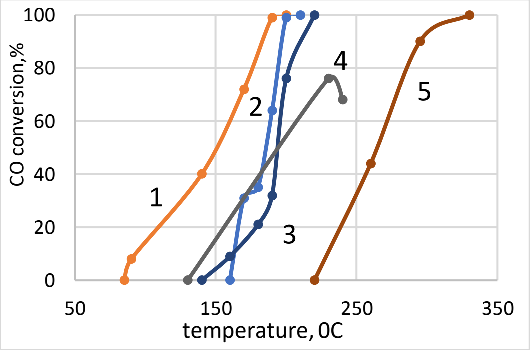


Fig.16. Temperature dependence of CO conversion in hydrogen-containing on oxide compositions with different compounds: 1- Co-Cu; 2-Co-Cu-Al; 3- Cu-Zn; 4- Cu-Zn-Al; Cu-Ni. (W=10800 h^{-1}; Cco=1,6 vol.%).

As can be seen from the fig. 16, Co-Cu systems turned out to be the most active, on which complete conversion was achieved at 190-200^{0}C. Complete CO conversion on Cu-Co-Al-O nanopowders obtained by heat treatment of synthesis products in ethylene glycol, glycerin and formaldehyde was observed at 210-216^{0}C.

This is due to the fact that the Cu-Co-Al-O surface is rich in aluminum compounds (according to EDS results), which apparently block the active centers.

It has been established that the activity of the latter does not depend on the nature of the synthesis environment. Figure 17 shows the results of studying the influence of the synergistic effect [55].

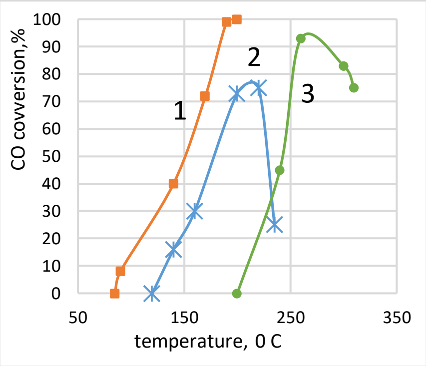


Fig.17. Temperature dependence of CO conversion on Cu-Co-O (1) and individual oxides: Co_3O_4 (2) and CuO (3). ($W=10800h^{-1}$).

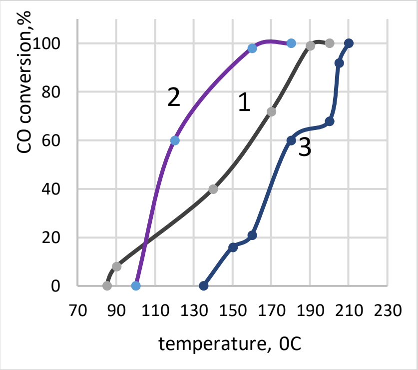


Fig.18. Temperature dependence of CO conversion at different Cu/Co ratios: 1-1:1; 2- 1:2; 3- 1:4. ($W=11016h^{-1}$).

As can be seen from Fig. 17, the bimetallic system exhibits the greatest activity. The high activity of the bimetallic system is probably associated with the high oxidizing ability of Co^{3+} to the states of Co^{2+}, leading to high oxygen mobility, and the adjustment of the composition by activation with a copper cation probably improves the ability of the surface to recover and leads to an improvement in the movement of oxygen from the lattice volume to the surface, which ultimately leads to efficient CO oxidation.

The effect of the Cu/Co metal ratio on activity was studied on Cu/Co nanopowders with ratios of ½ and ¼ (Fig. 18). As can be seen from the figure, the temperature of complete conversion is 180-210^{0}C. The catalyst with the Cu/Co=½ ratio, which has a smaller particle size (30-35nm), has the highest activity.

In addition, the high activity of this sample may also be due to Co_3O_4 faces and/or the presence of CoO with a tetraganal structure, which, oxidizing at high temperature, forms a faceted Co_3O_4 with a Co^{3+} enriched surface.

It should be mentioned that with prolonged use of the catalyst, it is possible to sinter and/or completely reduce, which can lead to a decrease in activity.

The replacement of copper oxide with manganese nanooxides showed that the cobalt-manganese system has a higher activity than individual oxides. Thus, the complete conversion of CO on the Co-Mn-O system (36.3 nm) was observed at 205^{0}C, which is 35^{0}C lower than on Mn-O (Mn_2O_3- 43,2 nm).

Thus, it has been experimentally shown that a complex oxide system is superior in its properties to individual oxides, even if they have a dimension in the nanometer range. Consequently, for the manifestation of high activity, the catalytic particle must have not only high dispersity, but also a structural organization, a certain morphology, and the nature of the surface. The reaction under study proceeds effectively on metal oxides, which replenish the surface of the material with lattice oxygen.

The reaction under study proceeds effectively on metal oxides, which replenish the surface of the material with lattice oxygen.

Cobalt oxides with a redox pair have a high lattice oxygen mobility, easily form electrophilic oxygen species, which is an important property for the manifestation of efficiency and makes this material interesting for study.

To improve activity and thermal stability, the researchers propose to introduce various ions into the composition of the material. An analysis of the literature data shows that the addition of Fe_2O_3 to the Co-O catalyst prevents the complete reduction of Co_3O_4 to CoO and, thereby, increases its stability in the oxidative process.

Based on these literature data, systems corresponding to the composition of $MnFe_XCo_{2-X}O_4$ (x=0-2) were synthesized and studied in the reaction of CO oxidation.

In the system under study, electronic exchange between ions of this type is possible:

$Co^{2+}_B + Fe^{3+}_A \leftrightarrow Co^{2+}_A + Fe^{3+}_B$ 1) $Co^{2+}_B + Co^{3+}_A \leftrightarrow Co^{2+}_A + Co^{3+}_B$ 4)
$Mn^{2+}_A + Fe^{3+}_B \leftrightarrow Mn^{2+}_B + Fe^{3+}_A$ 2) $Co^{2+}_A \leftrightarrow Co^{3+}_A$ 5)
$Mn^{2+}_B + Co^{3+}_A \leftrightarrow Mn^{2+}_A + Co^{3+}_B$ 3) $Co^{2+}_B \leftrightarrow Co^{3+}_B$ 6)

Obviously, depending on the nature of the resulting spinel (on the x region), one or another type of electron exchange predominates.

The influence of the ratio (x region) of the co-precipitated hydroxides $Mn(OH)_2$ - $xFeOOH$ - $(2-x)Co(OH)_2$ on the phase composition of the products obtained is presented in Table 9 [19, 20,24].

Table 9
Influence of the ratio of hydroxides $Mn(OH)_2 – {}_xFeOOH – {}_{(2-x)}Co(OH)_2$ on the phase composition of the products [24]

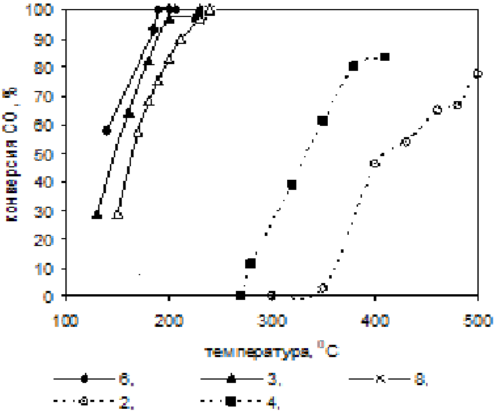
Sample №	Chemical composition		Fe/Co ratio, mol.	Phase composition
	x	formula		
1	0	$MnCo_2O_4$	–	solid solution α-$Mn(OH)_2$ to β-$Co(OH)_2$
2	0.25	$MnFe_{0,25}Co_{1,75}O_4$	0.14	Spinel+ CoOOH
3	0.5	$MnFe_{0,5}Co_{1,5}O_4$	0.33	Spinel+ CoOOH
4	0.75	$MnFe_{0,75}Co_{1,25}O_4$	0.6	Spinel
5	1.0	$MnFeCoO_4$	1.0	Spinel
6	1.25	$MnFe_{1,25}Co_{0,75}O_4$	1.67	Spinel
7	1.50	$MnFe_{1,5}Co_{0,5}O_4$	3.0	Spinel + α-FeOOH
8	1.75	$MnFe_{1,75}Co_{0,25}O_4$	7.0	Spinel + α-FeOOH
9	2	$MnFe_2O_4$	-	Spinel + α-FeOOH

An analysis of the data in the table shows that during boiling in systems, hydroxides interact with the formation of chemical compounds with a spinel structure.

This is due to significant differences in the acid-base properties and structure of α-FeOOH and α-$Mn(OH)_2$, β-$Co(OH)_2$. These hydroxides also differ in dehydration temperature ($Mn(OH)_2$-210^0C, $Co(OH)_2$-280^0C, FeOOH-300^0C). The nature of spinel depends on the ratio of hydroxides due to their mutual influence on the dehydration process and, consequently, on spinel formation. From the data in Table. it can be seen that the optimal ratios of hydroxides in this system, at which complete dehydration and the formation of single-phase spinel occur, are Fe/Co=0.60-1.67 (x=0.75-1.25).

To study the catalytic properties, samples with different Fe/Co ratios were selected: №3 (x= 0.5; Fe/Co= 0.33); № 6 (x=1.25;

Fe/Co= 1.67) and №8 (x=1.75; Fe/Co=7), which cover a wide range of compositions. The results of the study are presented in Fig.19.



Fiq.19. Temperature dependence of CO conversion on $MnFe_xCo_{2-x}O_4$ (x=0-2) with different chemical composition (CO=2.4 об. %; CO/O_2= 1.33; W=9000ч$^{-1}$)

As can be seen from Fig. 19, complete conversion of CO on samples №6 (x=1.25), 3 (x=0.5) and 8 (x=1.75) is ensured at T=190, 230 and 240^{0}C, respectively. The lower activity of №3 and 8 is apparently associated with the presence of the CoOOH and α-FeOOH phases (see Table 9).

In the $MnFe_xCo_{2-x}O_4$ system under study, in samples with a high iron concentration (x=1.25-1.75), as well as ferrous spinels, the presence of the amorphous phase γ-Fe_2O_3 should be expected. In this case, the chemical composition (x) and Fe/Co of the spinels obtained by boiling precipitates will be less than the nominal ones. In these spinels, all the above-mentioned electronic transitions can be active, which obviously ensures their high activity.

It is also impossible to exclude a positive effect on the activity of superparamagnetic γ-Fe_2O_3 (≤10 nm), which is characterized by the structure of defective spinel, in the unit cell of which out of 16 octahedral sites usually occupied by cations, 8/3 of the sites are vacant. The lower activity of sample no. 8 (x=1.75) is probably due to the presence of the FeOOH phase and, consequently, a smaller amount of γ-Fe_2O_3, and a larger Fe/Co.

From the foregoing, it is clear that it is not possible to unambiguously determine the effect of Fe/Co on activity in the study of only boiled samples. Therefore, samples calcined at 900^0C, characterized by a 100% structure of well-crystallized spinel with different Fe/Co ratios: №2 (x=0.25, Fe/Co=0.14) and № 4 (x=0.75, Fe /Co=0.6).

Their phase compositions are identical to № 3 and 6, respectively. As can be seen from Fig. 19, the operating temperature range of the calcined (№ 2 and 4) samples is much higher than that of the boiled ones (№ 3 and 6), which is associated with a significant decrease in their specific surface area. It can be seen that with an increase in the Fe/Co ratio in single-phase spinels, their activity increases. Probably, an increase in this ratio activates the electronic transitions given in equations 1 and 2 (see above).

Sample №6, calcined at 1000^0C, also formed a single-phase spinel, the composition of which corresponded to the nominal composition (x=1.25; Fe/Co=1.67).

The complete conversion of CO with its participation was observed at 500^0C, whereas on №2 and 4 at this temperature, only 77.5 and 80% conversion, respectively, was achieved. Therefore, single-phase spinel of composition (x=1.25), Fe/Co=1.67 has the maximum activity among those studied.

Therefore, the ratio Fe/Co=1.67 (the ratio of ferrites and cobaltites) can be considered optimal for the manifestation of maximum activity.

Thus, it has been experimentally shown that solid solutions with a spinel structure of the composition $MnFe_xCo_{2-x}O_4$ are effective catalysts for the oxidation of CO in air and hydrogen-containing mixtures, have a low operating temperature range, an oxide component that acts as a reversible source of oxygen (spinel) and retain activity at high temperatures.

The stability of the main lattice and the presence of metal ions in it in various oxidized states ensures the supply of electrons necessary for the implementation of the redox reaction.

An easily reproducible technique for obtaining highly dispersed ferrospinel and cobaltite (Mn-Fe-Co-O) with a specific structure has been developed, which allows to give the material the necessary functional properties.

A method of hydrothermal redox synthesis of systems in organic medium (ethylene glycol and glycerol) has been developed, allowing to obtain nanodispersed particles of metal-metalloxide compositions. The mechanism of particle formation was studied and the obtained compositions were characterized by instrumental methods of analysis. This allowed to reveal the relationship "synthesis-structure-surface properties-activity" and to reduce the temperature of the CO oxidation process.

The sixth chapter is devoted to the evaluation of the results of the dissertation research in other applications.

An important property of functional materials is their versatility, that is, the possibility of using them in other applications. The functional properties of the developed KM based on sludge, as well as zeolites, were studied in the process of reducing sulfur dioxide with hydrogen-containing gas and methane [1- 5, 33, 34, 36, 42, 60]. The advantage of using these KM is a significant reduction in the temperature of the sulfur dioxide reduction process with hydrogen-containing gas (up to 350^0C) and methane (up to $800\text{-}850^0$C), a cheaper process, and an expanded range of catalysts.

A scientifically based technique for obtaining materials by hydrothermal redox synthesis in an environment of organic reducing agents was used to obtain Li-Me-O (Co, Ni, Mn, Co-Ni) [59]. The choice is due to the prospect of their use as fuel cell electrodes.

These systems were obtained by heat treatment of precursors obtained by hydrothermal reduction of nitrates with glycerin at 270 °C (5 hours). The obtained powders were investigated by XRD, derivatographic, and SEM methods.

The evolution of the obtained precursors during heating was studied by the derivatographic method. In order to understand the process of structural reorganization during heating, intermediates accompanied by energy or weight changes were subjected to X-ray phase analysis.

Interpretation of the diffraction pattern of the synthesis product of the Li-Mn-O system, heat-treated at 200^0C (2 hours), showed the presence of: $LiH(C_2O_4)\cdot H_2O$ (#000491209) - 6.4; carbonates: Li_2CO_3 (#000221141) - 64.6 and $MnCO_3$ (#000440143) - 22.4; $Li_{0,5}MnO_2$ (#000440143) - 6.5 wt% At a temperature of 600^0C, carbonates and Li_2MnO_3 are observed; at 750^0C only lithium carbonate and Li_2MnO_3; at 850^0C, only lithium-manganese oxides: Li_2MnO_3 and $Li_{0.5}MnO_2$.

Thus, at 850^0C, a homogeneous product is formed - lithium-manganese oxides, which can be considered low-temperature.

The results of termoqravimetric studies of powdered products of Li-Me-O synthesis (Me-Co, Ni, Co-Ni) are shown in Fig.20.

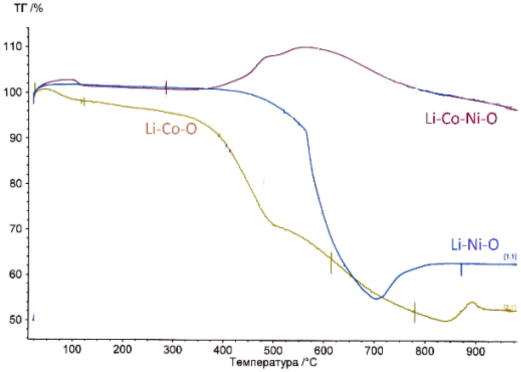


Fig.20. Combined TG curves of Li-Me-O (Me-Co; Ni; Co-Ni) precursor powders.

Here (fiq.20), the nature of the TG curve of a system with two transition metals (Co-Ni). attracts attention. So, with increasing temperature, the mass of the sample increases sharply. This is explained by the oxidation of metals and intermetallic compounds formed during the synthesis to oxides, which is reflected in the TG curve by a sharp increase in mass.

Indeed, the interpretation of the results of XRD analysis of the products of the synthesis of the bimetallic Co-Ni system, carried out in a glycerol/ethylene glycol medium, showed the formation of nano-sized (41–55 nm) particles of metals and inter metallic compounds (Co, Ni, $(Co_3Ni_7)_{0.4}$, CoNi, $Co_{0.75}Ni_{0.25}$).

The effect of temperature on changes in the qualitative composition of the products of the Li-Me-O system (Co, Ni, Co-Ni) is given in Table 10.

Table 10

The influence of temperature on the phase composition of Li-Me-O (Me-Co, Ni, Co-Ni)

Sistems	№	T, ^{0}C	Faza
Li-Co-O	1	200	Li_2CO_3; $LiCoO_2$
	2	480	Li_8CoO_6; Li_2O; $Co_{2,92}O_4$; $Li(CoO_2)$
	3	500	$LiCoO_2$; CoO_2
	4	820	$LiCoO_2$
	5	900	$LiCoO_2$
Li-Ni-O	6	200	Li_2CO_3; $LiNiO_2$; NiO
	7	580	Li_2CO_3; $(Li_{0,999}Ni_{0,001})$ NiO_2; Ni; NiO
	8	700	$Li_{30}Ni_{40}Ni_{30}O$
	9	780	$Li_{0,10}NiO_2$; Li_2O; NiO
	10	900	$Li_{0,09}Ni_{0,01}NiO_2$; NiO
Li-Co-Ni-O	11	200	Li_2CO_3; CoNi
	12	600	$LiNi_{0,85}Co_{0,15}O_2$; $Li_{0,26}Ni_{0,72}O$; $LiCoO_2$; CoNi
	13	800	$Li_2Ni_8O_{10}$; $Li(Ni_{0,5}Co_{0,5})O_2$
	14	900	$Li(Ni_{0,5}Co_{1,5})O_2$; $Li_{1,47}Co_3O_4$

As can be seen from Table 10, in the Li-Co-O system only at 820^{0}C, Li-Ni-O - 700^{0}C the only product is observed,

XRD results show that in the presence of alkali metal the main part of synthesized powder is represented by carbonates, in the manganese system there are also hydroxyoxalates. Cobalt-nickel systems form particles of metals and intermetallic compounds (alloys), which in the presence of lithium compounds form complex oxide systems.

These samples (No. 4, 8, 13) were studied by SEM and it was found that the particles are uniform in size and are in the range of 114-139 nm (Fig. 21).

As can be seen from the figure, the surface of $LiCoO_2$ (Fig. 21 (a, b)) is represented by plates that are collected in colonies. Particles corresponding to the composition $Li_{30}Ni_{40}Ni_{30}O$ (Fig. 21 (d, e)) have smooth rounded shapes.

A sample of Li-Co-Ni-O composition (Fig. 21 (c)), which, according to XRD results, contains two phases: $Li_2Ni_8O_{10}$; $Li(Ni_{0.5}Co_{0.5})O_2$, on SEM images, also consists of two phases: rounded and in the form of tubes with a diameter of about 137 nm.

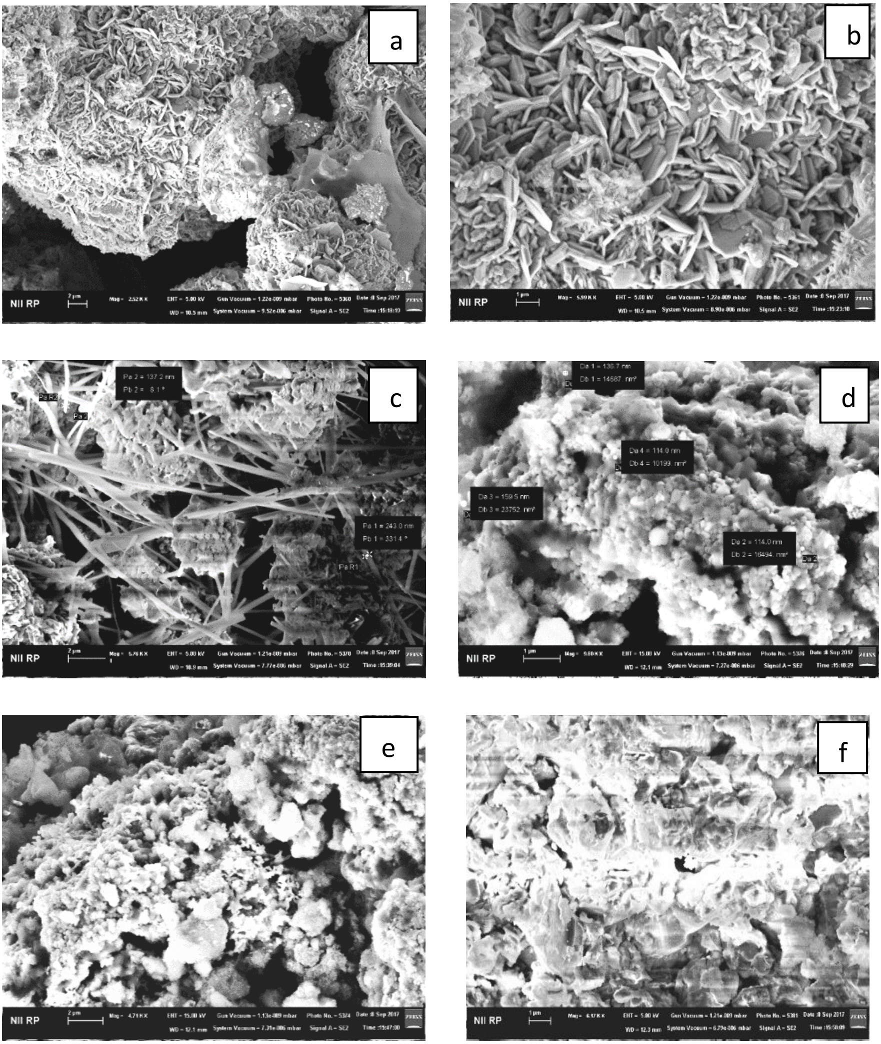


Fig 21. SEM images of the powders corresponding to the composition: a, b) $LiCoO_2$; c) $Li_2Ni_8O_{10}$; $Li(Ni_{0,5}Co_{0,5})O_2$; d, e) $Li_{30}Ni_{40}Ni_{30}O$; f) Li_2MnO_3 and $Li_{0,5}MnO_2$ [59].

By varying the temperature and duration of isothermal exposure during the hydrothermal synthesis from nitrates in ethylene glycol and glycerin materials with a pronounced nanostructure can be obtained. Synthesized systems with pronounced nanostructure can be considered as fuel cell cathodes in the future.

The data obtained in the dissertation work make it possible to select or purposefully synthesize the most promising materials with predetermined properties.

The dissertation ends with the discussion of the main results of the research and the list of references.

CONCLUSIONS

The scientific basis for the production of inorganic composite materials with functional properties in the main stages of the process of producing hydrogen from methane has been developed.

1. The basic methods for obtaining inorganic composite materials have been developed, allowing their composition to be varied, structure and texture to be controlled, imparting the required functional properties; a set of the most important physical and chemical properties ensuring the functioning of the materials has been determined.
2. Functional materials have been developed based on a combination of highly dispersed slurries, the macrocomponent composition of which is represented by Fe, Al, Ti, and montmorillonite oxides for the process of gas purification from sulfur compounds [1,30,40,41,44-46]. A rational dosage of montmorillonite has been determined, contributing to an improvement in texture, an increase in the tensile strength index (almost three times) and an increase in the ability to form in the form of various standard sizes (cylinders, tubes, rings, block structures) by increasing coagulation properties. The obtained composition ensures a high degree (95±1.8 vol.% at 250±15^{0}C and a volumetric flow rate of 750±250h^{-1}) of sulfur extraction from primary raw materials in the Claus process and has a high sorption capacity (0,23±0,01 mmol/g) concerning SO_2. It was found that these properties of the composition are provided by iron oxides in the composition of the sludge, which prevents the sulfation of the aluminium and titanium oxide

components, due to the formation of sulfate-sulfite iron compounds with their further reduction. This allows us to recommend them as forcontacts. A high correlation of activity with the presence of electron acceptor (r=1) and main (r=+0,91) centers on the surface is shown.

3. For the first time, the influence of the composition and type of structure of zeolite on their behaviour as a matrix of composite material for the synthesis gas production process from methane has been established [6-18, 40]:
   - screening of zeolites NaA, NaX, CaX, CaA, ZSM-5, clinoptilolite, mordenite, chabazite type, analcime, etc. as a matrix of nickel systems was carried out. The main differences in behaviour (NaY, NaX, CaX, CaA) were revealed: an increase in the $T_{80\%}$ index with an increase in the molar ratio of SiO_2/Al_2O_3; the effect of the exchange cation of zeolite, the relationship of the matrix structure with acid-base properties and activity was shown. A strong correlation has been established (r=0.94±0.01) of hydrogen yield with electron acceptor and main centers.
   - the role of the nature and concentration of cations (Na, K) present in the mother liquor during the synthesis of zeolite on the functional properties of nickel systems is shown. It is shown that the activity is determined by the value of the oxygen-catalyst bond energy. A correlation above the average concentration of Na^+ with $T_{80\%}$ (r=+0.689) and a strong correlation of weak acid centers with the amount of deposited coke (r=+0.99) was established.
   - the expediency of using clinoptilolite to obtain a composite material with increased activity and resistance to carbon deposition is shown. The influence of the composition and method of preparation, as well as chemical activation of the matrix on the characteristics of the composite system has been revealed. It has been established that the design features, consisting of the unique structure and composition of the carrier, contribute to a high dispersion of the active component and provide the required functional properties.
4. The developed composition with functional properties in the process of obtaining synthesis gas from methane based on zeolite is characterized by [53,56]:
   - having an optimal combination of acid-base properties, weak acid

(electron-acceptor) centers with an ionizing power of 9.69±0.01eV, moderately strong acid (proton-donor) centers with an ionizing power of 10.59±0.01eV and The particle with a dissociation constant of 9.89±0.01 consists of the presence of weak basic centers capable of ionizing, which distinguishes it from samples containing Co, Cr, Mo, Fe.

- –having optimal topology, activity on dehydrated natural zeolites correlates with void volume;
- –the optimal concentration of alkali and alkaline earth metals
- –with the amount of the active component being less than in industrial system.
- – functional properties comparable to the industrial catalyst brand GIAP-16.

5. The composition and mode of obtaining Co-Mn-O compositions with a spinel structure with a small tetragonal distortion of the cubic lattice (c/a=1.015) have been experimentally substantiated, ensuring complete deep oxidation of methane at a temperature 110^0C lower than on tetragonal spinel (c/a=1.15) obtained under similar conditions [22,25]. Conditions have been established to regulate the spinel structure and obtain spinels with the necessary characteristics. A positive effect on the activity of $CoMnO_3$, which is formed in addition to spinel during low-temperature processing, has been shown.
6. Design features of a ferrospinel with a nominal composition of $Mn_{0.5}Co_{0.5}Fe_2O_4$ provide the required functional properties in the CO steam conversion reaction [26]. The composition is characterized by a mixed spinel structure with a reversal parameter of 0.6, high dispersion, and thermal stability at high temperatures and causes high activity at high volume load ($3900h^{-1}$), temperature 450^0C, H_2O/ CO = 3.2. The advantage of this composition is its non-toxic composition (does not contain chromium) and its production from sulfur raw materials, which makes it safe for the environment.
7. The composition and mode of obtaining $MnFe_xCo_{2-x}O_4$ (x=0-2) iron-substituted cobaltites with a spinel structure with a low-temperature range ($180\text{-}240^0$C) in the oxidation reaction of CO in a hydrogen-containing medium has been developed [20,24]. It was found that at x=0.75-1.25 (Fe/Co=0.60-1.67), a single-phase spinel is formed; at

x=0.25;0.5, in addition to the spinel phase, there is a phase of CoOOH, and at x=1.50;1.75, the α–FeOOH phase; oxyhydrooxides have a negative effect on activity, increasing the temperature at 40-50^{0}C; at x>1, the possible presence of the γ-Fe_2O_3 phase (≤ 10 nm) with a defective spinel structure is shown; its positive effect on activity has been established. An increase in activity with an increase in the Fe/Co ratio in single-phase spinels was revealed, which is presumably associated with the activation of electronic transitions. It was found that the single-phase spinel of $MnFe_{1,25}Co_{0,75}O_4$ composition has the highest activity.

8. A technique has been developed for the production of metal-metal oxide compositions (Cu-Me-O (Me-Co, Zn, Ni); Co-Mn-O; Cu-Me-Al-O (Me -Co, Zn); Li-Me-O (Me-Co, Ni, Mn)) from nitrates by hydrothermal reduction with ethylene glycol or glycerin. It has been established that the process of formation of metal-metal oxide compositions proceeds through the formation and subsequent decomposition of hydroxy oxalates (oxalates) [28, 29, 31, 32, 35, 48, 49, 52, 55, 57]. The influence of the nature of metal on the morphology and structural-spatial organization of particles is shown: Cu-Co-O - nanoplates (30-35nm), and Cu-Zn-O-nanorods (12.5-20nm). The influence of the resulting properties of nanostructures (structure, size, morphology) on the activity during the oxidation of CO in a hydrogen-containing medium has been determined. The conditions for obtaining the Cu-Co-O system and its characteristics have been determined, which make it possible to reduce the temperature of the beginning of oxidation ($T_{50\%}$) of CO to less than 115^{0}C.
9. By hydrothermal redox-synthesis in glycerin medium, powders with a clear nanostructure $LiCoO_2$; $Li_{30}Ni_{40}Ni_{30}O$; Li_2MnO_3 и $Li_{0,5}MnO_2$; $Li_2Ni_8O_{10}$; $Li(Ni_{0,5}Co_{0,5})O_2$ were obtained, which in the future can be considered as cathodes [59].

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