

REPUBLIC OF AZERBAIJAN

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ABSTRACT

of the dissertation for the degree of Doctor of Science

**PHYSICAL-CHEMICAL FOUNDATIONS OF THE
SELECTION OF CATALYSTS FOR THE PROCESS
OF HYDROGENATION OF CARBON DIOXIDE**

Specialty: 2316.01 – Chemical kinetics and catalysts

Field of science: Chemistry

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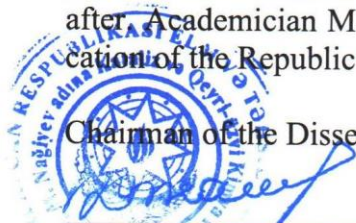
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GENERAL CHARACTERISTICS OF THE WORK

Relevance of the work and degree of development of the topic. Over the past centuries, the use of carbon-rich fossil fuels– coal, oil, and natural gas – has led to an unprecedented era of human development. However, burning fossil fuels releases large amounts of carbon dioxide into the atmosphere. An increase in the amount of carbon dioxide leads to the so-called “greenhouse effect” and, as a consequence, to climate change and various natural disasters on the planet. Carbon dioxide is recognized as a powerful climate regulator on Earth. Despite the fact that carbon dioxide ranks second after water vapor in terms of its greenhouse properties, the increase in the “greenhouse effect” is associated with an increase in CO₂ concentration. If carbon dioxide emissions continue at this rate, CO₂ emissions are expected to exceed 40 Gt by 2030. The European Union has set a strict target to reduce greenhouse gas emissions by around 60–80% by 2050¹. Reducing carbon emissions is a global and long-term goal. Therefore, it is necessary to find a solution to reduce CO₂ emissions, among which its capture, storage and processing into fuels or chemicals are essential to reduce emissions².

The first strategy requires energy-efficient processes and a transition from fossil fuels to lower carbon fuels and to other energy sources such as hydrogen and renewables. Carbon dioxide storage involves the development of new technologies to capture and sequester CO₂. There are promising projects in this direction.

Fuel demands are increasing with increasing energy consumption, fossil fuel resources are currently decreasing, and fuel prices have fluctuated greatly in recent years. The involvement of carbon dioxide in chemical syntheses is currently considered as one of the

¹ Rafiee, A. Chapter 8 - CO₂ Conversion and Utilization Pathways /A.Rafiee, K. R. Khalilpour, D. Milani // Polygeneration with Polystorage for Chemical and Energy Hubs For Energy and Chemicals, – 2019, –p. 213-245.

² Saravanan, A. A Comprehensive review on different approaches for CO₂ utilization and conversion pathways /A.Saravanan, P.Senthil-kumar, D-V.N.Vo, S. Jeevanantham, V. Bhuvanewari, V. A.Narayanan, P.R. Yaashikaa, S. Swetha, B. Reshma //Chemical Engineering Science, –2021, – V. 236, p. 116515.

possible options for replacing petroleum (fossil) raw materials with non-petroleum (alternative) ones. For chemists, recycling technology is more attractive, i.e. converting CO₂ into valuable chemical products. Once captured and concentrated, CO₂ can serve as a starting material for the production of many chemical products. Currently, the annual volume of its industrial use is about 120 million tons of CO₂, which represents less than 0.5% of the total annual anthropogenic emissions – 34 billion. t. CO₂. In this regard, expanding the use of carbon dioxide as a starting reagent for chemical processes is an urgent task aimed at solving issues of environmental safety and the use of CO₂ as a chemical raw material in industry is limited to several processes - the synthesis of salicylic acid, urea, methanol and ethylene carbonate. The use of CO₂ as a feedstock for various syntheses in the petrochemical industry will greatly ensure the rational use of natural resources and lead to an improvement in global climate change caused by rising CO₂. One of the promising and important methods of recycling CO₂ are hydrogenation reactions. However, involvement the presence of a stable CO₂ molecule in chemical processes is hampered by the lack of effective catalysts that allow the hydrogenation of CO₂ to be carried out with high yields and selectivity. Currently, numerous studies are underway related to the development of highly efficient catalysts for CO₂ hydrogenation processes. Despite noticeable progress in this area, many questions remain unresolved related to the selection of an effective catalyst for CO₂ hydrogenation, in particular, many questions regarding the nature of the active centers, mechanism, chemistry of the CO₂ hydrogenation process, activity, selectivity and stability of the catalytic system remain unresolved. Thus, it is necessary to develop a scientific basis for the selection of effective catalysts for CO₂ hydrogenation, and to search for new effective catalytic systems for CO₂ hydrogenation that avoid the disadvantages of known catalytic systems. And one of the most promising areas of search is the selection of effective catalysts for CO₂ hydrogenation, based on studies, including in-situ dynamics of elemental and phase composition, distribution of active components in the structure of the catalyst.

Object and subject of research. The object and subject of re-

search of the dissertation work are, respectively, the process of hydrogenation of carbon dioxide at atmospheric pressure in the presence of Fe–Ni, Co–Pd containing catalysts based on aluminum oxide and aluminosilicates and the development of the scientific basis for the preparation of catalysts for this process.

Purpose and tasks of the work. The purpose of the dissertation is to develop the physicochemical foundations for the preparation of highly effective Fe–Ni, Co–Pd containing catalysts for the hydrogenation of CO₂ into methane and methanol based on aluminum oxide and aluminosilicates, to establish the patterns of the dynamics of the structure and size of the active components of these reactions by monitoring the surface structure and chemical composition of the catalysts a combination of methods of electron scanning microscopy, X-ray fluorescence microscopy, X-ray diffractometry, infrared spectroscopy, electron magnetic resonance, thermal analysis and chromatography-mass spectrometry, measuring their textural characteristics.

To achieve this goal there were:

- samples of iron, nickel, cobalt, palladium containing catalysts for the hydrogenation of CO₂ into methane and methanol were synthesized, their catalytic properties were studied under continuous conditions in the temperature range of 473–773 K and atmospheric pressure, their elemental and phase compositions, texture, and surface structure were determined;

- the influence of the conditions of preliminary heat treatment of catalysts and the reaction medium on their surface elemental composition, structural-porous characteristics, phase composition, and magnetic properties was studied;

- the laws of the reaction of hydrogenation of carbon dioxide into methane and methanol on synthesized catalysts were studied depending on their elemental, phase composition and pre-treatment conditions;

- the nature of active centers, the mechanism of hydrogenation reactions into methane and methanol, factors influencing the activity, selectivity and stability of the catalyst were studied;

• the kinetics of CO₂ hydrogenation reactions into methane and methanol were studied, regression equations for these reactions were compiled, the composition of the catalysts was optimized, and a technology for the preparation of catalysts for the hydrogenation of CO₂ into these products was developed.

Methods of research. To determine the elemental and phase composition of the catalysts, textural parameters, distribution of active components, the structure of their local environment and the degree of oxidation, a Hitachi S-3400 N scanning electron microscope, Japan, with an energy-dispersive elemental analyzer, an XGT-7000 X-ray fluorescence microscope, and X-ray XRD diffractometers TD3500, China and PHASER D2, Bruker, Germany, spectrometer for diffuse reflection of ultraviolet and visible ranges Specord M40, Jena, Germany, infrared Fourier spectrometer FT-IR Alfa II, Germany, electron paramagnetic resonance spectrometers JES-PE-3X, Jeol, Japan and EMXmicro, Bruker, Germany, thermal analyzer TG/DTA/DTG, STA 449F3, Jupiter, NETSCHZ, Germany, device for measuring texture parameters of catalysts Belsorp Mini II from BEL, Japan, mass spectrometer coupled with thermal analyzer STA PT1600, Linseis, Germany, for identifying gases released during thermal desorption, studying intermediate products of the hydrogenation reaction of carbon dioxide, dynamic light scattering analyzer LB 550, Horiba, Japan, for measuring the size of catalyst granules and particles, their size distribution in their dispersions in alcohols (methanol, ethanol, propanol) before and after the reaction; To analyze the products of the conversion of carbon dioxide into methane and methanol, an Agilent 7890A gas chromatograph, USA, and a Thermo Fisher Scientific GC/MS Focus chromatography-mass spectrometer were used.

Catalytic studies of the synthesized samples were carried out in a laboratory flow-type installation with a fixed catalyst bed in the temperature range of 473–773 K and atmospheric pressure, followed by analysis of the desorbed products by chromatographic and gas chromatography-mass spectrometric methods. The initial catalytic systems were synthesized by impregnation of supports (γ -Al₂O₃ and Siral-1,10,40 aluminosilicates) with the corresponding salts of the active components.

Two types of γ -Al₂O₃ carrier were used: conventional (purchased) with a specific surface area of 120 m²/g and a specific pore volume of 0.39 cm³/g, and γ -Al₂O₃ with a specific surface area of 394 m²/g and a specific pore volume of 0.68 cm³/g, prepared by us hydrothermal treatment in the presence of organic structure formers (urea, citric acid, triethanolamine) of aluminum trihydroxide of pseudoboehmite structure. The constancy of catalyst activity was monitored by periodically returning to conditions accepted as standard.

The main results and provisions submitted for defense:

–results of studies of transformations occurring on the surface of the catalyst under the influence of the reaction medium using scanning electron microscopy in combination with elemental analysis, X-ray fluorescence microscopy, X-ray diffractometry, spectrophotometry in the UV and visible ranges, IR-Fourier spectroscopy, electron magnetic resonance, thermal desorption from the surface catalyst adsorbed molecules obtained by combining a thermal analyzer with a mass spectrometer, interpretation of data obtained by these methods, correlations between the structural features of the studied catalysts and their activity in the reactions of hydrogenation of carbon dioxide into methane and methanol;

–results of a study of the dependence of the activity of iron-nickel and cobalt-palladium containing catalysts on the distribution of active components on the surface of the catalyst, the ratio of their quantities and the use of the results of these studies in the preparation of effective catalysts for the hydrogenation of carbon dioxide into methane and methanol;

–technology for the preparation of aluminum oxide with a developed surface, optimal volume and pore size and catalysts for these reactions based on it;

–results of studies of hydrogen production by steam reforming, carbon dioxide conversion of methane with the participation of iron-nickel, nickel-magnesium containing oxide systems as catalysts for these reactions, photochemical decomposition of water in the presence of sensitizers based on aromatic hydrocarbons of the heavy fraction of oil;

–results of studies of the kinetics and mechanism of these reac-

tions with the participation of the synthesized catalysts.

Scientific novelty of research. A combination of scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS), X-ray fluorescence microscopy (XRF), X-ray phase analysis (XRD), ultraviolet and visible electron spectroscopy (UV/Vis.), infrared (IR)-Fourier spectroscopy, electron magnetic resonance (EPR), mass spectrometry and thermal analysis (TG/DTG/DTA) studied the transformations occurring under the influence of the reaction medium on the surface of iron-nickel, cobalt-palladium containing catalysts based on aluminum oxide and aluminosilicates, the connection of these transformations with the activity of the catalysts in the reactions of hydrogenation of carbon dioxide into methane and methanol, the dependences of the catalytic activity of the synthesized systems on their structural features, quantity and ratio of active components on the surface of the catalyst were established.

Nano-sized iron-oxide structures FeO_x have been identified and electronic transitions between iron ions in these structures have been established, nickel particles activating, respectively, carbon dioxide and hydrogen, on catalysts with an iron-nickel active component;

It has been shown that the hydrogenation of carbon dioxide into methanol in the presence of cobalt-palladium containing catalysts based on aluminosilicates is determined by the activity of dispersed nano-sized palladium particles. It is believed that the reaction of converting CO_2 into methanol occurs stepwise and at the initial stage molecular hydrogen interacts with Pd particles to form PdH particles. In the next step, CO_2 reacts with PdH particles to form formate structures, which are further converted into methanol;

A methodology has been developed for the preparation of CO_2 hydrogenation catalysts with a developed surface, optimal volume and pore size using structure-forming reagents;

The patterns of hydrogenation of CO_2 into methane and methanol using the indicated catalytic systems have been established.

Theoretical and practical value. Physicochemical principles have been developed for the selection of effective catalysts for the hydrogenation reactions of CO_2 into methane and methanol with alumina and aluminosilicate bases, based on studies of highly in-

formative methods SEM/EDS, XRF, XRF, UV/Vis/IR, EMR spectroscopy, thermal analysis in combination with mass spectroscopy of the dynamics of the elemental and phase composition of active components, the composition of gas-phase products during these reactions, the dependence of catalytic activity on the composition of active components, their distribution in the structure of the catalyst. From a practical point of view, the results of the above studies provide a valuable basis for the development of technologies for the targeted synthesis of catalysts for converting CO₂ into methane and methanol. From an environmental point of view, the hydrogenation of carbon dioxide into methane and methanol is one of the most promising ways to process CO₂.

Approbation and application of the work. The main results of the dissertation were reported and discussed in the form of oral and poster presentations at: Republican and international conferences: XXVII Symposium, 2015, Tuapse (Russia). Modern chemical physics; Eleventh International Symposium on Heterogeneous Catalysis 2015, Varna, Bulgaria; International Conference on Chemical Sciences and Application, 2016, Alex., Egypt; XXVIII Symposium Modern chemical physics. Skopje, Macedonia 2016; IX Baku International Mamedaliev Conference on Petrochemistry, 2016 INHP (2 theses); Republican scientific conference dedicated to the 80th anniversary of the Institute of Catalysis and Inorganic Chemistry named after M. Nagiyev, Baku 2016; International Conference – Physicochemistry of nanostructured catalysts 2016 Zvenigorod, Russia; XIII International Conference “Development of Science in the 21st Century”, Kharkov, Ukraine, 2016; Modern chemical physics, XXVIII Symposium, 2016, Tuapse, Russia; II All-Russian Scientific Conference “Current Problems of Adsorption and Catalysis”, Ivanovo, Russia, 2017; II Symposium Modern problems of nanocatalysis – NANOCAT-2017, Ukraine, Kyiv; The 3rd International Conference on Nanomaterials Fundamentals and Applications, 2017, Slovak republic, Bratislava; - ICINSE 2018, Turkish Republic of Northern Cyprus; Symposium on Heterogeneous Catalysis: A motor of economy, 2018, Sofia, Bulgaria; 5th International school - Conference on Catalysis for Young Scientists, Moscow, 2018; International scien-

tific and practical conference “Innovative prospects for the development of oil refining and petrochemistry”, dedicated to the 110th anniversary of academician V.S. Aliyev, INHP-2018, Baku; 2018; - 2nd International Conference innovations in Natural Science and Engineering 2018, Kyiv, Ukraine (ICINSE); International Conference on Catalysis Science, Engineering and Technology, Stockholm, Sweden, - 4-7 November, - 2018ITWCCST 2019; 5th International Turkish World Conference on Chemical Sciences and Technologies, 2019, Sakarya/Turkey; IV All-Union (with international participation) scientific symposium “Current problems of the theory and practice of heterogeneous catalysts and adsorbents”, 2019, Ivanovo-Suzdal, Russia, 2019; 4th International Turkish Congress on Molecular Spectroscopy (TURCMOS-2019); The International Scientific Conference “Current Problems of Modern Chemistry”, Dedicated to the 90th Anniversary of the Academician Y.H. Mammadaliev Institute of Petrochemical Processes, October 2-4, 2019, Azerbaijan; The 1st international student research and science conferences, 2020, Baku, Azerbaijan;- “Chemistry, Physics and Technology of Surface”, 2021, Kiev, Ukraine; - ROSKATALIZ - IV Russian Congress on Catalysis, 2021 Kazan, Russia; Intern.Conf. “Modern problems of theoretical and experimental chemistry” BSU, Baku, 2022.

Publications. On the topic of dissertation work 55 scientific works were published, including 26 articles and 29 abstracts.

Author's personal contribution. The applicant owns the main ideas, defining the purpose and direction of the work, collecting and summarizing literary data, direct participation in setting up and conducting the experiment, analysis, systematization and discussion of the results obtained, formulation of conclusions, scientific and practical value of the dissertation, design of the dissertation.

Place of creation of the dissertation work. The dissertation work was carried out at the Institute of Petrochemical Processes named after academician Y.H. Mammadaliev of the Ministry of Science and Education of the Azerbaijan Republic.

The structure and scope of the dissertation. The dissertation consists of an introduction, seven chapters, a conclusion, main conclusions, and a list of references, including 326 titles of domestic and

foreign authors. The total volume of work is 281 pages, including 43 tables and 59 figures and diagrams.

The introduction substantiates the relevance of the topic, formulates its purpose and objectives, and characterizes the scientific and practical significance of the research results.

The first chapter, which is a literature review, discusses the current state of work in the field of research and development of processes for the hydrogenation of carbon dioxide into methane and methanol.

The second chapter of the dissertation outlines the methodology for experimental research, preparation of catalysts, analysis of raw materials and reaction products.

The third chapter discusses the hydrogenation reaction of carbon dioxide into methane on Fe, Ni/Al and Fe, Zr/Al oxide catalysts. The results of studies of catalytic properties and the influence of conditions of preliminary thermal reduction treatment on the catalytic activity, magnetic properties and textural parameters of catalysts are presented. The mechanism of hydrogenation of CO₂ into methane is considered.

The fourth chapter presents the results of a study of the hydrogenation of CO₂ into methane and methanol in the presence of Co-, Pd-containing catalysts on alumina and aluminosilicate bases, and discusses the mechanism of methanol formation on these catalysts.

The fifth chapter presents the results of studies on the production of hydrogen by the decomposition of water by the photochemical method on reduced iron - nickel - aluminum oxide catalysts in the presence of oil sensitizers.

The sixth chapter provides a thermodynamic justification for the process of water decomposition on reduced iron-nickel-containing catalysts based on aluminum oxide and examines the participation of carbon dioxide in the abiogenic synthesis of hydrocarbons in oil and gas fields.

The seventh chapter discusses the kinetics of the processes under study and the technology for preparing catalysts for the hydrogenation of carbon dioxide into methane and methanol.

At the end of the dissertation, the main conclusions, a list of references and abbreviations are given.

MAIN CONTENT OF THE WORK

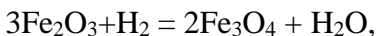
Below are the results of research in the main areas presented in the dissertation. The dissertation presents the results of a study of iron-nickel-containing and cobalt-palladium-containing catalysts with an alumina and aluminosilicate base in the hydrogenation reaction of carbon dioxide into methane and methanol, respectively, in order to establish a connection between the surface structure of these catalysts, the distribution of active components in their structure and catalytic activity in these reactions, the influence of these parameters on the direction of the CO₂ hydrogenation reaction; The results of a study of iron-nickel catalysts in the reactions of steam and carbon dioxide conversion of methane, photochemical decomposition of water to produce hydrogen, coupling reactions of decomposition of water vapor and hydrogenation of carbon dioxide into hydrocarbons are also presented. Our approach is to control the reconstruction of the surface of these catalysts by high-temperature treatment in various gas environments, in a vacuum in which time, temperature and atmosphere vary, and to study them using scanning electron microscopy in combination with elemental analyzes using energy-dispersive spectroscopy, X-ray fluorescence microscopy, X-ray diffractometry, electron spectroscopy of diffuse reflection in the UV-Visible region, Fourier transform infrared spectroscopy, electron magnetic resonance combined with thermogravimetry and mass spectrometry methods; understand the chemical features of the oxide surface, the correlation of the elemental composition, the distribution of active components in the structure of catalysts, the structure of surface structures with the activity of the latter in the above reactions. For example, the Fe₃O₄ (0001)-terminated α -Fe₂O₃ surface was found to be active for methyl radical chemistry. The formation of catalytic structures active in the hydrogenation of carbon dioxide into methane and methanol in iron-nickel and cobalt-palladium catalysts with an alumina and aluminosilicate base is discussed below. In iron-nickel catalysts, iron and nickel are excellent candidates for redox chemistry and are known to be active in many catalytic reactions. Iron and nickel in these reactions can be in different oxidation states. Nickel in these systems is characterized by oxidation states of +3, +2, 0 and for nickel - +2, +1 and 0. Cobalt is characterized by oxidation states of

+2, +1, 0 and in some cases +3, for palladium – +2, +1, 0. In this case, they are active components of catalysts with alumina and aluminosilicate bases. The dissertation describes in detail experimental methods for studying these catalysts and procedures for their preparation, with particular emphasis on sample preparation methods for studying oxide surfaces using SEM and X-ray fluorescence microscopy (XRF). In this study, along with SEM and XRF, a range of techniques were used, including X-ray diffraction, diffuse reflectance electron spectroscopy, Fourier transform infrared spectroscopy and electron magnetic resonance in combination with thermal analysis and mass spectrometry methods, and measurements of textural characteristics by adsorption methods.

1. HYDROGENATION OF CARBON DIOXIDE TO METHANE

This section presents the results of a study of iron-nickel and iron-zirconium containing alumina catalysts for the hydrogenation of carbon dioxide into methane depending on the pre-treatment conditions, the content of active components in them and the reaction conditions, the relationship between their composition, structure and catalytic properties.

The choice of iron-nickel containing oxide systems is due to the fact that these systems are well known as catalysts for CO₂ hydrogenation. Monometallic nickel-containing catalysts are most active in this reaction; however, the stability of these catalysts is low. To increase the stability of catalysts, iron is introduced into nickel-containing catalysts and their composition is optimized. It has been shown that the most active catalysts for CO₂ hydrogenation are catalysts previously reduced in a stream of hydrogen. Treatment of pre-oxidized samples in a hydrogen stream leads to the reduction, first of all, of nickel from the oxidized ionic to the “metallic” state. Depending on the reduction conditions, clusters and nickel particles of various sizes are formed. The catalytic properties of these systems are directly determined by the size of these particles and their distribution in the catalyst structure. In addition, in bimetallic systems, during treatment with hydrogen, depending on the treatment temperature, the initial oxidized states of nickel (NiO, NiAl₂O₄, etc.) are immediately reduced to clusters, Ni particles, and the initial oxidized states of iron Fe₂O₃, NiFe₂O₄ are reduced to magnetite:



magnetite and nickel particles:



The composition of the studied Fe,Ni/Al oxide catalysts and their activity in the CO₂ hydrogenation reaction are given in Table 1.

The results of catalytic studies (Table 1) showed that the most active catalysts are iron-nickel catalysts with a ratio of Fe: Ni = 1: 3, the maximum yield (58%) is observed on a catalyst with a composition of 5% Fe, 15% Ni / 80% γ -Al₂O₃, which was chosen as the optimal catalyst, and the entire bulk of research was carried out on this composition. Table 2 below shows the results of studying the reaction of CO₂ methanation on a Fe(5%)-, Ni(15%)-containing catalyst with a “purchased” aluminum oxide base and obtained from ground aluminum trihydroxide by its hydrothermal treatment using organic structure formers.

Table 1
Composition of Fe, Ni/Al oxide catalysts and their activity in hydrogenation of CO₂ (CO₂ : H₂ = 1:4, P = 0.1MPa, W=200h⁻¹)*

Catalyst	T,K	Conversion of CO ₂ , %	Yield of CH ₄ , %	Yield of CO, %
35%Fe,15%Ni/Al	573	36.5	29.0	7.5
	673	41.5	32.0	9.5
	773	47.5	34.0	13.5
20%Fe,15%Ni/Al	573	36.0	30.0	6.0
	673	43.5	35.0	8.5
	773	45.5	34.0	11.5
15%Fe,15%Ni/Al	573	41.0	35.5	5.5
	673	46.0	38.0	8.0
	773	49.5	39.5	10.0
10%Fe,20%Ni/Al	573	53.0	48.5	4.5
	673	59.0	52.0	7.0
	773	58.5	50.0	8.5
5%Fe,15%Ni/Al	573	55.0	53.0	2.0
	673	62.0	58.0	4.0
	773	58.0	52.0	6.0
15%Ni/Al	573	58.0	56.0	2.0
	673	55.5	53.0	2.5
	773	44.0	41.0	3.0
5%Fe /Al	573	17.0	8.0	9.0
	673	23.5	11.5	12.0
	773	27.5	12.0	15.5

The results are given in table. 2 indicate a noticeable influence of the textural characteristics of the catalyst on its activity in the hydrogenation of CO₂ into methane, the yield of which increases from 58 to 68%.

Table 2

Hydrogenation of CO₂ on a 5% Fe, 15% Ni/ γ -Al₂O₃ catalyst with an alumina base: conventional γ -Al₂O₃ and γ -Al₂O₃ obtained with a developed surface

Catalyst	T, K	Conversion of CO ₂ , %		Yield, CH ₄ , %	
		1	2	1	2
5% Fe- 15% Ni/ γ - Al ₂ O ₃	573	55	65	53	63
	673	62	72	58	68
	773	58	67	52	62

Table 3 shows the test results of catalyst for the methanation reaction at optimal composition 5% Fe, 15% Ni/80% Al₂O₃, subjected to preliminary reduction at different temperatures.

Table 3

The results of testing CO₂ hydrogenation catalysts 5% Fe, 15% Ni/ γ -Al₂O₃, reduced in a hydrogen flow for 1 hour at 573, 673 and 773K (CO₂: H₂= 1: 4, p=0.1 MPa, W= 200 h⁻¹)

Catalyst	Temperature, K		Conversion of CO ₂ , %	Yield and selectivity of CH ₄ , %		
	Reduction temperature, K	Reactions		B	C	
Fe, Ni/ γ - Al ₂ O ₃	573	573	52	50	96.2	
		673	63	56	88.9	
		773	56	52	92.9	
	673	573	65	63	63	96.9
		673	72	68	68	94.4
		773	69	62	62	89.9
	773	573	42	34	34	80.9
		673	46	38	38	82.6
		773	44	32	32	72.7

The greatest activity in the methanation reaction is shown by iron-nickel-aluminum oxide catalysts reduced for 1 hour at 673K. The maximum methane yield – 68% is observed at a temperature of 673K. As the reaction temperature increases from 673 to 773 K, the reaction selectivity for methane decreases from 96.9 to 72.7 wt%.

To establish the reasons for the influence of the conditions of preliminary thermal reduction treatment of the catalyst with hydrogen on its activity, in the reaction of carbon dioxide hydrogenation, along with measurements of catalytic activity, the elemental composition of the surface, phase composition and magnetic characteristics of the synthesized systems were studied. In table Figure 4 shows the results of studying the elemental composition of a 5% Fe, 15% Ni / γ -Al₂O₃ catalyst by scanning at each of 4 surface points using an X-ray fluorescence microscope.

X-ray fluorescence analysis data (Table 4) show an almost uniform distribution of active components in the structure of the 5%Fe, 15%Ni/ γ -Al₂O₃ catalyst.

Table 4

The content of elements in each of the 4 points of the scanning surface of 5%Fe, 15%Ni/ γ -Al₂O₃ catalysts

Element	weight, %	Formula	weight, [%]
²⁶ Fe	4.1	Fe ₂ O ₃	5.8
²⁸ Ni	13.3	NiO	16.9
¹³ Al	39.6	Al ₂ O ₃	74.8
O	43.0	–	–
²⁶ Fe	3.4	Fe ₂ O ₃	4.9
²⁸ Ni	12.1	NiO	15.4
¹³ Al	40.1	Al ₂ O ₃	75.7
O	44.4	–	–
²⁶ Fe	5.18	Fe ₂ O ₃	7.4
²⁸ Ni	14.0	NiO	17.8
¹³ Al	39.1	Al ₂ O ₃	73.8
O	41.7	–	–
²⁶ Fe	4.3	Fe ₂ O ₃	6.1
²⁸ Ni	14.9	NiO	19.0
¹³ Al	40.7	Al ₂ O ₃	76.9
O	40.1	–	–

Below in Fig.1–4 show SEM images and the results of elemental analysis (Table 5) of the surface composition of a 5%Fe, 15%Ni/80% γ -Al₂O₃ oxide catalyst, the original one, oxidized at 773 K in a flow of air for 4 hours and reduced in flow of hydrogen for 1 hour at temperatures 573, 673 and 773K.

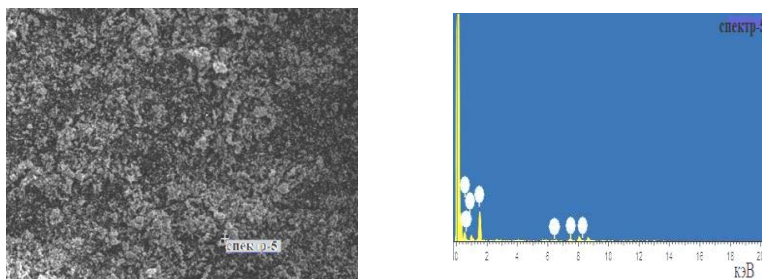


Fig.1. SEM image of surface energy dispersive elemental analysis of oxidized 5%Fe,15%Ni/Al catalyst

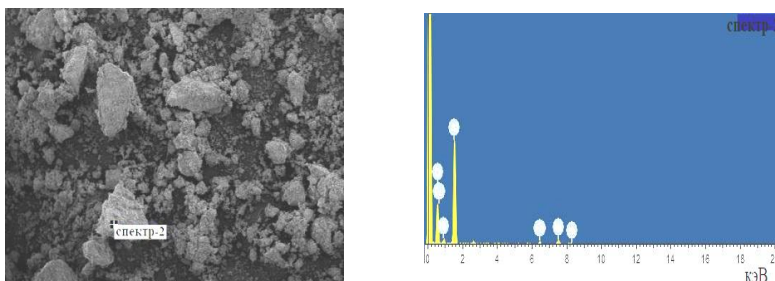


Fig. 2. SEM image of the surface and energy dispersive elemental analysis of the 5%Fe,15%Ni/Al catalyst reduced in a hydrogen flow at 573K

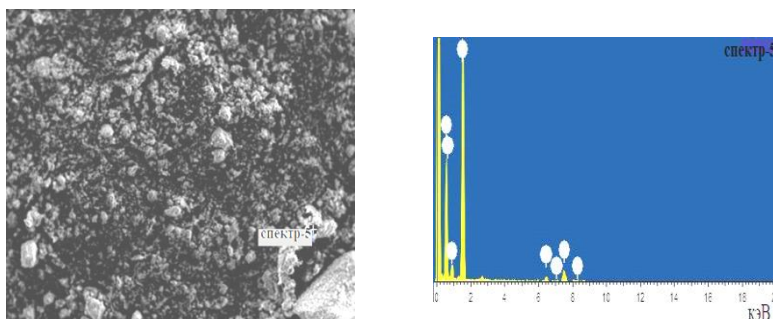


Fig. 3. SEM image of the surface and energy dispersive elemental analysis of the 5%Fe,15%Ni/Al catalyst reduced in a hydrogen flow at 673K

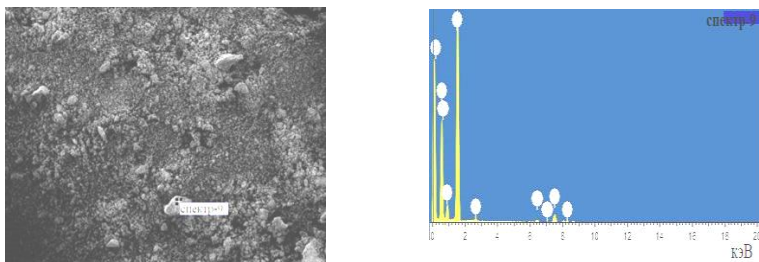


Fig. 4. SEM image of the surface and energy dispersive elemental analysis of hydrogen reduced in a stream at 773K 5%Fe,15%Ni/Al

Table 5

Distribution of elements in 5%Fe,15%Ni/Al* oxide catalyst - oxidized and reduced at 573, 673 and 773 K according to ED analysis

Element	weight %	At-om.%	weight %	At-om.%	weight %	at-om.%	weight %	At-om.%
	1		2		3		4	
AlK	43.75	35.86	42.77	35.86	40.06	34.49	41.91	35.97
FeK	2.80	1.48	3.47	1.38	3.10	0.88	3.15	1.20
NiK	10.79	3.69	11.16	3.79	15.53	6.01	12.04	3.98
O	42.66	58.97	42.60	58.97	41.31	58.62	42.90	58.85

*Samples - original (1), restored at 573K (2), 673K (3), and 773K (4).

As can be seen from the table above, there is a tendency towards a decrease in oxygen content with increasing temperature of sample treatment with hydrogen. There is a noticeable discrepancy in the nickel content in the oxidized and reduced samples, and its concentration is noticeably higher in the samples subjected to hydrogen treatment at 673K than in the samples subjected to hydrogen treatment at 773K, as indicated by the X-ray diffraction patterns of 5% Fe, 15% Ni/Al oxide catalyst – original and reduced at 573, 673 and 773K, shown in Fig. 5. This fact can be explained by the characteristic feature of nickel - its segregation to the outer surface during reduction, the highest content of which is observed when the sample is reduced with hydrogen at 673K. Reduction at 773K leads to a decrease in the nickel content on the outer surface.

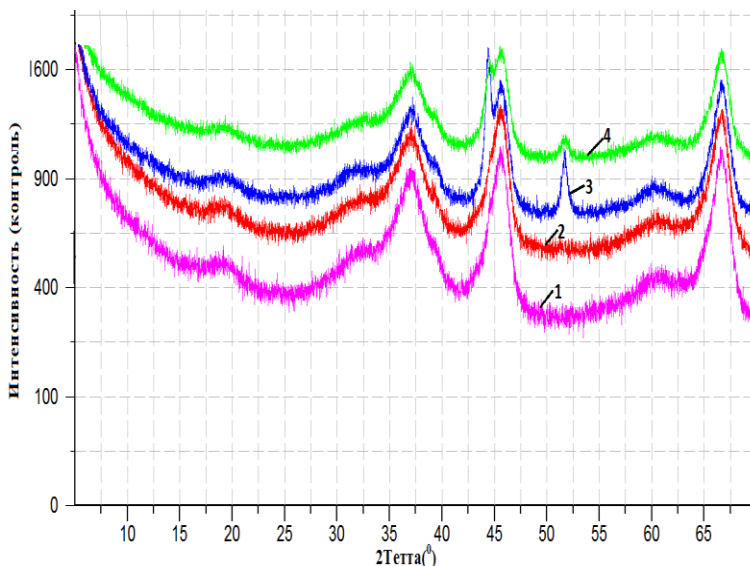


Fig.5. X-ray diffraction patterns of 5%Fe,15%Ni/Al oxide catalyst: 1-initial and reduced in a hydrogen flow at 573 (2), 673 (3), and 773K (4)

The results of X-ray phase analysis showed that with increasing temperature of the preliminary reduction of the catalyst in a flow of air, the phase composition of the catalyst noticeably changes. The phase composition and size of crystallites, estimated using the Debye–Scherrer equation, are presented in Table 6. Table 6 data show that the oxidized catalyst is characterized mainly by the phases of hematite Fe_2O_3 , nickel aluminate NiAl_2O_4 and NiO .

Catalysts reduced at temperatures of 573 and 673K contain magnetite Fe_3O_4 , metallic nickel and small amounts of nickel oxide and nickel aluminate, while those reduced at 773K contain mainly FeNi_3 alloy, metallic nickel, metallic iron and a small amount of magnetite Fe_3O_4 .

Since the maximum yield of the target product is observed for samples reduced at a temperature of 673 K, then from the data in table. 6, it can be assumed that the phases of magnetite Fe_3O_4 and metallic nickel Ni are responsible for the process of hydrogenation of carbon dioxide into methane.

Table 6

Phase composition and average crystallite size of 5%Fe,15%Ni/ γ -Al₂O₃ catalyst oxidized at 773K and reduced at 573, 673, 773K

Phases	The content of the identified phases, in relative % and the average crystallite size (P)							
	Original catalyst		Preliminary reduction temperature of the initial catalyst in a hydrogen flow, K					
	%	P	573		673		773	
			%	P	%	P	%	P
γ -Al ₂ O ₃	71.3	23.1	69.2	23.1	68.7	23.1	63.5	23.1
Fe ₂ O ₃	4,2	28.9	3.8	26.8	—	—	—	—
Fe ₃ O ₄	—	—	5.0	30.5	17.5	28.9	2.5	27.5
NiAl ₂ O ₄	18.0	22.8	9.8	21.2	—	—	—	—
Ni	—	—	4.4	13	10.5	11	5.0	15
FeNi ₃ -	—	—	—	—	—	—	14.3	16.5
NiO	6.5	30.8	7.7	28.4	3.3	20.8	—	—
Fe	—	—	—	—	—	—	14.7	14

Figure 6 shows the EPR spectra of a 5%Fe, 15%Ni/Al oxide catalyst: a) original, b) reduced in a stream of hydrogen for 1 hour, at temperatures: 1) 573, 2) 673, 3) 773K.

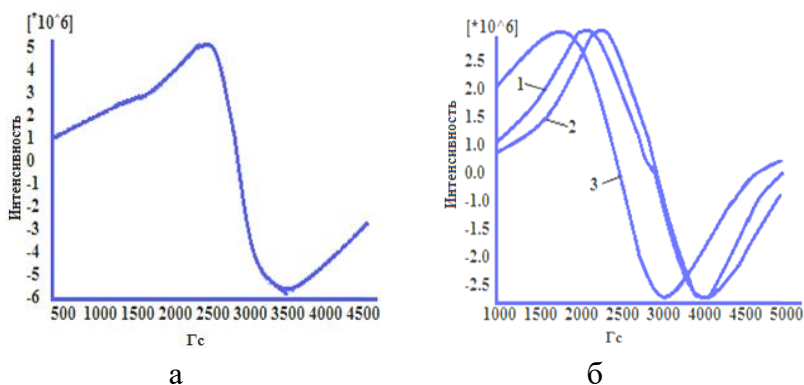


Fig.6. EPR spectra of 5%Fe,15%Ni/Al oxide catalyst: a) original, b) reduced in a hydrogen flow at: 1 - 573K; 2 - 673K; 3 - 773K

Next, in fig. 6 was shown the EPR spectra of 5%Fe,15%Ni/Al oxide catalyst: a) initial (oxidized) and b) reduced in a hydrogen flow for 1 hour, at temperatures: 1) 573, 2) 673, 3) 773K.

The EPR spectra shown are typical for samples of iron-nickel containing catalysts of superpara/ferromagnetic nature. The values of magnetic resonance parameters determined from the EPR spectra are given below in table 7.

Table 7

Values of magnetic resonance parameters of 5%Fe,15%Ni/Al oxide catalyst, initial and reduced in a hydrogen flow at 573, 673 and 773 K

Catalyst reduced at T, K		Spectral width ΔH , mT	Particle size, in nm	Resonance field, mT
5%Fe,15% Ni /Al	573	1350	11.9	2400
	673	1900	6.8	2700
	773	1600	7.9	2800
	initial	1250	26.5	3000

As can be seen from Fig. 6 and Table 7, the conditions of thermal reduction treatment of samples significantly affect the intensity, type and values of the magnetic resonance parameters of the ESR spectra. The difference is due to a change in the magnetic state of the catalyst. Research shows that under reaction conditions the catalyst is superparamagnetic and is a nanostructured oxide system with a magnetic particle size of less than 10 nm.

The results of chromatographic analysis of the composition of gas-phase products of hydrogenation of CO₂ into hydrocarbons on Fe, Zr/Al and Zr/Al oxide catalysts are presented in table 8. As can be seen from table. 8, the yield and distribution of gas-phase CO₂ hydrogenation products depend on the composition of the catalyst and the content of active components in them. The main products of CO₂ hydrogenation in the presence of the above catalysts are methane, ethane, carbon monoxide and water. The maximum activity of the catalysts in the formation of methane was found at 673 K on the 35% Fe, 15% Zr/Al catalyst. The data obtained show that iron-nickel

containing catalysts are more active in the methanation of carbon dioxide than iron-zirconium catalysts; there is also a noticeable influence of the textural characteristics of the aluminum oxide base on the catalytic properties. Thus, the maximum yield of the target methane product in the case of a catalyst with a “purchased” aluminum oxide base is 18.5%, and in the case of a catalyst with a developed surface – 26.5%. A comparison of data from catalytic studies of iron-nickel and iron-zirconium containing catalysts shows that Fe-Ni containing catalysts are more active in the reaction of hydrogenation of carbon dioxide to methane.

The results of chromatographic analysis of the composition of gas-phase products of hydrogenation of CO₂ into hydrocarbons on Fe, Zr/Al and Zr/Al oxide catalysts are presented in Table 8.

Table 8

Gas-phase products of CO₂ hydrogenation to hydrocarbons on Fe, Zr/Al and Zr/Al oxide catalysts*. CO₂:H₂ = 1:4, P = 0.1MPa, temperature 573-773K

Catalyst	T,K	Conversion, %	CH ₄	C ₂ H ₆	CO
			Yield	Yield	Yield
5%Fe,15%Zr/Al	573	10,0	7.3	–	2.7
	673	14.0	11.4	0.40	2.2
	773	12,0	10.0	0.20	1.8
20%Fe,15%Zr/Al	573	16,0	11.4	–	4.6
	673	19,0	14.7	0.9	3.4
	773	17,0	14.3	0.5	2.2
35%Fe,15%Zr/Al	573	22.0	16.0	–	6.0
	673	23.5	18.5	1.0	4.0
	773	22.0	18.0	0.5	3.5
35%Fe,15%Zr/Al (γ-Al ₂ O ₃ - with de- veloped surface)	573	28.0	21.5	–	6.5
	673	31.5	26.5	0.5	4.5
	773	28.5	24.0	0.4	4.1
35%Fe /Al	573	19.5	8.0	–	11.5
	673	25.5	12.0	–	13.5
	773	24.5	9.5	–	15.0
15%Zr /Al	573	8.5	6.0	1.5	1.0
	673	13.5	8.5	3.5	1.5
	773	15.0	9.0	4.0	2.0

Table 9 shows the phase composition and average size of crystallites (coherent scattering regions), estimated from X-ray diffraction patterns of the original and reduced 35%Fe,15%Zr/ γ -Al₂O₃ catalyst. X-ray phase analysis data (Table 9) show that the original sample (not reduced) is characterized by the presence of γ -Al₂O₃, Fe₂O₃, ZrFe₂O₄ phases, and the reduced one is characterized by the presence of γ -Al₂O₃, Fe₃O₄ and ZrO₂ phases. The average crystallite size determined on the basis of X-ray diffraction patterns using the Debye-Scherrer method varies in the range from 23.6 to 37.5 nm.

Table 9

Phase composition and average crystallite size of 35%Fe, 15%Zr/ γ -Al₂O₃ catalyst oxidized with air at 773K for 4h and reduced at 673 K with hydrogen

phases	Phases and size of 35%Fe,15%Zr/ γ -Al ₂ O ₃ catalyst crystallites, in nm			
	Oxidized with air at 773K		Reduced at 673 K with hydrogen	
	Relative, %	Phase size, nm	Relative, %	Phase size, nm
γ -Al ₂ O ₃	44.5	23.6	43.2	23.6
Fe ₂ O ₃	31.2	37.5	–	–
Fe ₃ O ₄	–	–	34.8	32.2
ZrFe ₂ O	14.2	33.3	–	–
ZrO ₂	10.1	30.7	–	–

The EPR spectra of the 35%Fe–15%Zr/Al oxide sample, the original, spent and reduced catalyst are shown in Fig. 7. The presented EPR spectra of Fe,Zr/Al oxide catalysts indicate the presence of superpara/ferromagnetic particles in their composition.

Table 10 shows the parameters calculated from the EPR spectra for the 35%Fe–15%Zr/Al system of the original reduced at 673K), spent and reduced at 673K after working out. ($g_e = 2.0036$).

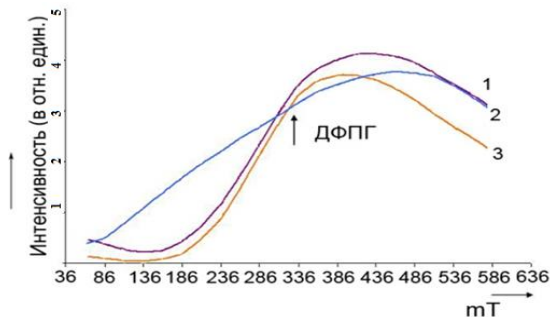


Fig.7. EPR spectrum of 35%Fe-15%Zr/Al oxide catalyst: 1-original, 2-spent, and 3-reduced.

Table 10

EPR parameters of 35%Fe–15%Zr/Al original (reduced at 673K), spent and reduced after working out

Catalyst	T, K	Particle size, nm	Resonance field, mT	Linewidth, mT
35%Fe,15%Zr/Al	original, reduced	10.0	302.2	125.0
	working out	22.5	276.7	131.8
	reduced after working out	11.5	298.5	120.4
35%Fe /Al	reduced	13.5	270.4	130.7
15%Zr/Al	—	—	—	—

Particle sizes estimated from EPR spectra range from ~10 to 22 nm. It should be noted that only iron-containing catalysts have magnetic properties. Samples containing only zirconium do not exhibit EPR signals. The monometallic, reduced iron catalyst has a magnetic particle size of 13.5 ± 3 nm. For a bimetallic iron-zirconium catalyst on an alumina base, an ESR spectrum characteristic of supersteam/ferromagnetic particles is also observed (Table 8). The effect of zirconium on the magnetic resonance characteristics of iron-zirconium samples is to reduce the particle size, and is most likely due to the redistribution of these magnetic particles within the catalyst. Note that the reduced catalysts at 673K are superpara/ferro-

magnetic with a particle size of 12 ± 3 nm, almost 2-3 times smaller than the average crystallite size (23.6-37.5 nm) determined from XRD patterns.

Below are the results of a study of the kinetics of the hydrogenation reaction of CO_2 into methane on the $\text{Fe,Ni}/\gamma\text{-Al}_2\text{O}_3$ catalyst. Figure 8(a,b,c,d) shows the results of a study of the influence of operating parameters on the yield of methane (U) in the reaction of CO_2 hydrogenation on a $\text{Fe,Ni}/\text{Al}$ oxide catalyst.

Below are give the results of a study on the optimization of the process of hydrogenation of CO_2 into methane and the kinetics on the catalyst $\text{Fe,Ni}/\gamma\text{-Al}_2\text{O}_3$.

Optimization of CO_2 hydrogenation on $\text{Fe,Ni}/\gamma\text{-Al}_2\text{O}_3$ catalysts

To study the optimization of CO_2 hydrogenation on the $\text{Fe,Ni}/\gamma\text{-Al}_2\text{O}_3$ catalyst, the effect of operating parameters on the yield of methane (Y) was studied.

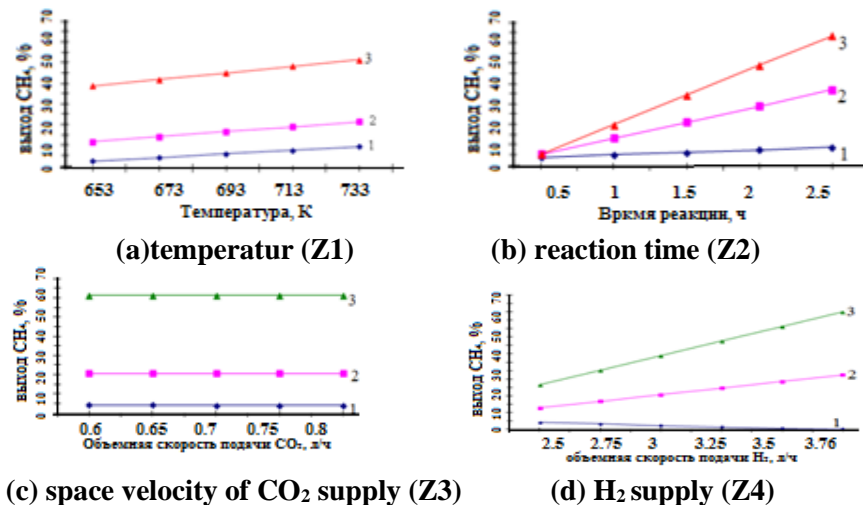


Fig. 8 (a, b, c, d). Dependence of CH_4 yield on temperature (Z1), reaction time (Z2), space velocity of CO_2 supply (Z3) and H_2 supply (Z4).

The output function, taking into account the regime parameters, presented in the form: $Y = a_0 + \sum_{i=1}^n \alpha_i \cdot Z_i + \sum_{i=1}^n \alpha_{ij} \cdot Z_i \cdot Z_j (i \neq j)$

Mathematical processing of experimental data for each factor was calculated according to this equation (Y). With the calculated optimal values of the input variables found, a control experiment was set up, which made it possible to determine the value of the methane yield $Y \sim 70\%$, which indicates the acceptability of the developed regression model.

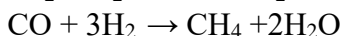
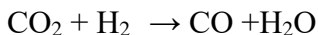
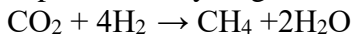
In order to identify the main kinetic regularities of the hydrogenation process, allowing us to suggest its probable mechanism, we studied the dependence of the concentration (Cp) of the initial and final products of the carbon dioxide hydrogenation reaction on the contact time (τ) and temperature (table 11).

Table 11

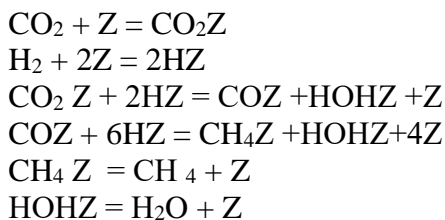
Concentration (Cp) of the initial and final products of the reaction of the interaction of carbon dioxide and hydrogen depending on the contact time (τ)

T, K	τ -sek	Starting reagents, Cp - mol/l		Final products, Cp - mol/l		
		CO ₂	H ₂	CH ₄	CO	H ₂ O
573	5	0.0164	0.066	0.00577	0.00865	0.00285
	10	0.00965	0.0574	0.0124	0.0175	0.00295
	15	0.0047	0.0504	0.0177	0.0245	0.00255
673	5	0.0152	0.065	0.0066	0.0098	0.0041
	10	0.008	0.054	0.0136	0.0208	0.0033
	15	0.0032	0.046	0.0194	0.028	0.0029
773	5	0.0129	0.063	0.0082	0.0115	0.0022
	10	0.0065	0.055	0.0148	0.0126	0.0035
	15	0.0025	0.050	0.0121	0.025	0.0033

The revealed patterns made it possible to propose a probable mechanism for the process of hydrogenation of CO₂ into methane:



Stage scheme of the mechanism:



To build a kinetic model, we used the equation

$$\frac{dC_i}{dt} = \sum Y_{ik} \cdot W_k$$

on the basis of which the kinetic parameters and kinetic constants are calculated (table 12).

Table 12

Kinetic parameters of the interaction of carbon dioxide and hydrogen

k_i	Temperature, K			Activation energy E_i -kcal/mol	Preexponential factor k_{0i}
	573	673	773		
k_1	0.00695	0.009	0.0357	17.53	0.815×10^4
k_2	0.0104	0.019	0.035	13.18	0.633×10^3
k_3	0.025	0.043	0.0646	10.41	0.313×10^3

The kinetic model, compiled on the basis of the chosen scheme of the reaction mechanism, at the found values of the rate constants, well describes the reaction of CO₂ hydrogenation.

2. HYDROGENATION OF CARBON DIOXIDE TO METHANOL

The results of a study of the hydrogenation of CO₂ into methanol at atmospheric pressure and a temperature range of 473–773K on Co–Pd-containing catalysts based on Siral aluminosilicates with various SiO₂/Al₂O₃ ratios of 1.10.40 are presented. Elemental and phase compositions, IR spectra, dynamic light scattering (DLS) spectra, electron magnetic resonance (EPR) spectra, and thermal characteristics of catalysts have been studied. The specific surface area and specific pore volume have been determined, and a proba-

ble mechanism for the formation of methanol has been proposed.

The content of active components in the catalysts correspond to: 10% Co, and 10% Co, 0.5% Pd on Siral 1, 10, 40. The values of the specific surface area and specific pore volume of Co and Co-Pd containing catalysts on Siral-1,10,40 aluminosilicates, pre-calcined at 823K in a stream of air and then reduced in a stream of hydrogen at 723K for 1 hour are given in table 13.

Table 13

Specific surface area and pore volume of 10%,Co,10%Co, 0.5% Pd - catalysts on Siral 1, 10, 40

Catalysts	SiO ₂ content, wt. %	Specific surface area, m ² /g	Specific pore volume, sm ³ /g
Co/S-1	1	284	0.46
Co/S-10	10	343	0.54
Co/S-40	40	409	0.63
Co,Pd/S-1	1	242	0,36
Co,Pd/S-10	10	298	0.45
Co,Pd/S-40	40	355	0.56

The textural characteristics of the samples indicate a certain sequence of increasing values of the specific surface area and specific pore volume, depending on the SiO₂/Al₂O₃ ratio. This behavior is due to the stabilization of oxide particles of cobalt and palladium metal on the surface of the substrate. Results of chromatographic analysis of the composition of the gaseous products of CO₂ hydrogenation on Co/Siral -1,10,40 and Co, Pd/S-1,10,40 catalysts are presented in Tables 14 and 15.

Data of Table14 show that on catalysts containing only cobalt, at a reaction temperature ≤ 573 K, practically only methane is formed, at a reaction temperature $T \geq 573$ K - methane and no more than 1% carbon monoxide, and with an increase in the SiO₂/Al₂O₃ ratio, a decrease in the methane yield is observed. The maximum methane yields (55% and 41%) at a reaction temperature of 573 K are observed on the Co/S-1 and Co/S-10 catalysts, respectively. The Co/Siral-40 catalyst exhibits little activity in the hydrogenation of CO₂ to methane, which indicates that the reaction of hydrogenation of CO₂ to methane depends on the SiO₂/Al₂O₃ ratio.

Table 14

Products of CO₂ hydrogenation on Co-containing catalysts on aluminosilicates Siral-1, 10, 40 (P = 0.1 MPa, CO₂ : H₂ = 1:3, vol. W=120 h⁻¹)

*Catalyst	T,K	Conversion of CO ₂ , %	CH ₄		CO	
			Sel.	Yield	Sel.	Yield
Co/Siral-1	473	51	100	51	–	–
	573	55	100	55	–	–
	673	52	98.7	51.3	1.3	0.7
	773	41	97.8	40	2.2	1.0
Co/Siral-10	473	38	100	38	–	–
	573	41	100	41	–	–
	673	37	97.3	36	2.7	0.99
	773	28	96.8	27.1	3.2	0.89
Co/Siral-40	473	29	100	29	–	–
	573	33	100	33	–	–
	673	28	96.4	27	3.6	0.98
	773	25	98.8	24.7	1.2	0.3

Table 15

Composition of CO₂ hydrogenation products on Co-containing catalysts based on aluminosilicates /Siral-1,10,40 (reaction conditions: P = 0.1 MPa, CO₂ : H₂ = 1:3, vol. W = 120 h⁻¹)

Catalyst	T, K	Con- version of CO ₂ , %	Selectivity and yield%					
			CH ₄		CO		CH ₃ OH	
			Sel.	yield	Sel.	yield	Sel.	yield
Co,Pd/S-1	473	49	98.8	48.4	1.2	0.6	–	–
	573	54	91.1	49.2	6.7	3.6	2.19	1.2
	673	56	75.5	42.3	11.96	6.7	12.54	7.0
	773	64	63.6	40.7	12.34	7.9	24.06	15.4
Co,Pd/S-10	473	54	98.5	53.2	1.5	0.8	–	–
	573	58	78.1	45.3	7.1	4.1	14.8	8.6
	673	62	70.0	43.4	5.0	9.8	18.5	12.5
	773	69	55.7	38.4	15.2	10.5	29.1	20.1
Co,Pd/S-40	473	41	99.2	40.6	0.57	0.4	–	–
	573	43	96.3	41.4	1.4	0.6	2.3	1
	673	44	91.8	40.4	2.32	1.2	5.88	2.4
	773	45	79.1	35.6	5.6	2.5	15.3	6.9

The introduction of palladium into the catalyst stimulates the formation of methanol (table 15), the yield of which increases with increasing reaction temperature and reaches its maximum value at a temperature of 773 K.

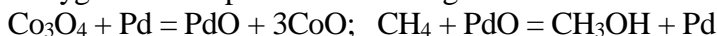
The maximum methanol yield (20.1%) is observed on the Co,Pd/S-10 catalyst at a temperature of 773 K and atmospheric pressure. It was shown that the activity of the Co,Pd/Siral catalyst containing S-1.10 compared to the catalysts with S-40 is noticeably higher, which indicates the dependence of the hydrogenation of CO₂ into methanol on the SiO₂/Al₂O₃ ratio. The dependence of the catalytic properties of these systems on the Al₂O₃/SiO₂ ratio is most likely associated with the textural features and acidic properties of the aluminosilicate base. One of the key properties of Siral aluminosilicates is their relatively high acidity. The concentration and type of acid sites (Lewis, Brønsted) strongly depend on the Al₂O₃/SiO₂ ratio. The highest concentration of Lewis acid sites is observed for Siral - up to 10, while the largest number of Brønsted acid sites are found for Siral – 30 and 40. Therefore, it can be assumed that Lewis acid sites play a significant role in the hydrogenation of CO₂ into methanol. The SiO₂/Al₂O₃ ratio in the samples significantly affects their X-ray diffraction patterns and EPR spectra. Table 16 shows the results of analysis by X-ray diffractometry of the phase composition of oxidized and reduced samples of the Co,Pd/Siral 10 catalyst.

Table 16
Phase composition and average crystallite size of the oxidized and reduced catalyst 10%Co, 0.5%Pd /Siral -10

phases	Phase composition and average crystallite size, in nm	
	Oxidized	Reduced
$\gamma\text{-Al}_2\text{O}_3$	23.6	23.6
SiO ₂	24.5	24.5
Co ₂ O ₃	31.5	–
PdO	27.8	–
PdCoO ₂	33.4	–
CoO	29.4	–
Co ₃ O ₄	–	32.5
Co-Pd	–	<10
Pd	–	<10

The initial sample of the Co, Pd/S-10 catalyst is characterized by the presence of Co_2O_3 , PdO, PdCoO₂ and CoO phases, and the reduced Co_3O_4 phase, CoPd and Pd particles. The crystallite sizes vary from ~10 to 34 nm.

A study of the activity of Co/S-1,10,40 catalysts revealed the formation of only methane and no more than 1% carbon monoxide. When palladium was introduced into the catalyst, the formation of methanol was observed. Based on the data obtained, it can be assumed that the formation of methanol occurs at active centers, which include cobalt and palladium. It can also be assumed that the introduction of palladium into Co-containing samples stimulates the oxidation reaction of methane to methanol. At the first stage of this reaction, the introduced palladium activates oxygen to form particles according to the reaction:



EPR analysis data showed that the composition of the matrix significantly affects the magnetic state of the Co, Pd/S-10 and Co/S-10 samples and, consequently, the catalytic activity (Fig. 9 - a, b).

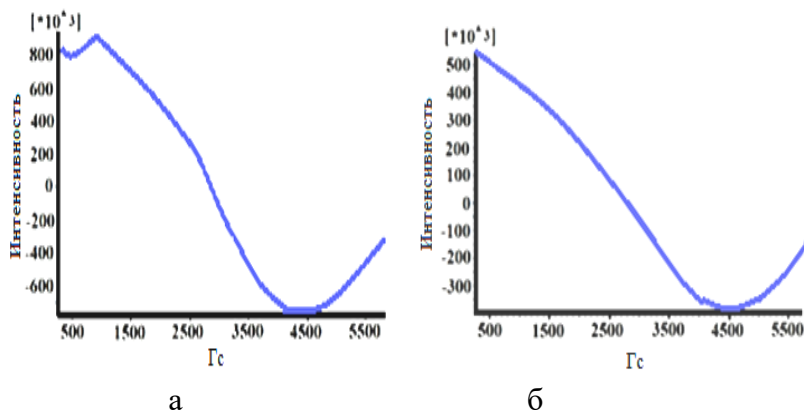


Fig. 9 (a, b). EPR spectra recorded at room temperature for the following catalysts: a) Co/S-10 and b) Co,Pd/S-10

Based on these EPR spectra, the parameters and sizes of magnetic particles were calculated. The values of the parameters and sizes of the magnetic particles of the Co/S-10 and Co,Pd/S-10 catalysts are indicated below in table 17.

Table 17

Parameters of EPR spectra and sizes of magnetic particles of 10%Co (1) and 10%Co,0.5%Pd (2) on Siral-10 reduced at 723K in a hydrogen flow

Catalyst Катализатор	Particle Size, in nm	Resonant field, in mT	Linewidth, in mT
Co/S-10	25	1710	2850
Co,Pd/S-10	15	2900	1600

When Pd is introduced into the Co/S-10 system, the shape of the signal from ferromagnetic Co_3O_4 particles changes noticeably. Definitely it can be argued that this change is due to a change the magnetic state of cobalt oxide particles as a result of the reaction of a certain number of palladium particles with Co_3O_4 particles and their redistribution in the catalyst structure, a change in the dispersed state of these particles, their size, causing a change in the magnetic interactions between them. In Co,Pd/S-10 samples calcined at 823K and then reduced in a stream of hydrogen at 723K, palladium is reduced to a zero-valent state and is stabilized in the form, most likely, of nano-sized particles, dispersing ferromagnetic particles of cobalt oxide in the surface layer of the catalyst. The palladium particles thus change their magnetic state, which also affects the particle size. The size of magnetic Co_3O_4 particles with the introduction of palladium into the Co/S-10 catalyst decreases from 25 to 15 nm (table 17). That is, it can be assumed that during thermal reduction treatment the magnetic state of the catalyst changes significantly. With a change in particle size, their distribution, as well as activation of oxygen with the formation of PdO particles as a result of the reaction $\text{Co}_3\text{O}_4 + \text{Pd} = \text{PdO} + 3\text{CoO}$, the direction of the carbon dioxide hydrogenation reaction changes.

Mechanism of methanol formation on palladium-containing catalysts with alumina and aluminosilicate bases

Below are thermograms of samples of the Co,Pd/S-10 catalyst with adsorbed methanol at room temperature (Fig. 10).

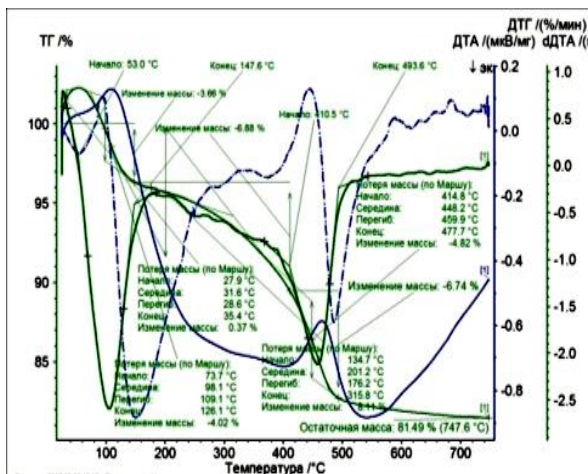


Fig. 10. Thermograms of the Co,Pd/S-10 catalyst with adsorbed methanol

Table 18 shows the values of mass loss with increasing heating temperature of catalyst samples with methanol adsorbed at room temperature.

Table 18

Parameters according to thermograms of the Co,Pd/S-10 catalyst with adsorbed methanol

Catalyst	Beginning, T, K	End, T, K	Weight loss, %	Residual mass, %
Co,Pd/S-10	330	430	4.02	81.49
	460	760	8.11	
	770	930	4.82	

Based on the thermograms in fig. 10 and table 18, we can say that the most clearly manifested peaks are observed at temperatures of 370 and 700K, which correspond to temperature intervals of ~ 330–430 and 460–760K. It should be noted that the first peak at relatively low temperatures contains mainly physically adsorbed methanol, as well as water. The second peak is the products of chemisorbed methanol – CO, H₂, CH₄, as well as oxygen-containing fragments. The third peak contains mainly products of deep oxidation. Because we observed the main peaks on the thermogram at temperatures of

370 and 700 K, then to establish the intermediate products formed at these temperature intervals, these peaks were studied by the IR method, heating the catalyst with methanol deposited on the surface in turn to a temperature of 370 and 700 K (Fig. 11, a, b).

The IR spectrum (Fig. 11b) shows new bands at 2977 and 2895 cm^{-1} . This suggests that methanol does not convert at low temperatures, and if it does, then it is very insignificant. At 700 K, decomposition of chemisorbed methanol is observed; at a temperature of intensive formation of methanol. Thus, we can say that methanol decomposes into methyl groups or transforms into oxygen-containing compounds (we believe that into formic acid or formate).

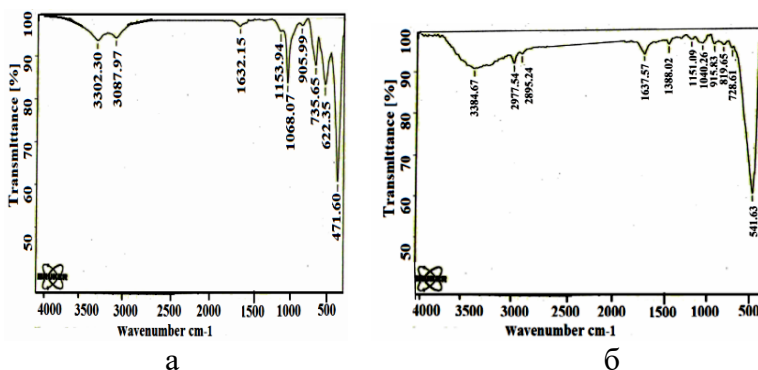
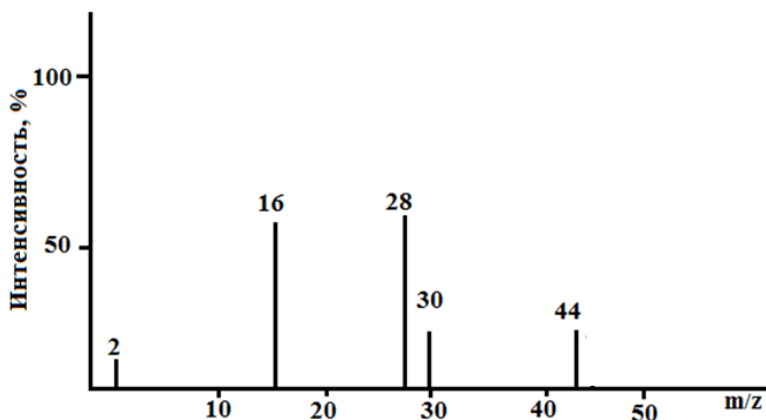


Fig.11 (a, b). IR - from the spectrum of the catalyst Co,Pd/S-10 with precipitated methanol: (a) - heated up to 370K; (b) - up to 700K

To confirm our assumptions, the Co, Pd/S-10 catalyst with methanol deposited on the surface and heated to 700K was studied by a combination of the thermal analysis method with a mass spectrometric method for studying the gas phase in an isothermal, dynamic mode (Fig. 12).

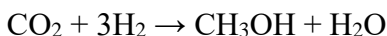
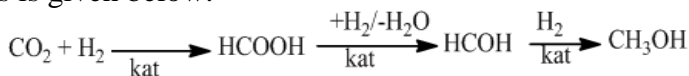
The data of mass-spectrometric analysis in combination with thermal analysis showed the presence of desorption products, the formation of formaldehyde. That is, on the basis of experimental data and literature data, it can be said that the probable mechanism of methanol formation on Co, Pd-containing catalysts proceeds along the formate pathway.



2 - H₂, 16 - CH₄, 28 - CO, 30 - CH₂O, 44 - CO₂

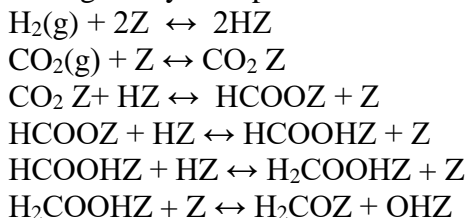
Fig.12. Mass-spectrometric analysis of methanol decomposition on Co,Pd/S-10 catalyst

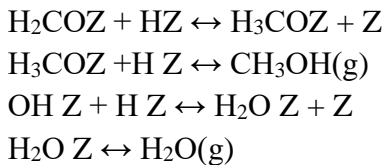
The probable mechanism of methanol formation on Co,Pd/S-10 catalysts is given below:



The given reaction mechanism consists of three successive stages: (1) conversion of CO₂ into formic acid; (2) the conversion of formic acid to formaldehyde and water; (3) conversion of formaldehyde to methanol.

The stepwise mechanism of methanol formation in the presence of Co, Pd-containing catalysts is presented below:





The given mechanism of CO₂ hydrogenation into methanol is based on the latest advances in the field of CO₂ hydrogenation research and our own data presented in the dissertation work. The results obtained in the presented dissertation work by combining chromatography-mass spectrometry, on-line thermogravimetric and IR spectroscopic studies indicate a number of features of the hydrogenation of CO₂ into methanol and make it possible to identify a number of stages of the hydrogenation reaction of CO₂ into methanol.

Kinetics of the process of thermal desorption of methanol adsorbed on the surface of the Co, Pd/S-10 catalyst

Kinetic studies of desorption from the surface of the catalyst Co, Pd/S-10, adsorbed methanol at room temperature were taken on the basis of thermal analysis curves. The study of thermal analysis shows that in the temperature range (according to TG data), 298–1023K, thermal stimulation occurs in at least five successive stages. If for the initial stage we take $\alpha=0$, the end $\alpha=1$, then in this case, to determine the speed of the process, we used the formula:

$$v = d\alpha / d\tau = \kappa(T) \cdot f(\alpha),$$

where: $\kappa(T)$ – dependence of temperature on constant speed; $f(\alpha)$ – a function that takes into account changes in the physico-chemical characteristics of the processes occurring in the system

$$\kappa(T) = \kappa_0 \exp(-E_a/RT)$$

where: E is the activation energy, A is the exponential constant.

Table 19 shows the values of the kinetic parameters of the thermal desorption of methanol from the surface of the Co,Pd/S-10 catalyst.

Table 19**Kinetic parameters of thermal desorption of methanol from the surface of the catalyst Co,Pd/S-10**

Stages	ΔT (T ₂ -T ₁)	$\Delta \alpha$	m	g(α)	Ea, kd/mol	lgA
1	62.5-100.2	0.01-7.84	1.99	$-\ln(1-\alpha)$	23.5	7.9
2	100.2-126.5	7.84-2.08	1.15	$-\ln(1-\alpha)$	38.3	6.8
3	126.5-409.7	2.08-2.31	0.92	$-\ln(1-\alpha)$	35.5	6.4
4	409.7-462.5	2.31-0.95	0.85	$(1-(1-\alpha)^{1/3})^2$	32.3	4.9
5	462.5-497.1	0.95-0.55	0.52	$(1-(1-\alpha)^{1/3})^2$	34.4	4.4

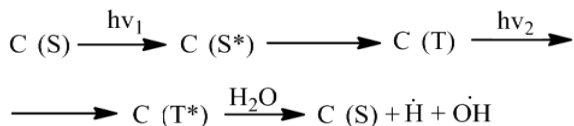
Where: ΔT – temperature interval, $\Delta \alpha$ – degree of conversion, m – % of the initial mass, the amount of moisture dehydrated from each stage, Ea – activation energy cd / mol, A – coefficient.

3. OBTAINING OF HYDROGEN

The main problem in implementing CO₂ hydrogenation is the economic feasibility of the process. Exhaust gases from petrochemical plants and air can be used as CO₂ resources. Human activities emit more than 30 billion tons of CO₂ into the atmosphere each year, almost 80% of which comes directly from fossil fuels. Hydrogen in industry is produced mainly by steam reforming of methane. It is expected that improvements in catalytic technologies for hydrogen production will improve energy efficiency, increase the range and reduce the cost of processes for producing useful products from CO₂. The hydrogen required for the technology can be produced by electrolysis and photodecomposition of water. Projects for integrated plants for the production of renewable methanol by hydrogenation of CO₂ are currently being developed.

Below are the results of a study of the photodecomposition of water with the participation of a number of zeolite (mordenite, clinoptilolite, NaX, NaY) catalysts in the presence of polycyclic aromatic hydrocarbons (PAHs) of oil isolated from the heavy pyrolysis resin fraction (fraction 473-573K) as sensitizers. It has been shown

that this fraction, rich in polycyclic aromatic hydrocarbons, is promising for the implementation of double sensitization during the decomposition of water using solar radiation. The reaction should be carried out under conditions under which “hot” hydrogen atoms are formed, extending beyond the “cage” due to their high kinetic energy. These conditions are realized with the participation of a sensitizer in the system, as well as compounds of elements of groups I and II of the periodic table.



where: S, S* and T, T* are the main and excited singlet and triplet states of sensitizer molecules, respectively.

Producing hydrogen by photodecomposition of water using solar radiation is one of the promising and environmentally friendly methods. However, the bulk of sunlight reaching the Earth is not enough to split the water molecule into hydrogen and oxygen. In this regard, of particular interest are the photochemical reactions of sensitized photolysis of water, where the elementary act uses the energy of two light quanta, sequentially absorbed by the sensitizer molecule. We used petroleum systems as sensitizer molecules, the electronic spectra of which cover a significant part of the solar radiation spectrum.

In industry, the only method used to produce hydrogen is steam reforming of methane. One of the most important chemical reactions suitable for the industrial production of hydrogen and giving rise to the synthesis of hydrocarbons (liquid fuel) and other technically valuable products is also the carbon dioxide conversion of methane into synthesis gas.

In the presented thesis, iron-nickel-containing oxide catalysts were tested as catalysts for the above reactions. These catalysts were prepared by impregnation based on metal nitrates using γ -Al₂O₃ as a binder, followed by calcination under reduced pressure (Growth = 10–15 mm Hg) and structure formers (urea, citric acid, triethanolamine), which made it possible to obtain samples of nanostructured catalysts with a developed specific surface area, optimal pore size and volume. When evacuating

Fe-Ni/Al oxide catalyst samples in the range of 573–773K, superpara/ferromagnetic particles with a certain size are formed that are active in the methanation of CO₂ and at 973–1123K - in the steam reforming of methane. The best results for steam reforming of methane were achieved on a catalyst with the composition wt.%: Fe₂O₃–65; NiO–15; γ -Al₂O₃–20. The same composition of Fe-Ni/Al oxide catalyst, evacuated in the range of 823–923K, was tested in water decomposition. This process occurs at the stage of reduction of samples of the original catalysts under vacuum conditions at a temperature of 823 K. It was found that the conversion of water occurs on the surface of the reduced iron. The role of nickel in the water conversion reaction is to modify and stabilize reduced iron with a certain structure and particle size. At this temperature, both the iron and nickel-containing oxide phases are reduced to “metallic” Fe, Ni and oxide phases with a reduced oxidation state of iron and nickel. The interaction of these structures with water at 553 – 573 K leads to the decomposition of water with the formation of hydrogen. The activity of the catalyst under reaction conditions remains unchanged in the presence of the reducing agent carbon monoxide in the reaction zone. The conversion of water to Fe,Ni/ γ -Al₂O₃ in the presence of carbon monoxide prevents the oxidation of free iron to its oxides, which eliminates catalyst deactivation. As a result of the experiments, it was established that the optimal reaction conditions are the ratio of carbon monoxide to water 1:1, at a temperature of 553–573 K, the hydrogen yield is 61.2% by weight, with a conversion of ~ 95%.

Below are the results of studies of the kinetic patterns of carbon dioxide conversion of methane into synthesis gas (CH₄ + CO₂ ↔ 2CO + 2H₂) on a nickel-magnesium catalyst, which is one of the methods for producing hydrogen. The process occurs at a temperature of 973 K. Note that recently this process has become the object of numerous studies. Methane and carbon dioxide, which are the main compounds causing the greenhouse effect, are converted into synthesis gas with a CO : H₂ ratio of ~ 1.0 - the feedstock for the production of liquid hydrocarbons and synthetic fuels.

The reaction kinetics is described by the first equation order in methane, the stage of interaction of methane with the catalyst surface is taken as the limiting stage. The dissertation presents the results of

constructing a kinetic model of the reaction of carbon dioxide conversion of methane into synthesis gas on a nickel-magnesium catalyst and a differential gradient-free reactor with a thin layer of catalyst.

Kinetic data for carbon dioxide conversion of methane on a nickel-magnesium catalyst are given in table 20.

Table 20

Kinetics of carbon dioxide conversion of methane at T= 1098K

Ni-MgO	$V^0_{mixture} \cdot \tau^{-1}$	x	$k, l \cdot \text{atm}^{-1} \cdot \text{q}^{-1} \cdot \text{h}^{-1}$
CH ₄ : CO ₂ = 1 : 1.5	2500	0.41	16.4
CH ₄ : CO ₂ = 1 : 1	2500	0.62	19.3
CH ₄ : CO ₂ = 1.5 : 1	2500	0.74	21.5
CH ₄ : CO ₂ = 1 : 1	5000	0.50	22.0
	7500	0.36	17.0
	10000	0.30	17.0

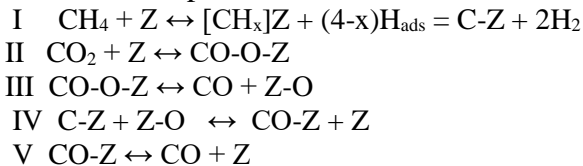
where: $k = 3.8 \cdot 10^{23} e^{\frac{114.5}{RT}}$

The kinetic equation is described as follows form:

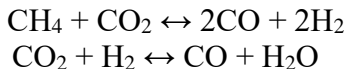
$$r^1 = \frac{k \cdot P_{\text{CH}_4}}{k_2 + k_1 P_{\text{H}_2}^2}$$

$\rightarrow 0 \leftarrow 0$

The presence of such a kinetic dependence unambiguously indicates that the rate-limiting stage is the stage of interaction of methane with the catalyst surface. In accordance with this, the mechanism of the process can be represented as:

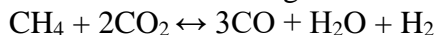


Simultaneously with the reaction of carbon dioxide conversion of methane into synthesis gas, the interaction of the resulting hydrogen with carbon dioxide occurs:



At atmospheric pressure and reaching a temperature of

1073K, the yields of hydrogen and carbon monoxide equalize, approaching 100%. In the limiting case, the process of carbon dioxide conversion of methane, taking into account the reverse reaction of water vapor, can be written in the following form:

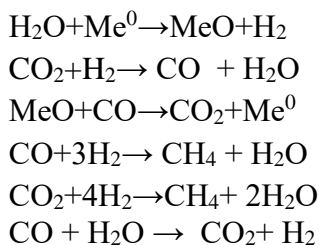


It is necessary to introduce a correction factor into the kinetic equation that takes into account this influence, i.e. actually the opposite reaction. However, this is true, in our opinion, only if the reverse reaction is implied in its classical version, and the initial $\text{CH}_4:\text{CO}_2$ ratio is equal to unity. The reversibility of chemical reactions in classical kinetics means that the products formed from them can, in principle, interact, turning back into the original substances within the limits limited by thermodynamic equilibrium under given conditions. It follows from this that the observed experimental reaction rate can be determined not only by the rate of transformation of the starting substances, but also by the rate of the simultaneously occurring reaction of the resulting products.

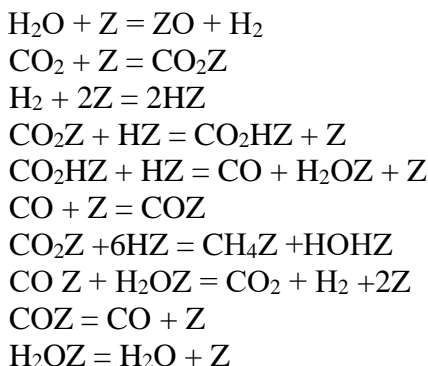
4. CONJUGATION OF REACTIONS OF DECOMPOSITION OF WATER VAPOR AND HYDROGENATION OF CARBON DIOXIDE INTO HYDROCARBONS

For the first time, the fundamental possibility of producing hydrocarbons (using methane as an example) by reacting water vapor with carbon dioxide according to a stage scheme on specially synthesized samples of Fe,Ni/ Al_2O_3 oxide catalyst at moderate temperatures and atmospheric pressure was experimentally demonstrated. The hydrogen required to construct the hydrocarbon molecule is not supplied from outside into the reaction zone, but is produced during the water conversion process itself. The synthesized catalysts were characterized by X-ray fluorescence microscopy, X-ray phase analysis, UV/Vis diffuse reflectance electron spectroscopy, and EMR spectroscopy. X-ray phase analysis of samples of this catalyst (Fe_2O_3 – 65%; NiO – 15%; $\gamma\text{-Al}_2\text{O}_3$ – 20% wt.) after vacuum treatment showed the presence of $\alpha\text{-Fe}$, Fe_3O_4 , NiAl_2O_4 phases; after treatment with a reducing agent – $\alpha\text{-Fe}$, $\gamma\text{-Fe}$, NiAl_2O_4 ; after working with water Fe_2O_3 , NiO, $\alpha\text{-Fe}$, Ni, NiAl_2O_4 and $\gamma\text{-Al}_2\text{O}_3$. After treatment with a reducing agent, a transition from the

low-temperature phase to the high-temperature phase is observed. After the experiment, some of the α -FeO is oxidized to Fe₃O₄ and Fe₂O₃ is formed. The diffuse reflectance electron spectroscopy method does not detect the presence of oxides on the outer surface of the samples, but the presence of iron and nickel oxides is detected in the bulk. The oxidation of iron and nickel with oxygen occurs first on the outer surface of the pores, and as work progresses in the water conversion mode, oxides accumulate in the inner surface. This is indicated by the appearance in the ESDR spectra of nickel ions Ni²⁺ and iron Fe³⁺ in the composition of the NiAl₂O₄ and Fe₂O₃ phases. Below are the reactions occurring in this system:



Where: MeO is the Fe, Ni/\(\gamma\)-Al₂O₃ catalyst, and stage diagram of the mechanism of this process is presented below:



The direct interaction of carbon dioxide and water vapor with the formation of hydrocarbons is thermodynamically impossible, since the value of the Gibbs energy for the initial compounds exceeds the corresponding values for the final products. In addition, it is assumed that water is also not capable of spontaneously decomposing into hydrogen and oxygen without the supply of significant energy

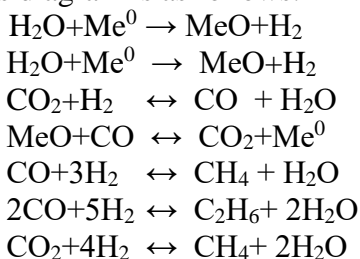
from the outside under normal thermobaric conditions. However, numerous facts and publications indicate that the decomposition of water is widespread in nature, and the presence of carbon dioxide under these conditions leads to the formation of hydrocarbons of various structures. These coupling reactions of the decomposition of water vapor and the hydrogenation of carbon dioxide into hydrocarbons can be considered as models of macroprocesses, the purpose of which was an attempt to substantiate the possibility of catalytic abiogenic synthesis of hydrocarbons in the earth's crust, which could have occurred (are currently occurring) in different periods of the geochemical history of the Earth.

Modern ideas about the genesis of oil and gas fields are based on abiogenicity, i.e. it is argued that their hydrocarbon resources are renewable. Deep catalytic processes occurring in the thickness of the earth's crust are responsible for the formation of hydrocarbon deposits. This is especially clearly seen in the example of gas fields: annually, as a result of degassing of the planet, up to 1 trillion. m^3 of methane is released from the depths into the earth's crust and atmosphere, which is comparable to its global annual production (2.5 trillion m^3). Very often, in old operating oil and gas fields, there is an increase in well production and an excess of the forecast indicators of the total hydrocarbon reserves in relation to the actual values.

A very recent example on this topic: recently new oil wells were drilled at the Oil Rocks field, as there was an unpredicted increase in its estimated reserves. For the synthesis of hydrocarbons in the conditions of the Earth's upper mantle, carbon and hydrogen donors are required, as well as a favorable reducing environment. Carbon donors can be carbon dioxide, graphite, carbonates, and metal carbides. Hydrogen donors are water; a reducing environment can be created by the presence of unbound iron(II) – (FeO). In the presence of hydrogen, CO_2 is reduced along various routes, the course of which depends on thermobaric conditions and the presence of various minerals, i.e. potential catalysts. As a result of primary processes, molecules of hydrogen, carbon oxides and hydrocarbons are formed. These reactions can occur both thermally and catalytically.

We have established that when carbon dioxide reacts with water vapor on a reduced iron-nickel catalyst, methane hydrocarbons (methane and ethane) are formed. In our opinion, there is a combination of the processes of online formation of hydrogen from water vapor and its hydrogenation of carbon dioxide into hydrocarbons. The reaction of carbon dioxide with water vapor on the surface of a Fe,NiAl oxide catalyst should be considered as proceeding through the stages of dissociation of carbon dioxide with the formation of either dissociatively adsorbed carbon monoxide or carbides as intermediate products. Hydrogenation of carbon fragments occurs quickly, which leads to the formation of methane and other paraffin hydrocarbons.

The overall process diagram is as follows:



where: MeO is the Fe,Ni/ γ -Al₂O₃ catalyst.

These reactions are thermodynamically allowed. Carbon dioxide is the “starter” compound in the formation of carbon monoxide, the subsequent interaction of which with hydrogen via the Fischer-Tropsch reaction subsequently leads to the formation of a complex mixture of products of different molecular weights.

We have studied in detail the patterns of hydrogenation of carbon dioxide with molecular hydrogen on the same iron-nickel catalyst for water conversion, and determined the optimal conditions for the formation of C₁-C₂ hydrocarbons and carbon monoxide. Catalytic tests of samples in the CO₂ hydrogenation reaction were carried out at CO₂/H₂ molar ratios of 1:1, 1:2, 1:3. The obtained data are shown below in the table 21.

Table 21

Composition of products of CO₂ hydrogenation to hydrocarbons on Fe-Ni/Al oxide catalyst

Catalyst Fe,Ni/Al	T,K	Conver- sion ,%	Selectivity%		
			CH ₄	C ₂ H ₆	CO
CO ₂ /H ₂ =1:1	623	31.4	49.2	13.8	37,0
	723	42.2	56.2	15.0	28.8
	793	39.8	69.0	14.7	16.3
CO ₂ /H ₂ =1:2	623	34.6	52.3	11.2	36.5
	723	41.9	60.7	7.0	28.3
	793	38.7	69.6	11.1	19.3
CO ₂ /H ₂ =1:3	623	41.9	61.4	10.3	28.3
	723	49.5	68.3	10.1	21.6
	793	39.8	72.0	10.5	17.5

The results show that the main products of the reaction of the CO₂+ H₂ mixture on the samples of the studied catalyst are methane, ethane and carbon monoxide.

In conclusion, we can conclude that technologies for abiogenic inorganic synthesis of hydrocarbons make it possible to achieve natural variations in their composition - from predominantly methane to a mixture of liquid hydrocarbons (C₂₀₊) with varying contents of olefins, n-alkanes, isoparaffins, and aromatic hydrocarbons. The synthesis of hydrocarbons on inorganic catalysts from mixtures of CO₂, CO and H₂ can simulate macrogeochemical processes that occurred in the early stages of the geological history of the Earth.

CONCLUSIONS

1. Based on studies of the evolution of morphology, elemental composition of the surface, and phase rearrangements in the in-situ mode, features of the relationship between the dynamics of the elemental composition of the catalyst surface and its activity in the reaction of hydrogenation of carbon dioxide into methane and methanol have been established. The elemental and phase composition, textural characteristics of iron-nickel and cobalt-palladium-containing catalysts based on aluminum oxide and aluminosilicates in this reaction have been optimized.

2. It has been shown that high-temperature ($T > 573\text{K}$) hydrogen treatment of an iron-nickel-containing catalyst with an aluminum oxide base is accompanied by the enrichment of its surface with nickel. The elemental composition of the surface changes and, along with a change in the elemental composition, a change in the particle size of the active components and their size distribution is observed. As the temperature of the reduction treatment increases, the particles of the active components of the catalyst become larger. The depth of penetration of active components into the structure of the carrier was studied and its dependence on the conditions of sample pretreatment was shown. The revealed behavior of the active components allows us to better understand the structural dynamics of the bimetallic catalyst during its interaction with the reaction medium, which is a necessary condition for the development of effective catalysts for such reactions.
3. Using the EPR spectroscopy method, it was shown that under the conditions of the reaction iron - nickel and cobalt - palladium-containing catalysts with alumina and aluminosilicate bases are superpara/ferromagnets and are nanostructured oxide systems with the size of nickel and palladium magnetic particles less than 10 nm. The magnetic properties of these systems change significantly due to changes in particle size, their size distribution and the presence of a catalyst in the structure during its heat treatment in a reducing environment and under reaction conditions. It has been shown that the active components of the Fe, Ni/Al oxide catalyst for the hydrogenation of CO_2 into methane are Fe_3O_4 phases with a CSR size of 30–40 nm and Ni particles with a size of less than 10 nm.
4. It has been shown that reduced Co, Pd - containing catalysts with an aluminosilicate base are characterized by the presence of a Co_3O_4 phase and “metallic” Pd, Co-Pd particles that catalyze the hydrogenation reactions of CO_2 into methane and methanol, respectively. In the case of cobalt-containing aluminosilicate-based catalysts, CO_2 is hydrogenated almost exclusively into methane with traces of CO (no more than 1% CO at a reaction temperature $T \geq 573\text{K}$). The introduction of palladium into the catalyst stimulates the formation of methanol, the yield of which increases with

increasing reaction temperature and reaches a value of 20.1% at a temperature of 773 K and atmospheric pressure.

5. The kinetics and mechanisms of reaction of CO₂ hydrogenation into methane and methanol were studied, the factors influencing the activity, selectivity and stability of the catalysts were determined. It has been established that the hydrogenation of CO₂ into methane occurs directly, through the stage of formation of carbon monoxide with the participation of catalytically active nano-sized particles of nickel and iron oxide Fe₃O₄. It has been shown that the hydrogenation of CO₂ into methanol is catalyzed by nano-dispersed palladium particles and a step-by-step mechanism for the conversion of CO₂ into methanol is realized. At the initial stage, molecular hydrogen reacts with palladium particles to form Pd-H particles ($\text{Pd}_n + \text{H}_2 = 2\text{Pd-H} + \text{Pd}_{n-2}$), then CO₂ is hydrogenated by interaction with Pd-H particles to form formate structures, which are then converted to methanol through a number of intermediate products.
6. The production of hydrogen by photochemical decomposition of water, sensitized aromatic hydrocarbons of oil, isolated from the heavy pyrolysis resin fraction (fr. 473–573K) was studied. It has been shown that this fraction is rich in aromatic hydrocarbons, which, under the influence of photoradiation, easily transform into radical ion structures that are directly involved in the photodecomposition of water.
7. Reactions for the production of hydrogen by steam and carbon dioxide conversion of methane on Fe–Ni and Ni–Mg containing oxide catalysts have been studied. It has been shown that the decomposition of water on iron- and nickel-containing catalysts based on aluminum oxide, synthesized under low vacuum conditions, at a residual pressure of ~ 10–15 mm Hg, at a temperature of 553–593 K, proceeds with ~ 95% water conversion and the hydrogen yield is 61.2 wt.%.
8. The fundamental possibility of producing methane by combining the reactions of water decomposition and hydrogenation of carbon dioxide with the participation of a Fe, Ni/Al oxide catalyst at 553–593K and atmospheric pressure has been shown. It is assumed that the synthesis of hydrocarbons on inorganic catalysts from mixtures of CO₂,

CO and H₂ can simulate macrogeochemical processes that occurred in the early stages of the geological history of the Earth and technologies for abiogenic inorganic synthesis of hydrocarbons allow variations in their composition – from predominantly methane to a mixture of liquid hydrocarbons (C₂₀₊) with different olefin content of olefins, n-alkanes, isoparaffins, aromatic hydrocarbons.

**The main content of the dissertation is published
in the following works**

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