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A B S T R A C T

of the dissertation for the degree of Doctor of Sciences

**ACTIVATION OF METHANE AND LOW
MOLECULARWEIGHT HOMOLOGUES ON
THE CATALYSTS, CONTAINING HIGHLY DISPERSED
METAL NANOPARTICLES**

Speciality: 2314.01 – Petrochemistry
2316.01 – Chemical Kinetics and Catalysis

Field of science: Chemistry

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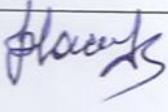
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GENERAL DESCRIPTION OF WORK

Relevance of the research topic. The current state of the industry is characterized by high energy consumption and oil derived from petroleum feedstock. Reduction of oil reserves on the background of the rapid growth of global consumption increases the importance of natural gas as an energy source and raw material for the production of chemical products. An economically and environmentally acceptable safe routes processing gaseous hydrocarbons (natural gas and liquefied petroleum gas) in the process of obtaining valuable products has considerable practical and theoretical importance. This issue received much attention in recent years. Therefore, catalytic transformations studies of low molecular weight hydrocarbons, especially methane, in motor fuels and hydrocarbon products are valuable actual direction modern petrochemical industry. Certain advances have been made in the direction of activation of methane and its lower homologues by using as catalysts high-silicone zeolites. This shows the possibility of alternatively crude oil, with high yields to obtain aromatic hydrocarbons, a component of motor fuels, oligomers, etc. from cheap and available hydrocarbon gas feedstock. motor manufacturing processes of fuels based on methanol, the resulting methane-base gas, are promising, and its stages: MtO/MtP and COD (MtSynfuels process) are currently the subject of intensive research aimed at the selection and synthesis of catalysts for the optimization of methanol enterprises through combining synthetic steps of methanol to other stages extract the desired products. Taking into account the high energy intensity of the production of synthesis gas from methane is also required to search for new, single-stage paths turning it into more valuable products, including high molecular weight hydrocarbons. MtO/MtP and COD (MtSynfuels process) are currently the subject of intensive research aimed at the selection and synthesis of catalysts for methanol optimize alignment enterprises through methanol synthesis stage with other stages extract the desired products. Taking into account the high energy intensity of the production of synthesis gas from methane is also required to search for new, single-stage paths turning it into more valuable products, including high

molecular weight hydrocarbons. MtO/MtP and COD (MtSynfuels process) are currently the subject of intensive research aimed at the selection and synthesis of catalysts for methanol optimize alignment enterprises through methanol synthesis stage with other stages extract the desired products. Taking into account the high energy intensity of the production of synthesis gas from methane is also required to search for new, single-stage paths turning it into more valuable products, including high molecular weight hydrocarbons.

Thus, to obtain valuable products, including hydrocarbons, is fundamentally important to the development of alternative methods for producing petrochemicals valuable products and organic synthesis from methane and other gaseous hydrocarbons using active heterogeneous catalysts capable of effectively engage natural and passing the gases in the processes of formation of C-C bonds. Catalysts such conversions of methane and other gaseous alkanes may be metal oxide and zeolite system. Therefore, the research aimed at the development of processes involving methane and other gaseous alkanes in the processes of the formation of intermolecular C-C bonds with new catalytic systems containing highly dispersed metal particles on oxide and a zeolite carrier and their composites, relevant and promising.

Object and subject of research. The object of research is low-molecular organic compounds (methane, propane, dimethyl ether).

The subject of research is the possibility of catalytic involvement of low molecular weight organic compounds into the formation of intermolecular carbon-carbon bonds for obtaining of valuable products (benzene, cumene and hydrocarbons of unsaturated and branched structure).

Purpose and tasks of work.

The establishment of bases laws of the intermolecular C-C bonds formation with gaseous alkanes, especially methane, participation, both directly and throw syntheses gas, methanol /DMP , into C₂₊ hydrocarbons over bimetalumina and zeolites catalysts containing the highdispersed nanoparticles of VIII B group elements as well as on their compositions.

To achieve the aim set in the work the following tasks:

- Application of C-C bond formation laws of the methane DHCH activation on the conversion of others law molecular alkenes (for instance propane) with participation of bimetal alumina catalysts highly dispersed nanoparticles of VIII B group established;
- Created of the high productive catalysts to methanol dehydration into DME;
- The synthesized and selection of catalysts and conditions for an effective translation of a separate stages of Mt synfuels process to DMEt sinful one.
- Established of the peculiarities of the methanol transformation into initial ethylene and its influence on following distribution of MtO and DMEtO conversions product;
- Established of the methanol influence on an intermediate products formation at low molecular olefins conversion to distillate(COD) ;
- Basis of the methane activation mechanism and formation of the initial intermolecular C-C bond by results generalized of systematic study of methane DHCH; benzene dehydroalkylation with propane and methanol / DME conversion to hydrocarbons have been solved scientific novelty of the work. The systematic studies were first conducted :
- Straight dehydrocyclohexanization methane into benzene over bimetal alumina catalysts contained VIII B group elements (Ni,Co or Pt) ;
- Propane involved in the process of benzene dehydroalkylation and dehydrogenation to propylene at lower temperatures over the composite catalytic system consisting of the methane DHCH and H-zeolite (Y,MOR or ZSM-5)
- Methanol dehydration into DME and following conversion to various structures hydrocarbons : intermediate interactions of methanol with its products transformed
- The dependence of the formation of the end products of these reactions on bimetallic aluminum and zeolite catalysts on the composition and synthesis conditions of their compositions.
- The laws of the C-C bonds of methane molecules, propane,

oxydatively functionalized methane-methanol (methoxymethane (DME) over bimetal alumina - H - zeolite composite catalysts and modified zeolite ones

- The high active and selective $M/\text{ReO}_x/\text{Al}_2\text{O}_3$ ($M=\text{Ni}$ or Co) catalysts activating direct methane conversion into benzene ($T=600-700^\circ\text{C}$ at atmospheric pressure) have been synthesized
- the composite catalysts consisted of $M/\text{ReO}_x/\text{Al}_2\text{O}_3$ ($M=\text{Ni}$ or Co) and H-zeolite (Y, MOR or ZSM-5) synthesis capable of activation of the low-temperature benzene by propane and propane dehydrogenation to propene.
- establishing methanol influence on the formation of intermediate products of low molecular weight conversion of olefins in the distillate (COD), have been solved.

Research methods. When performing the work, the following methods were used: gas chromatography, high-temperature adsorption of ammonia, hydrogen chemisorption, IR spectroscopy, differential thermal analysis and thermogravimetry (DTA), programmed thermal desorption (PTD), and x-ray phase analysis (XRPA).

The main provisions submitted for protection:

- The methane dehydrocyclization to benzene proceeding over bimetal alumina catalysts containing highly dispersed VIII B group elements particles of the size less 2 nm;
- Arising of the reactivity in homogenous oxygen in oxide phase under the influence of VIII B group elements with a particle size less 2 nm;
- The formation of the intermolecular C-C bond with reactivity inhomogeneous oxygen participation;
- The role of bimetal alumina catalysts modifying by carbonaceous deposits at methane DHCH
- Applicability of the formation of intermolecular C-C bond with participation of methane two molecules to gaseous alkanes (propane) activated;
- Evidence of C-C bond formation with participation of oxygen connected of the instance of the methanol / DME conversion to the initial ethylene and other hydrocarbons.

Scientific novelty of the work. The systematic studies first con-

ducted:

- straight dehydrocyclohexamerization methane in benzene at bimetal aluminum oxide catalysts containing elements of group VIII b;
- process involving propane dehydroalkylation of benzene and propylene in dehydrogenation at lower temperatures for composite catalytic systems consisting of the catalysts for methane dehydrocyclohexamerization and H-zeolites (Y, MOR, ZSM-5);
- sequential dehydration of methanol to DME, followed by conversion to hydrocarbons of various structures; intermediate interactions with methanol transformation products thereof;
- depending on the formation of the end products of the reactions selected conditions of synthesis of zeolite and alumina catalysts and their compositions;
- of the formation of C-C bonds of molecular methane, propane, oxidatively functionalized methane-methanol /methoxymethane (dimethyl ether) at bimetal aluminum oxide, composite bimetal aluminum oxide, H-zeolite and modified zeolite catalysts;
- synthesized highly active and selective catalysts $M, \text{ReO}_x / \text{Al}_2\text{O}_3$ ($M = \text{Ni}, \text{Co}$), activating the direct conversion of methane into benzene ($T = 600\text{-}700^\circ\text{C}$ at atmospheric pressure);
- $M, \text{ReO}_x/\text{Al}_2\text{O}_3$ ($M = \text{Ni}, \text{Co}$) composition with H-zeolite (Y, MOR, ZSM-5) the low-temperature component dehydroalkylation benzene propane and the dehydrogenation of propane;
- as a result of a comparative study of the dehydrocyclohexamerization of methane to benzene, the dehydroalkylation of benzene with propane and the conversion of methanol / DME to hydrocarbons with the participation of bimetal alumo oxide and zeolite catalysts, as well as their mechanical mixtures, first substantiated the non-contradictory mechanism of the formation of the primary C-C bond from molecules methane and its gas homologues, including cyclic redox changes in the metal system associated with the formation and dehydration of an intermediate of the Alk-O-R type (where Alk - $\text{CH}_4, \text{C}_3\text{H}_8$, and R - $\text{CH}_4, \text{C}_6\text{H}_6$).

The practical and theoretical significance of the work:

- The possibility of replacing the expensive platinum on nickel or

cobalt in the synthesis of aluminum oxide catalysts for the selective dehydrocyclohexamerization of methane into benzene.

- Simplification technology of isopropyl benzene (cymene) by low temperature direct dehydroalkylation of benzene with propane to isopropylbenzene on composite catalyst systems, including those based on modifying industrial zeolite catalysts.
- Developed a high performance catalyst for an environmentally friendly fuel - dimethyl ester and one-step processing of methanol / DME from synthesis gas to hydrocarbons of various structures.

Publications. On materials of thesis published 54 scientific papers in national and international journals, collections of scientific papers, theses of republican, Russian and international conferences, symposia, including 29 articles and 24 thesis and 1 patent of the Russian Federation.

Approbation of work. The results of the thesis were presented at: III Международный Конгресс по окислительному катализу (Сан-Диего, 1997); The 5th European Congress on Catalysis - EuropaCat-V, (Ireland, 2001); Proceedings of the 14th International Zeolite Conference, (Африка, 2004); Europacat VIII conference From Theory to Industrial Practice (Finland, 2007); III International Conference “Catalysis: Fundamentals and Application” dedicated to the 100th anniversary of Academician G.K. Borekov (Novosibirsk, 2007); XVIII Mendeleev Congress (Москва, 2007), 5-ая Всероссийская цеолитная конференция «Цеолиты и мезопористые материалы: Достижения и перспективы» (Звенигород, 2008); V Российская конференция «Проблемы дезактивации катализаторов и VI Российская конференция «Научные основы приготовления и технологии катализаторов» (Туапсе, 2008); Республиканская конференция по нефтехимии и нефтепереработке, посвященная 100-летию В.С. Алиева (Баку, 2008); VIII International Conference «Mechanisms of catalytic reactions», dedicated to the 70th anniversary of the birth of prof. K.I. Zamaraev (Novosibirsk, 2009); VII Бакинская Международная Мамедалиевская конференция по нефтехимии, посвященная 80-летию Института нефтехимических процессов НАН

Азербайджана (Баку, 2009); International conference catalysis for renewable sources: fuel, energy, chemicals (St. Petersburg, 2010), 6-ая Всероссийская цеолитная конференция. «Цеолиты и мезопористые материалы: Достижения и перспективы» (Звенигород, 2011); Российский Конгресс по катализу «РОСКАТАЛИЗ» (Москва, 2011); Azərbaycan Respublikası Təhsil Nazirliyi Gəncə Dövlət Universiteti “Müasir biologiya və kimyanın aktual problemləri” Elmi-Praktiki Konfransının məruzələri (Gəncə, 2015); 7-ая Всероссийская Цеолитная Конференция «Цеолиты и мезопористые материалы: Достижения и перспективы» (Звенигород, 2015); XII Европейский Конгресс по катализу - Eurocat XII - 2015 (Россия, Казань, 2015); “RR2017” International Conference “Renewable Plant Resources: Chemistry, Technology, Medicine” (St. Petersburg, 2017).

Venue of the dissertation work.

The work was carried out at the Institute of Petrochemical Processes named after academician Y.H. Mamedaliev National Academy of Sciences of Azerbaijan, in accordance with the work program 14/2016 under registration number 0106Az00010.

The personal involvement of the author. The author outlines the key research objectives and tasks to achieve them, research areas identified, carried out processing, systematization and discussion of the results. The author has been directly involved in the formulation and conduct of laboratory tests.

The structure and volume of work. The dissertation is presented on 307 pages, consists of an introduction, VI chapters, including 49 tables, 38 graphs and 3 figures, a list of references, consisting of 450 titles and amounts to 399,680 characters.

In the introduction the urgency of the problem, the purpose and objectives of the dissertation, scientific novelty and practical significance of the research data.

The first chapter generalized and systematized literary sources on the current status scale chemical processing of methane, including chemical processing methods alkanes, alternative production of hydrocarbons from natural gas via syn-gas and methanol, oxidative conversion of methane, and benzene alkylation with low molecular

weight alkanes C₁-C₃.

The second chapter shows methods of synthesis of catalysts for dehydrocyclohexamerization by methane dehydration of methanol and to obtain mechanical mixtures of the catalysts, methodology for catalytic studies, as well as methods for conducting physico-chemical studies of catalysts.

The third chapter describes results for methane dehydrocyclohexamerization on mono- and bimetal alumo oxide catalysts. Studied DGTSG methane on Ni (Co) ReO_x/Al₂O₃, the conversion of methane in the composite catalysts, and also studied the effect of the interaction of the reactant-catalyst of methane conversion to benzene.

The fourth chapter devoted to the study of low-temperature catalytic dealkylation of benzene propane, studied the influence of the nature of the zeolite at low temperature conversion of benzene-propane mixtures in the catalyst systems M,ReO_x/Al₂O₃ + H-zeolite.

The fifth chapter has the results of studies on the processing of dimethyl ether into hydrocarbons of various structures on the catalysts prepared on the basis H-ZSM-5; studied particularly the conversion of methanol on zeolites H-ZHS and effect of the modification on the H-ZSM-5 conversion of dimethyl ether.

The sixth chapter devoted to the study of the dynamics, and the mechanism of formation of intermolecular C-C bonds in the presence of methanol and methane, identifying features methanol conversion mechanism and dimethyl ether into hydrocarbons on the modified zeolite systems study catalytic conversion involving spatially separated active sites, as well as cyclic transport of protons between the space – separated centers.

In the dissertation work generalized results of modifying effects on treason of catalyst, acid, and other microporous physic-chemical properties of the catalyst systems investigated revealed and features of the formation and redistribution of C-C bonds in the hydrocarbon conversions.

MAIN CONTENT OF WORK

Based on the main objectives of the dissertation work – estab-

lishing the basic laws of formation of intermolecular C-C bonds systematic research of direct dehydrocyclohexamerization methane were carried out in benzene, low temperature dehydroalkylation benzene propane, sequential dehydration of methanol to dimethyl ether, followed by conversion to the C₂₊ hydrocarbons; studied the formation of patterns of C-C bonds in these processes, were synthesized bimetal alumo oxide, zeolite catalysts and their compositions for the above processes was researched reacting H₂, CO, CH₄ catalysts M (M = Co, Ni, Pt) ReO_x/Al₂O₃, prepared by adsorption (a) and impregnating (i) methods. It is shown that the reactivity of ReO_x oxygen depends on the application M, it was found that the oxygen contained in the sample (a), unlike the sample (i), the reaction has heterogeneity, discussed the role of oxygen in the activation of methane, the mechanism of formation of the primary C-C bond.

Below are the results of catalysts synthesized studies in direct processes dehydrocyclohexamerization methane to benzene, low temperature dehydroalkylation benzene propane, sequential dehydration of methanol to dimethyl ether to C₂₊ hydrocarbons.

1. Catalysts and research methods

Objects of the study served as contacts, containing Ni, Co, Pt, Re (M) and M,ReO_x/Al₂O₃ alumo-metal rhenium contacts AMR, prepared by applying on these elements γ -alumina AMR adsorption of solutions (a) and impregnating AMR (i). For this purpose, previously calcined at 750 °C spherical γ -Al₂O₃ adsorption method from aqueous solutions of NiCl₂ was applied and NH₄ReO₇. Sample Ni, ReO_x/Al₂O₃ (a) was filtered, then dried at 80 of 120 °C and further calcined at 750 °C for 3 hours. The amount of applied substances was determined by the AAS method according to the difference in the concentrations of these substances in the initial and final solutions. For comparison, by impregnating the carrier with solutions of appropriate, c, followed by evaporation, drying at 100 and 120 °C, calcination at 750 °C (3 h) it was also synthesized sample Ni, ReO_x / Al₂O₃ (i). Monometallic-platinum- and cobalt-containing contacts were synthesized in a similar manner. In the case of synthesis of platinum-containing catalysts, the specified solutions of hexachloroplatinic

acid were used contents M and Re (in terms of metal) in the catalyst preparation were respectively 0.5 and 0.3-1.0 % by weight. by mass of the sample. The catalysts are also used decationized and dealuminated H-form zeolites H MOR, HY and HZSM-5 and the predetermined mechanical mixtures AMR (a) H-zeolites.

As reagents used natural gas (methane 99.6 %), methanol, benzene, propane. Experiments were conducted at flow unit equipped with a quartz reactor with a fixed catalyst bed. The reaction products were analyzed by gas chromatography. The selectivity and yield of benzene was calculated based on the amounts of starting and unreacted carbon atoms. Analysis of carbon deposits was performed by differential thermal analysis and thermogravimetry. Measurement of amounts of CD accumulated on the catalyst during the reaction and their residues after regeneration was carried out by thermoprogrammed-oxidation (TPO) using derivatograph IOM Q-1500. The influence of catalyst synthesis methods on their structural properties and dispersion of supported elements of group VIII b were respectively characterized by adsorption methods using benzene and hydrogen as adsorbates. The measurements were carried out in volumetric-vacuum units equipped with a McBen scale and/or a McLeod pressure gauge. The acidic properties of the samples were determined by thermal desorption of ammonia adsorbed by the sample, the state of the deposited elements was determined by diffuse reflection infrared spectroscopy of a carbon monoxide probe molecule sorbed by bimetal alumina contacts. The phase composition of the samples was monitored by X-ray diffractometry.

2. Methane dehydrocyclohexamerization on Ni (Co), $\text{ReO}_x/\text{Al}_2\text{O}_3$ bimetal-aluminum oxide contacts

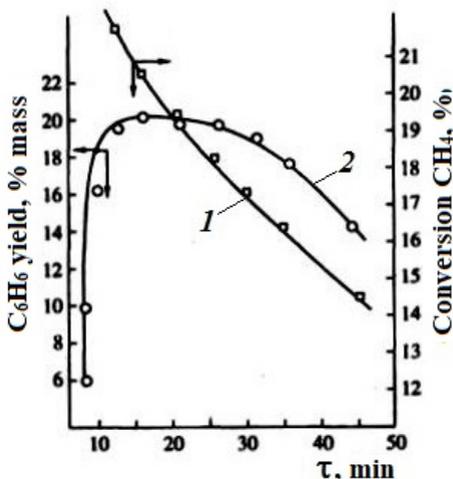
To establish the general laws, activate C-H and the formation of C-C bonds were investigated conversion of methane and its homologues in low molecular weight aromatic hydrocarbons in $\text{M}_i\text{ReO}_x/\text{Al}_2\text{O}_3$ catalysts.

The conversion of methane to synthesis M, $\text{ReO}_x / \text{Al}_2\text{O}_3$ catalysts was studied: a) after activation of an unreduced sample of air; b) recovery of the sample after hydrogen; c) after re-oxidation of the

reduced sample.

Studies have shown that regardless of the method of synthesis aluminum metal rhenium (AMR) of the catalyst, the reaction with their prior states (a, b, c) in the presence of gaseous oxygen occurs only deep oxidation of methane. The contacting of pure methane with AMR catalysts subjected to reduction also did not lead to the formation of any higher hydrocarbons. Only unreduced catalysts AMR series (i) prepared by applying the adsorption of the active components, exhibit activity in benzene formation.

The graph 1 shows the characteristic of the unreduced catalyst AMR dependent conversion of methane and benzene yield from the duration of the experiment.



Graph 1. The dependence of the conversion of methane (1) and the yield of benzene (2) on the duration of the reaction to ANR the catalyst. $T = 650 \text{ }^\circ\text{C}$, $V = 1450 \text{ h}^{-1}$

For dehydrocyclohexamerization methane (DHCH) in benzene on catalyst AMR characteristic that in the initial stage (first 5-10 min) are formed only of deep oxidation products. Subsequently the activity of the sample is reduced, and the reaction products appear benzene and hydrogen, which exits with the duration of the experiments increased to a maximum quasi-stationary. Then the product yield reduction occurs, which corresponds to a reduction of the me-

thane conversion (graph 1). It should be noted that the only reaction to hydrocarbon product AMR catalyst is benzene.

Benzene formation is preceded by activation of the catalyst, followed by a period of its relatively stable dehydrocyclohexamerization activity. Further there is catalyst deactivation. Subsequent reactivation of the catalyst is achieved by treating AMR sample air at temperatures experience.

At the same time, as can be seen from these data, the interaction of methane with an AMR catalyst is accompanied by the formation of carbonaceous deposits (CD), and this reaction is an additional source of hydrogen (table 1).

Table 1
Conversion of methane to catalyst AMR
(T = 650 °C, V = 1450 h⁻¹, τ = 20 min)

| Content activating components, % mass. | | CH ₄ conversion, % | Yield, % mass | | |
|--|-----|-------------------------------|-------------------------------|----------------|------|
| Ni | Re | | C ₆ H ₆ | H ₂ | CD * |
| 0.3 | 0.3 | 24.1 | 14.4 | 4.2 | 5.5 |
| 0.5 | 0.3 | 24.9 | 12.3 | 4.7 | 7.9 |
| 1.0 | 0.3 | 26.4 | 14.3 | 4.8 | 7.3 |
| 0.3 | 0.5 | 23.3 | 11.8 | 4.4 | 7.1 |
| 0.3 | 1.0 | 23.4 | 13.6 | 4.2 | 5.6 |

* The hydrogen content of CD is less than 1.5 % mass.

The initial moment of interaction of the reactant with the catalyst can be considered as a stage of preliminary treatment of the DHCH catalyst of methane. During this stage, as can be seen from the data in Table 1, the catalyst undergoes, on the one hand, reduction with methane, the result of which is the conversion of oxygen in its composition and the formation of oxidation products (CO₂, H₂O), and on the other hand, is covered with carbonaceous deposits. Probably, these modifying factors contribute to the formation of a Ni, ReO_x / Al₂O₃ catalyst which is active in the DHCH of methane.

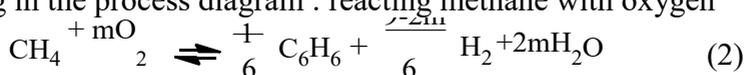
Thermodynamic calculations show relatively low equilibrium yield of benzene by the reaction:



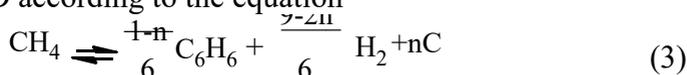
In the experimental conditions, it is about 1.1 mol % (which corresponds to about an 8 % CH₄ conversion).

As can be seen from the data shown in graph 1 the amount of methane subjected DHCH approximately twice this value. This indicates that the formation of benzene from methane, most likely occurs in other ways.

Thermodynamic reaction difficulty can be eliminated by including in the process diagram : reacting methane with oxygen



where in the yield of benzene (2) is 19 % and / or the formation of the CD according to the equation



Calculations show that the equilibrium yield of benzene according to (3) is 25 %.

From the data obtained it follows: a) the total activity in the absence DHCH prerduced catalysts AMR; b) development of the oxidation catalyst, provide enhanced activity with their DHCH a duration interaction with methane; c) the possibility of catalyst regeneration by treatment with air. These features may be classified as to the accumulation of the CD, and associated of bound oxygen contained in oxidized samples during the process.

Standard regeneration air AMR catalysts functioning on the quasi-stationary regime results from one side to the total drop in catalyst activity, and on the other – under the influence of the reactant, the catalyst, after a certain time (activated), again recovers its reactive properties, i.e. deactivation observed under the influence of the oxidation treatment is reversible. Unlike standard regeneration, reducing the processing time used in the reaction of the catalyst with air affects the yield of benzene at DHCH methane.

The activation period can be regarded as a step of pretreatment of the catalyst. Table 2 presents quantitative data methane interaction with Ni, ReO_x/Al₂O₃ catalyst in a non-oxidizing methane DHCH

showing the removal of oxygen from the catalyst volume in the form of CO₂ and H₂O and the sample recovery.

Table 2
The conversion of methane on Ni, ReO_x / Al₂O₃;
T = 650 °C, V = 1450 h⁻¹

| Time, min | Conversion,% | | Selectivity,% C | | |
|-----------|-----------------|-----------|-------------------------------|-----------------|------|
| | CH ₄ | O bound * | C ₆ H ₆ | CO ₂ | CD |
| 3 | 28.0 | 60.0 | - | 96 | 4.0 |
| 5 | 20.0 | 71.0 | 8.0 | 17 | 75.0 |
| 10 | 18.2 | 76.0 | 68 | 0.0 | 32.0 |
| 15 | 18.7 | 78.0 | 75 | 0.0 | 25.0 |
| 20 | 17.9 | - | 77 | 0.0 | 23.0 |
| 30 | 15.8 | 80.0 | 80 | 0.0 | 20.0 |
| 40 | 13.4 | 81.5 | 87.5 | 0.0 | 13.0 |
| 60 | 11.5 | 85 | 93.0 | 0.0 | 6.0 |

* – oxygen, which is part of the catalyst, the maximum the amount of which is 0.139 mmol / g_{cat}

An analysis of the products showed that the formation of CO₂ is almost completed within the initial 5-7 minutes, and the formation of H₂O, despite a decrease in its concentration is observed throughout the experiment.

During activation, as shown in table 2, the catalyst is subjected, on the one hand, reactant recovery which results in the conversion of oxygen entering its structure and the formation of oxidation products (CO₂, H₂O), and on the other is coated carbonaceous deposits. Probably these modifying factors contribute to the formation of the active methane in DHCH M, ReO_x / Al₂O₃ catalyst.

Table 3 shows the titration of the catalyst with hydrogen. From these data it follows that the maximum amount of bound oxygen contained in the Ni, ReO_x / Al₂O₃ is 0.139 mmol / g_{kat} and hydrogen released practically at the first minutes of the experiment, and the catalyst is irreversibly deactivated.

From Table 3 it follows that the reaction of methane with deactivated (reduced) catalyst, similar to the interaction of the sample with hydrogen. Considering the average size of supported nickel, determined by hydrogen chemisorption, is 1.3 nm (dispersion 0.8) and the fact that the interaction of methane with an active (unreduced)

catalyst is characterized by some kinetics of oxygen eduction, it can be assumed that the bound oxygen in the composition Ni, ReO_x / Al₂O₃ active in DHCH is reactively inhomogeneous with respect to methane. Given the similarity in the interaction with the methane oxidized deactivated AMR (a) and inactive AMR (i) samples may be assumed that Ni or Co in the active AMR, as well as Pt localized on Al₂O₃ as before crystallized particle size of less than 2 nm.

Table 3
Recovery of bound oxygen from Ni, ReO_x / Al₂O₃
by reaction with CH₄ and H₂

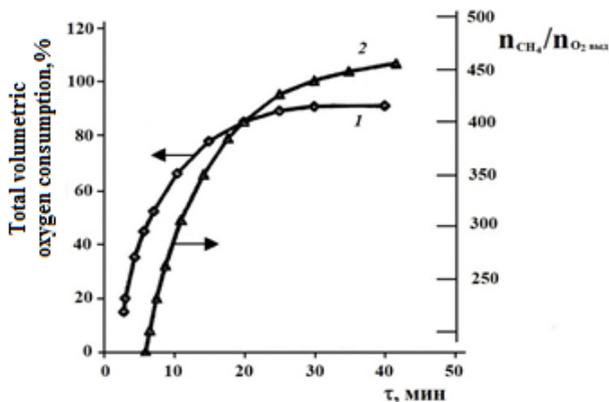
| Reducing agent | Recovered O, mmol·/r ⁻¹ _{katt.} | Time, min | | | | | | |
|--|---|-----------|-------|-------|-------|-------|-------|-------|
| | | 3 | 7 | 10 | 15 | 30 | 60 | 120 |
| Ni, ReO _x / Al ₂ O ₃ | | | | | | | | |
| CH ₄ | n ₁ | 0,028 | 0,040 | 0,045 | 0,048 | 0,050 | 0,057 | 0,062 |
| | n ₂ | 0,056 | 0,059 | 0,061 | 0,061 | 0,061 | 0,061 | 0,061 |
| | n _Σ | 0,084 | 0,099 | 0,106 | 0,109 | 0,111 | 0,118 | 0,123 |
| H ₂ | n ₂ | 0,130 | 0,126 | 0,139 | 0,139 | | 0,139 | |
| Ni, ReO _x / Al ₂ O ₃ (restored H ₂) | | | | | | | | |
| CH ₄ | n _Σ | 0,120 | 0,138 | 0,138 | 0,140 | | 0,140 | |

n₁ and n₂ – corresponds to the amount of oxygen selected as H₂O and CO₂; n_Σ – the total amount of oxygen separated in the form of CO₂ and H₂O

Studies carried out using methane-oxygen mixtures have shown that, regardless of the previous treatment of the catalysts, only deep oxidation of methane occurs in all cases. The contact of pure methane with bimetalum-alumina contacts subjected to reduction and subsequent reoxidation also did not lead to the formation of any higher hydrocarbons.

From the data (tables 2 and 3) it follows that the methane conversion is associated with the presence of bound oxygen. This follows from the comparison of the amounts of methane converted into the target product (benzene) with the amounts of liberation of bulk oxygen from the catalyst during the reaction by the products of deep oxidation of methane. It should be noted that the practical cessation

of the formation of carbon dioxide corresponds to the beginning of the fixation of the formation of the DHCH product of methane, observed after the fifth minute of the experiment. The rate of evolution of bulk oxygen, starting from the tenth minute, decreases linearly. However, the DHCH of methane in this time interval is more complex.



Graph 2. Dependence of the total oxygen consumption (1) and the ratio of the amount of converted methane per one atom of oxygen released. (2). Catalyst Ni, ReO_x / Al_2O_3 , $T = 650^\circ C$, $V = 1450 h^{-1}$

In graph 2 have been compare the curve of the total consumption of volumetric oxygen with curve of the number of methane molecules undergoing DHCH, per one atom of oxygen released.

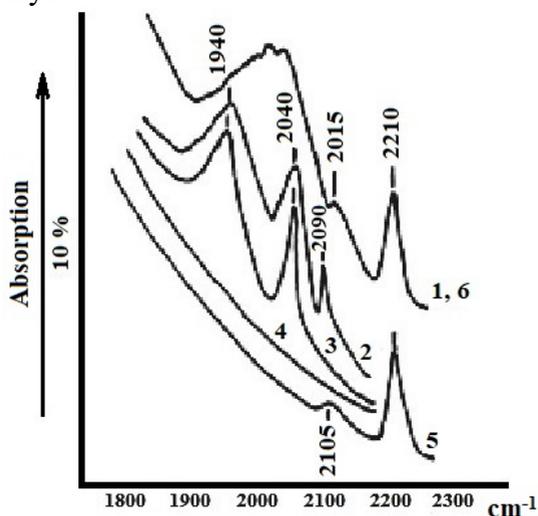
As can be seen from graph 2, the total evolution of bulk oxygen with the duration of the experiment has the character of saturation, while the number of methane molecules subjected to DHCH and per one atom of oxygen released from the volume (n_{CH_4}/O_{rel}) increases monotonically. The data of graph 2 (curve 1) show that the dependence of the volumetric oxygen consumption on the time of the experiment has an extreme character, tending to the value of 82%. Thus, only a small fraction of bulk oxygen (about 20%) participates in the formation of benzene. However, as this part of the bulk oxygen

is consumed, the $n \text{ CH}_4 / n \text{ O}_2$ value increases (graph 2, curve 2). Thus, one atom of bulk oxygen is repeatedly involved in the activation of the formation of the C – C bond from two methane molecules. At the same time, a decrease in the content of bulk oxygen during the reaction is the reason for a decrease in the activity of the catalyst. Consequently, the replenishment of this oxygen form can lead to the stabilization of the DHCH process of methane. Analyzing the contribution of bound oxygen to the DHCH of methane, we note that the presence of even a small amount of oxygen in the gas phase (~ 3 mol %) completely inhibits the formation of benzene. In addition, analysis of the products of the interaction of methane with the catalyst oxidized after regeneration (for 3 h) (Table 3) shows that 65% of the total volumetric oxygen is removed from the sample in the form of deep oxidation products in the first five minutes. Thus, according to Table 2, for the stable operation of the AMR catalyst, it is required to maintain the content of bulk oxygen in the range of 18-22%.

Used as an oxidizing agent, carbon dioxide exhibits a complicated character of action on the DHCH process of methane. Graph 2 shows how, after the completion of the development of the catalyst, as a result of introducing 3 mol % CO_2 into the reaction medium, the deactivation of the C-C bond of the catalyst slows down somewhat. Thus, the introduction of CO_2 into the reaction as an oxidizing agent, in general, does not significantly affect the stability of the catalyst functioning. At the same time, these data show that oxygen-containing compounds introduced into the reaction medium affect the concentration of oxygen in the AHP catalyst. Bound oxygen, which is part of the Ni, $\text{ReO}_x / \text{Al}_2\text{O}_3$ catalyst active in DHCH, is reactively heterogeneous with respect to methane.

Really, under the influence of M (Ni, Co, Pt), the reduction temperature of rhenium oxide decreases sharply. However, as can be seen from the IR spectra of the adsorbed test molecules of CO ($1700\text{-}2300 \text{ cm}^{-1}$) (graph 3), the reduced rhenium in the AMP composition is quite readily oxidized even by the hydroxyl groups of the support (spectrum 6). Such behavior indicates the mutual influence of M and rhenium oxide. Possibly, as a result of this interaction, structures are formed containing a bridged form of bound oxygen $\text{M} - \text{O} - \text{ReO}_x$,

which changes the redox characteristics of the supported rhenium oxide in the catalyst.



Graph 3. IR spectra of CO adsorbed on the catalyst $M,ReO_x/Al_2O_3$ (a), reduced H_2 at 200 °C and 15 torr: 1 – 20 °C, 15 torr; 2 – 100 °C, 3 – 300 °C 4 – 450 °C (all three evacuated to $P = 10^{-4}$ torr); 5 – 20 °C, 15 torr; 6 – 20 °C, 15 torr, CO recovery after H_2 (two samples with repeated adsorption of CO)

Possibly, as a result of such interaction, structures are formed containing the bridged form of bound oxygen $M - O - ReO_x$, contained in the volume of the catalyst, which change the reactivity. On the other hand, it is the presence of a bond like $M - O - ReO_x$ that helps to maintain a stable state of supported M and prevents irreversible deactivation of the active catalyst.

Analyzing the role of inhomogeneity's in the reaction of methane DHCH note that the presence of even small amounts of oxygen in the gas phase (~ 3 mol %) completely inhibited the formation of benzene. In addition, analysis of the products of the interaction of methane with an oxidized AMP catalyst (within 3 h) (Table 4) shows that 65 % of the total volume oxygen in the first 5 minutes is removed from the sample in the form of deep oxidation products.

This time corresponds to the time of activation of the catalyst.

About 12 % of the oxygen is not removed from the catalyst volume and for 2 hours. Thus, in reaction (2) may participate only 23 % volume of firmly bound oxygen.

Comparing this value with the amount of benzene formed (table 4) shows that one atom of oxygen evolved over 70 benzene molecules and one oxygen atom, in the remaining amount of catalyst AMP, up to 40 molecules of benzene.

The dependence of the reactivity of bound oxygen from the method of preparing M (M = Ni, Co, Pt) $\text{ReO}_x/\text{Al}_2\text{O}_3$ -catalysts was studied on the example of the interaction of the oxidized M, $\text{ReO}_x/\text{Al}_2\text{O}_3$ -contact with the H_2 , CO and CH_4 in the catalytic install flow-type atmospheric pressure, and temperature 650 °C.

Table 4

**The yield of benzene and the balance of volume oxygen
by reacting methane with the catalyst
0,3 % Ni + 1,0 % Re/ γ - Al_2O_3 T = 650 °C, V = 1450 h⁻¹**

| Experience duration, min | Number of forming. C_6H_6 , mmol | [O] rest* mmol | [O] rel ** mmmol | $[\text{C}_6\text{H}_6] / [\text{O}]$ rest | $[\text{C}_6\text{H}_6] / [\text{O}]$ rel |
|--------------------------|--|----------------|------------------|--|---|
| 0 | 0 | 0,331 | 0 | 0 | 0 |
| 3 | 0 | 0.156 | 0,175 | 0 | 0 |
| 5 | - | 0,114 | 0,042 | - | - |
| 10 | 1.45 | 0.097 | 0,017 | 9 | 42 |
| 15 | 3.43 | 0.097 | 0,017 | 12 | 58 |
| 40 | 10.16 | 0,053 | 0,044 | 40 | 76.5 |

* - the amount of oxygen remaining in the volume of catalyst

** - the amount of oxygen released from the catalyst consisting of deep oxidation products

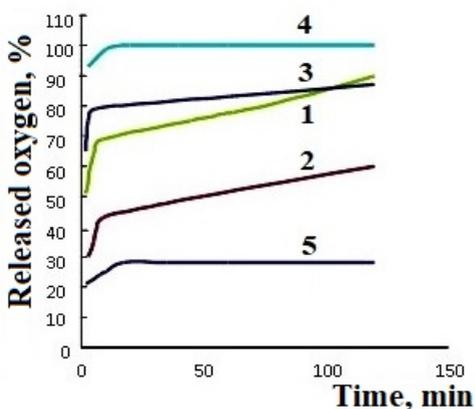
Graph 4 shows the results of the interaction of hydrogen and CO with a catalyst $\text{M,ReO}_x/\text{Al}_2\text{O}_3$ (a).

Practically all of the oxygen amount released from the catalyst with hydrogen in the first minutes of the experiment. According to the analysis, by reacting with hydrogen of the catalyst $\text{M, ReO}_x/\text{Al}_2\text{O}_3$ (a) released 1.07 mg $\text{g}^{-1}_{\text{kat}}$ oxygen in the form of water molecules. This value is taken as the maximum value of oxygen contained in the catalyst.

The reaction of CO with $\text{M, ReO}_x/\text{Al}_2\text{O}_3$ (a) can be characterized by two portions of CO_2 emissions. In the initial stage of the interac-

tion of the catalyst removed most of the oxygen (70 %), while the remaining part thereof is reacted with CO slower and CO₂ separation, despite the decrease observed throughout the experiment.

According to graph 4, the reaction of methane with M, ReO_x/Al₂O₃ (a) leads to the appearance of oxidation products (CO₂ and H₂O), and, as a consequence, the catalyst is recovered. The methane oxidation products can be associated with rhenium oxide deposited by reduction, which is promoted with platinum. It should be noted that the formation of CO₂ is practically complete within the first 5-7 minutes, and the formation of H₂O is observed throughout the experiment.



Graph 4. Released oxygen with the oxidized M, ReO_x/Al₂O₃ catalyst (a) in the form oxidation products (CO₂ and H₂O) T = 650° C. From reducing methane (1) – CO₂ + H₂O, (2) – H₂O, (3) – CO₂, hydrogen (4) – H₂O; carbon monoxide (5) – CO₂

Analogous researches of the interaction of reducing the sample with an inactive M, ReO_x/Al₂O₃ (i) showed the absence of the slow stage of the reaction of CH₄ and CO with this sample. In this case, almost the entire volume oxygen in this catalyst, is fully allocated in the first minutes of contacting the sample with a stream of reducing agents.

The research results show that pre-reacting with unreduced CH₄ hydrogen and air oxidized M, ReO_x/Al₂O₃ (a) affects the subsequent reaction of the reducing agent with the catalyst sample. The reduction

of oxygen from the catalyst by methane becomes identical to the reduction of hydrogen.

Thus, the reactivity of oxygen after reduction treatment of sample M, $\text{ReO}_x/\text{Al}_2\text{O}_3$ (a) with hydrogen to that of the sample M, $\text{ReO}_x/\text{Al}_2\text{O}_3$ (i), which is not active in the reaction of aromatization of methane or dehydroalkylation of benzene with propane.

Reduction treatment with CO does not lead to changes in the reactivity of the oxygen contained in the catalyst M, $\text{ReO}_x/\text{Al}_2\text{O}_3$ (a). In contrast to hydrogen reduction, the oxygen reduction of CO from a re-oxidized sample reproduces the curve, and in the case of CO, approximately 14 % of the bound oxygen remains in the catalyst.

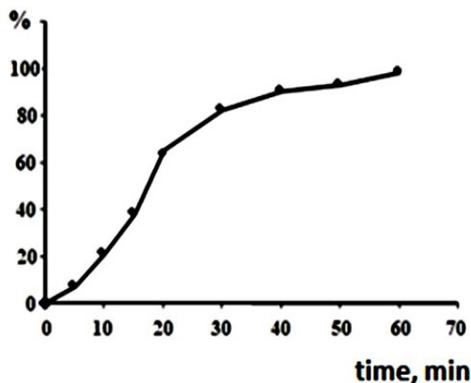
Thus, the laws governing the release of bound oxygen in the form of oxidation products during the interaction of methane and CO with the sample M, $\text{ReO}_x/\text{Al}_2\text{O}_3$ (a), which is active in the methane aromatization reaction, are quite similar to the above reactivity of oxygen bound to high dispersion platinum ($d_{\text{Pt}} = 1.0\text{-}2.0$ nm).

Aromatization of methane is occurring with the participation of oxygen entering consist of the catalyst. Thus the formation and benzene yield increase may be associated with a second, slow, stage of recovery of the sample M, $\text{ReO}_x/\text{Al}_2\text{O}_3$ (a), which is characterized by the formation of H_2O molecules with decreasing duration of the experiment.

The conversion of methane in an active $\text{Ni,ReO}_x/\text{Al}_2\text{O}_3$ catalyst and the inactive $\text{Ni,ReO}_x/\text{Al}_2\text{O}_3$ (i) leads to the formation of carbonaceous deposits (CD) and the subsequent decrease in their activity.

According to graph 5 resulting from this regeneration treatment with air that has accumulated on the catalyst AMR CD, during DHCH methane completely released from the catalyst in the form of CO_2 and H_2O .

The catalyst deactivated during the reaction completely restores its catalytic properties after treatment with air for 1 h at the experiment temperature. As a result of this regeneration treatment with air, the CD accumulated on the AMR catalyst in the process of methane DHCH are completely released from the catalyst in the form of CO_2 and H_2O . The dynamics of burnout of carbonaceous deposits is shown in graph 5.



Graph 5. Effect of treatment time on the air removing carbonaceous deposits from Ni, $\text{ReO}_x/\text{Al}_2\text{O}_3$ (650°C)

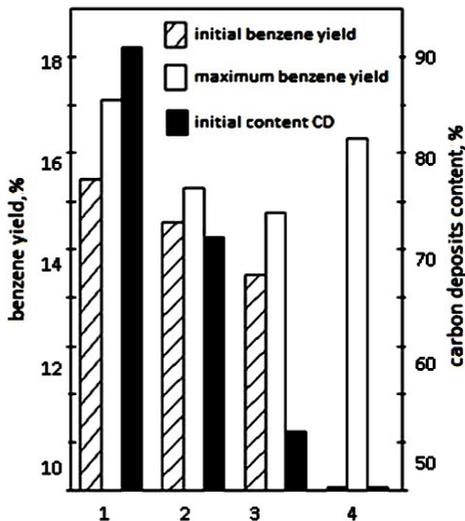
If we assume the third minute after the beginning of the reaction (minimum catalyst activity), and 15th minute – to achieve maximum activity, then as shown in graph 5, decrease in the catalyst regeneration time of from 60 to 5 minutes resulting to an increase in initial benzene yield from zero to 13 %, i.e., activation of the catalyst decreases.

At the same time, with a decrease in the treatment of the catalyst with air, the dependence of the benzene yield on the time of the experiment changes.

If we take the third minute as the beginning of the reaction, corresponding to the initial (minimum) activity of the catalyst, and 15 minutes as the achievement of the maximum activity, then, as shown in graph 5, a decrease in the catalyst regeneration time from 60 to 5 minutes leads to an increase in the initial yield of benzene from zero to 13 wt%, i.e. the catalyst activation time is reduced.

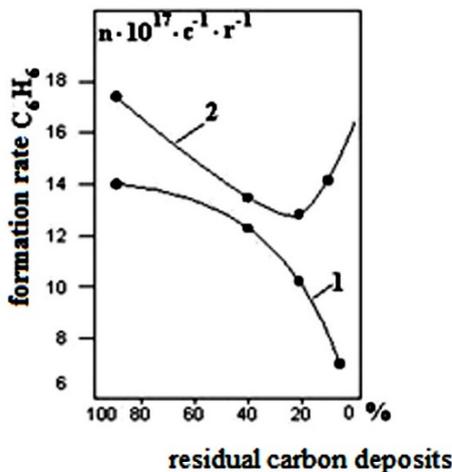
Graph 6 shows the dependence of the initial benzene yield on the amount of surface CD remaining. This indicates the participation of the latter in the formation of an active methane aromatization catalyst, the result of which is a change in both the time and the form of the reaching dependence of catalyst to maximum activity on the bimetal-alumina contacts. Thus, the magnitude of the maximum

activity of the catalyst depends on the duration of the catalyst regeneration.



Graph 6. Relationship between the precursor carbonaceous deposits initial and maximum yields of benzene in the conversion of methane to Ni, ReO_x/Al₂O₃; regeneration time, min : 1 – 5; 2 – 15; 3 – 30; 4 – 60

The achievement of maximum activity by the catalyst also depends on the duration of catalyst regeneration, i.e. from the content of residual CD in its composition (graph 6). Short-term treatment of the deactivated catalyst with air (for 3-5 minutes) makes it possible to increase its DHCH activity without significantly affecting the amount of deposited carbon monoxide. Consequently, such treatment helps to restore the concentration of the bound form surround sour kind necessary for the implementation DHCH methane.

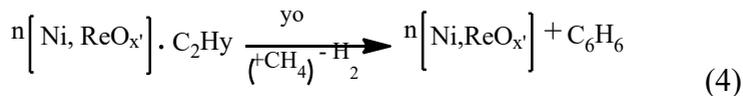


Graph 7. Dependence of the rates of benzene formation on residual amounts of carbon deposits on the Ni, ReO_x/Al₂O₃ catalyst. 1 – initial speed corresponding to 3 minutes experience; 2 – maximum speed corresponding to 20 min. experience

As shown in graph 7, with decreasing catalyst regeneration time (from 60 min to 5 min), the initial rate of benzene formation increases from 0 to $14 \times 10^{17} \text{ mol C}_6\text{H}_6 \text{ s}^{-1} \text{ g}^{-1}$, i.e. the catalyst activation time is reduced. In this case, the amount of CD remaining on the catalyst increases from 0 to a maximum value of 93%, the value of which is taken to be the weight of CD accumulated on the catalyst for 50 minutes of the experiment, $0.032 \pm 0.003 \text{ mg / gcat}$. The presence of a relationship between the rate of the initial yield of benzene and the amount of CD remaining on the bimetal-alumina catalyst indicates their participation in the formation of the active catalyst of DHCH of methane. The achievement of the maximum activity by the catalyst also depends on the duration of the catalyst regeneration, i.e. from the content of residual DC in its composition. For example, as can be seen from graph 7, a decrease in the catalyst regeneration time, from 60 to 30 minutes, leads to a decrease in the maximum benzene yield, but at the same time, the formation of benzene begins to be observed as early as 3 minutes of the experiment. Subsequent, successive reductions in the pretreatment time of the catalyst with air promote an

increase in both the initial and maximum DHCH activity of methane. Moreover, after 5 minutes of catalyst treatment, the rate of maximum benzene yield reaches an even higher value in comparison with the standard treatment of the catalyst with air. Thus, the change in the initial and maximum yield of the DHCH product of methane (graph 7), i.e. the development time of the catalyst is associated with the presence of residual CD.

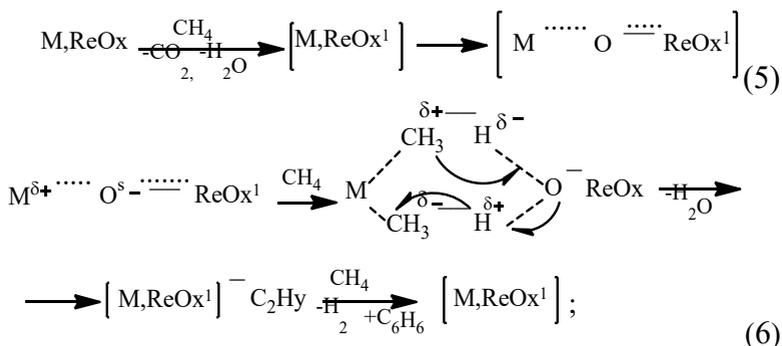
It should be noted that the reason for the change in the rate of maximum benzene yield is apparently a change in the structure and composition of carbonaceous deposits as a result of interaction with air. As a result, it is possible that the centers responsible for the formation of CD responsible for the stage of oligomerization of C_2H_y fragments into the target product are reduced (blocked). To establish the functions of CD in the formation of benzene from methane, it should be noted that the catalyst reduced by hydrogen, Ni, ReO_x / Al_2O_3 , loses its activity in the DHCH of methane. Therefore, in the case of DHCH of methane on bimetalum-alumina catalysts, for example, Ni, ReO_x / Al_2O_3 , it is natural to assume that the subsequent oligomerization of C_2H_y fragments and their transformation into benzene proceeds with the participation of surface carbonaceous deposits:



here: $n = 2 \div 3$, CD-carbonaceous deposits

These carbonaceous deposits can be in various forms responsible for oligomerization of C_2H_y fragments and dehydrocyclization of intermediate oligomers, or deactivate the catalyst.

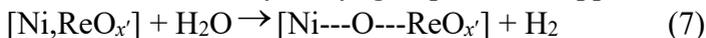
Based on the literature data and the assumption is made that the role of carbon deposits on the catalyst surface AMR along with the catalyst deactivation is reduced to dehydrocyclization and oligomerization C_2H_y intermediates formed from methane molecules involving bulk oxygen:



Indeed, the profiles obtained thermally programmed oxidation (TPO) of carbonaceous deposits (CD) on Ni catalyst, $\text{ReO}_x/\text{Al}_2\text{O}_3$ is characterized by two bands with maxima at 420 °C (low-temperature LT) and 457 °C (high temperature-HT). LT-peak characterized by a sharp decrease in the intensity and disappears after 30 minutes. HT-peak intensity monotonously decreases to zero with the duration of treatment with air coked Ni catalyst, $\text{ReO}_x/\text{Al}_2\text{O}_3$ and appears even after 60-minute treatment.

From a comparison of the data with the data TPO CD graph 6 that the activation reaction times (the difference between the initial and maximum yields of benzene) is limited by the residual amounts of LT-form carbonaceous deposits.

It has been suggested that the decrease in the dehydrocyclohexamerizing activity of the catalyst with the duration of the experiment is the result of a decrease in the concentration of bound oxygen, since after the completion of the cycle of benzene formation from methane, the reduced $[\text{Ni}, \text{ReO}_x^1]$ is again activated, being reoxidized by the formed H_2O molecules or hydroxyl groups of the support:



3. The conversion of methane in the composite catalysts $\text{M}/\text{Al}_2\text{O}_3 + \text{ReO}_x/\text{Al}_2\text{O}_3$

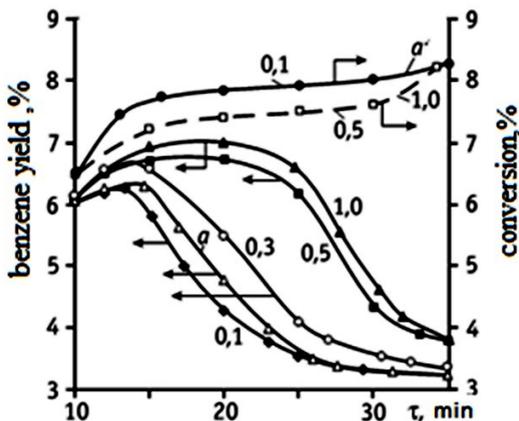
In the example composite mechanical mixtures of the catalysts are presented results of studies preparation conditions influence the individual components M, $\text{ReO}_x/\text{Al}_2\text{O}_3$ (M = Ni, Co or Pt) catalysts dehydrocyclohexamerization of methane into benzene. The interac-

tion of alkanes with composite catalysts (CC) during the reaction is shown. The initial interaction of the reactant with the catalyst is characterized by the yield of products of deep oxidation of methane. CO₂ yield practically stops in the first 7-10 minutes of the experiment and coincides with the onset of detecting the formation of benzene and increase its output. In contrast to the CO₂ release of H₂O is observed throughout the experiment, but decreased with the duration of the experience. For comparison, it was shown dynamics eduction of bound oxygen in the form of CO₂ and H₂O in the interaction of C-C respectively with H₂ and CO. In the case of the reduction of CK, which is active in DHCH methane with hydrogen, all oxygen is released in the first 5 minutes, and under the influence of CO there is some dynamics (after 2 hours) in the release of bound oxygen, and part of it (~ 13 %) remains in the catalyst. Influence H₂ and CO in the catalyst is also different. Processing of the catalyst with hydrogen leads to its irreversible deactivation; in this case, during the interaction of CH₄ with the catalyst, the release of bound oxygen after subsequent standard processing with air, without changing quantitatively, becomes similar as in the interaction with hydrogen, i.e. all bound oxygen is also released during the first 10 minutes of the experiment Unlike H₂ CO reconstitution sample leads to the reversible deactivation of the catalyst. Follow standard processing with air leads to complete reproduction data when DHCH catalytic methane and reproduced by the above dynamic allocation of bound oxygen in the interaction of the reactant with the unreduced catalyst.

The absence of DHCH activity of the catalyst in the CH₄ conversion can be due to the instability of the platinum oxide phase under DHCH methane. In this case, the activity of C-C in the conversion of methane is the result of the interaction of M with Re, which has a stable oxide phase under the reaction conditions. Therefore, taking into account the data presented: a) the dynamics of oxygen eduction during interaction with CH₄, H₂ and CO; b) complete catalyst deactivation during hydrogen reduction; c) reversible deactivation of the catalyst during the processing of CO, as well as; d) activation of the catalyst during interaction with the reactant and an increase in the activity of the aluminum-nickel catalyst upon pulsed introduction of

air into the reaction mixture, it is possible to assume with a high degree of probability that part of the oxygen bound to the catalyst is involved in the reaction.

This is confirmed by the effect of the promoting effect of supported rhenium oxide on DHCH, the activity of a monometallic catalyst during methane conversion on a mechanical catalyst mixture $M/Al_2O_3 + ReO_x / Al_2O_3$ catalyst = 1 : 1. Using the example of a mechanical mixture of catalysts Ni/Al_2O_3 catalysts: $ReO_x/Al_2O_3 = 1 : 1$, graph 7 shows the results of such a promoting effect on M/Al_2O_3 .



Graph 8. Effect concentrate-talkie ReO_x output benzene in the conversion of methane in the mechanical mixture of Ni / Al_2O_3 : $ReO_y/Al_2O_3 = 1 : 1$. $T = 650 \text{ }^\circ\text{C}$; $V = 1500 \text{ h}^{-1}$.

**Contents ReO_x % by weight. (In terms of Re) – the curves:
a, a' – $Ni/Al_2O_3 : ReO_x/Al_2O_3 : Al_2O_3 = 1 : 1 : 1$**

From the presented data show that with increasing amount of rhenium deposited from 0 to 0.5 % by mass the reaction period of the action of the mechanical mixture of catalysts for the DHCH process of methane increases, which is also accompanied by a slight increase in the yield of the target product.

An additional “argument” in favor promoting action ReO_x/Al_2O_3 on M/Al_2O_3 – is the diluting of the carrier system Al_2O_3 , which as can be seen from a comparison of curves in the graph 8 leads to a sharp decrease in the reaction period of the mixed catalyst. However,

co-deposition of nickel and rhenium solid catalysts not only leads to an increase in reaction period, but also increases the activity of the system in the conversion of methane and the yield of benzene, to the values given above. Thus ReO_x , inactive in DHCH methane, regardless of its use in the form of a mechanical mixture ($\text{Ni}/\text{Al}_2\text{O}_3 + \text{ReO}_x/\text{Al}_2\text{O}_3$) or in the form of the catalyst $\text{Ni}, \text{ReO}_x/\text{Al}_2\text{O}_3$ promotes affects non-oxidative DHCH of methane, increasing reaction catalyst period and its activity.

Note: additional studies have shown that the activity of $\text{C-C M}/\text{Al}_2\text{O}_3 + \text{ReO}_x/\text{Al}_2\text{O}_3$, unlike $\text{M}/\text{Al}_2\text{O}_3$, does not depend on the method of application Re , i.e. a method the synthesis of the second component. The resulting patterns of reactivity bound oxygen and the promotional effect of rhenium (graph 8) are not changed by replacing one of the elements M (Ni, Co or Pt) on the other, and all C-C as and $\text{M}, \text{ReO}_x/\gamma\text{-Al}_2\text{O}_3$ -catalysts prepared by described methods irreversibly deactivated by reduction with hydrogen. Thus, these data indicate identical interference between the used M elements and rhenium in $\text{M}, \text{ReO}_x/\gamma\text{-Al}_2\text{O}_3$ or their compositions and mechanical mixtures.

Studies of DHCH methane on solid $\text{M}, \text{ReO}_x/\gamma\text{-Al}_2\text{O}_3$ (mainly platinum-containing) systems shown the possibility of activation of this reaction due to the fixation of M to the carrier in the form of particles with high dispersion (in the form of pre-crystalline nanoparticles of 1-2 nm) and the effect of such formations on the reactivity of oxygen contained in the composition of the applied ReO_x .

The above data on the synergic effect of ReO_x on $\text{M}/\text{Al}_2\text{O}_3$ in the composite systems shows that such explanations are not enough, because the question of the transfer of the impact of $\text{M}/\text{Al}_2\text{O}_3$ on $\text{ReO}_x/\text{Al}_2\text{O}_3$ not only in composite systems, but also in solid. It should be noted that $\text{M}, \text{ReO}_x/\text{Al}_2\text{O}_3$ are among the deeply studied catalytic systems in connection with the fact that they are reforming catalysts (dehydrocyclization) straight-run gasolines.

Our studies on $\text{Pt}, \text{Re}/\text{Al}_2\text{O}_3$ reforming catalysts with a high dehydrocyclizing and dehydro-oligomerizing ability showed that these catalysts are not active in the DHCH of methane and in the formation of the primary C-C bond from two methane molecules.

However, contacting this catalyst with C₂₊ alkanes leads to the formation of aromatic hydrocarbons. This is an additional argument in favor of the formation of a C–C bond between methane molecules with the participation of oxygen contained in rhenium oxide.

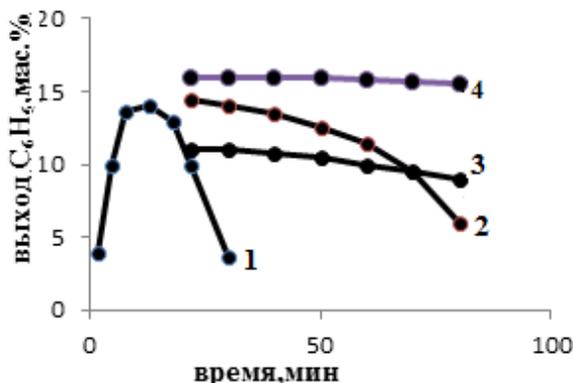
4. Stabilization of nonoxidative dehydroaromatization of methane to benzene on bimetal alumina catalysts

The formation of the primary C-C bond from two CH₄ molecules proceeds with the participation of a small part of the bound oxygen, which is part of the bimetal alumina catalyst. From a comparison of the curves of the total consumption of volumetric oxygen with the number of methane molecules undergoing DHCH per atom of oxygen () it follows that the dependence of the volumetric oxygen consumption on the time of the experiment has an extreme character, tending to a value of 82%. Thus, about 20% of the volume oxygen is involved in the formation of benzene. The presence of even a small amount of oxygen in the gas phase (~ 3 mol%) completely inhibits the formation of benzene. The maintenance of the catalyst in an oxidized state corresponding to its stable functioning can be achieved by introducing oxygen-containing ingredients into the reaction medium. Hence it follows that the ingredients can be H₂O, CO₂, CH₃OH or (CH₃)₂O (DME), which are formed in the process of DHCH methane on bimetal alumina M, ReO_x/ Al₂O₃ catalyst.

To maintain a similar state of the AMR catalyst, approximately 3 mol% H₂O or CO₂, which are reduction products, were introduced into the reaction medium after activation of the sample. At the same time, under the influence of H₂O, a sharp deactivation of the catalyst occurs (graph 9). However, the treatment of the catalyst with an inert gas (N₂ or He) at the experimental temperature results in the reproduction of the data corresponding to the DHCH of methane after the standard treatment of the catalyst.

Used as an oxidizing agent, carbon dioxide exhibits a complex character of action on the DHCH process of methane. As a result of introducing 3 mol % CO₂ into the reaction medium of DHCH methane after completion of the catalyst development, the deactivation of the C

– C bond of the catalyst slows down somewhat.



Graph 9. Influence of oxidized ingredients on DHCH methane in the presence of AMR catalyst. T-650°C; V = 1450h⁻¹, Ingredients: 1-without; 2- CO₂; 3-CH₃OH; 4-DME

The introduction of this ingredient into the reaction as an oxidizing agent, in general, does not significantly affect the stability of the catalyst functioning. These data show that oxygen-containing compounds introduced into the reaction medium affect the concentration of oxygen in the AMR catalyst.

The release of H₂O molecules during the process and the influence of the addition of H₂O additives on the course of the reaction (graph 9), and the multiple participation of oxygen atoms in the catalyst composition in the formation of C - C intermediates indicate the importance of the role of this molecule for this process.

The formation of the primary C – C bond by methane molecules is realized through an intermediate with a structure similar to DME. Therefore, methanol or DME were introduced into the reaction medium as additives instead of water molecules.

The introduction of methanol into the reaction helps to reduce the formation of benzene, but the stability of the process increases sufficiently (graph 9). The use of DME has a significant positive effect on the stability of the catalyst functioning. Due to the introduction of

DME into the reaction medium (graph 9), the DHCH process of methane acquires a sufficiently high stability.

To elucidate the influence of the ingredients on the content of bound oxygen in the composition of the AMR catalyst, the latter was subjected to titration with hydrogen after its prolonged operation, preceding deactivation.

Table 5
Influence of oxidized ingredients on methane DHCH and bound oxygen content in AMP catalyst. T-650°C; V =1450h⁻¹

| Ingredient | - | H ₂ O | CO ₂ | CH ₃ OH | DMЭ |
|-----------------------------------|------|------------------|-----------------|--------------------|------|
| Time, min | 40 | 10 | 60 | 120 | 180 |
| Conversion of CH ₄ , % | 13,4 | + | 12,1 | 11,9 | 16,5 |
| Residual O _{boun} * % | 19,5 | 100 | 28 | 25 | 21 |
| Selectivity | 87 | - | 84 | 96 | 98 |

* 100% residual bound oxygen O_{boun} corresponds to 0.139 mmol/g catalyst

In table 5 the corresponding catalytic parameters of the reaction and the presence of residual bound oxygen on the catalyst sample were compared. It can be seen from these data that the presence of an excess of H₂O molecules in the reaction medium brings the catalyst not only to the initial oxidized state, but also blocks the methane-catalyst interaction. Unlike H₂O, in an environment with CO₂, the sample partially replenishes the content of bound oxygen, in relation to the initial one. The presence of CO₂ in the reaction zone insignificantly increases the stability of the process, which leads to a decrease in the selectivity for the target product.

Of particular interest for the DHCH process of methane are additions of methanol and dimethyl ether, which make it possible to maintain the concentration of bound oxygen at the required level. The presence of these ingredients in the reaction zone makes it possible to sharply stabilize the DHCH process of methane in the presence of an AMR catalyst while maintaining high selectivity for the target product. At the same time, a comparison of the effects of methanol and DME on the process shows that in the case of the former, the catalyst is less active and contains 4% more bound oxygen.

Taking into account the influence of H₂O molecules on the

DHCH process of methane and the oxidative effect on the AMR catalyst, it is possible to associate the stabilizing effect of CH₃OH and DME and differences in the number of water molecules formed during the interaction of these ingredients with the AHP catalyst.

The results obtained indicate the importance of the role of the oxidized state of the AMR catalyst and H₂O molecules for maintaining the concentration of active centers involved in the formation of primary C-C bonds in the DHCH process of methane in benzene.

DHCH of methane in benzene proceeds with the participation of a small part (18-22%) of bound oxygen, which is part of the M, ReO_x / Al₂O₃ catalyst. The introduction of small additions of methanol or DME into the reaction medium makes it possible to maintain the catalyst in a pseudo-equilibrium oxidized state, which is necessary for the stable course of the process.

5. Dehydration dimerization of methanol

Possible use of DME as a clean energy source, implies a sharp increase in the production of this compound. Combination preparation with methanol to DME by dehydration improves the conversion of synthesis gas in a single pass over the catalyst with 15 % (preparation CH₃OH) to almost 90 %. For this purpose, use a mechanical mixture of catalysts for methanol production from synthesis gas and dehydration to DME. Given the nature of the acid catalysts in the dehydration of alcohols, ethers, for dehydration of methanol were used and HSZM HY-5 zeolite catalysts. From Table 8, it follows that the conversion of methanol to HSZM-5 (2) is accompanied by formation of substantially hydrocarbon products, but the catalyst is not stable, and for 30 minutes at 360 °C reduces its activity from 75.6 % to 8 %.

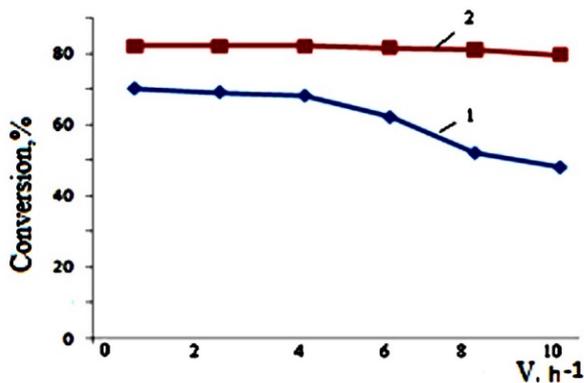
Despite the stability, selectivity of the catalyst for both of DME and hydrocarbons is low. Positive results in the conversion of methanol exhibit zeolite catalysts impregnated with phosphoric acid.

As seen from Table 6, HZSM-5 catalyst in this case becomes stable conversion of methanol to hydrocarbons and cannot create a catalyst having high activity and selectivity in the dehydration of methanol to DME based on Y zeolite.

Table 6
The conversion of methanol on zeolite catalysts modified H₃PO₄. T = 300 °C, V = 3 h⁻¹

| Time, min | Composition of the reaction mixture, % C | | | | |
|--|--|-------------------|------------------|------|--------------------|
| | CH ₄ | ΣC ₂₊₌ | ΣC ₂₊ | DME | CH ₃ OH |
| | HY + Al ₂ O ₃ | | | | |
| 15 | 1.7 | 14.8 | 5.7 | 56.5 | 21.3 |
| 120 | 1.6 | 16.5 | 4.5 | 55.8 | 21.6 |
| HZSM-5 + Al ₂ O ₃ | | | | | |
| 15 | 2.4 | 60.85 | 21.84 | 10.6 | 24.4 |
| 120 | - | - | - | 7.4 | 92.0 |
| 5% P ₂ O ₅ / HY + Al ₂ O ₃ | | | | | |
| 120 | 2.6 | 0.25 | 0.23 | 95.7 | 1.25 |
| 5% P ₂ O ₅ / HZSM-5 + Al ₂ O ₃ | | | | | |
| 15 | 2.8 | 60.75 | 18.1 | 10.6 | 7.8 |
| 120 | 2.5 | 60.8 | 21.6 | 10.8 | 4.3 |

Moreover, as can be seen from the graph 10, Y-containing catalyst retains its activity even at space velocities greater than 10 h⁻¹, i.e. it has high productivity, it is very important not only for the direct conversion of syngas to DME, but regulation methanol/DME by simply changing the amount of load of a dehydrating catalyst.



Graph10. Effect of volume speed on conversion of methanol on the catalyst P₂O₅/HZSM-5. 1 – 260 °C; 2 – 300 °C

From the above data it follows that not all types of acidic catalysts, even of the same nature (alum inosilicates) may be effective for

obtaining alignment and dehydration of methanol to DME in a single reaction space. It should be noted that the use of a mechanical mixture of catalyst as the second component contacts, based on structural analogs ZSM-5, (combining the production of methanol from synthesis gas and its conversion to hydrocarbons), leads to the deactivation of the first catalyst.

This implies that the primary product synthesis catalyst in a mechanical mixture of the contacts should not experience negative effects of the final products, and the conversion of the primary product in the end to be shifted towards the latter, as occurs in the conversion of syngas to DME. Therefore, for effective selection of mechanical components of the mixture contacts for subsequent stages or MtSynfuels DMETSynfuels required to establish the causes of the primary product.

6. The conversion of methanol and DME to hydrocarbons

Contacting the DME and methanol H-ZSM-5 catalyst modified with phosphoric acid under otherwise equal conditions leads to a different distribution of hydrocarbon products.

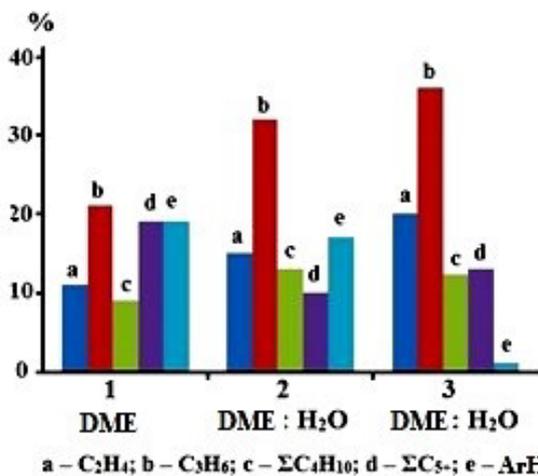
Comparison of DME conversion products with the products of methanol conversion on 5 % P₂O₅/HZSM-5 shows that in the first case to form hydrocarbons of higher molecular weight ΣC_{5+} and aromatic hydrocarbons (ArH) except benzene, i.e. occurs deeper hydrocarbon oligomerization primary intermediates.

Product conversion of methanol and DME to P₂O₅/HZSM-5 are very different from the products formed by contacting the methanol and DME with a mechanical mixture consisting of phosphate HZSM-5 and HY. As follows from the data presented in Table 7, in the presence of P₂O₅/HY, the main products of methanol conversion are a C₂-C₄ olefins yield reaches almost 80 %. However, conversion of DME in the presence of P₂O₅ HY has no significant impact. This difference in the conversion products of these substances possibly associated with different water vapor content in the reaction medium for the conversion of these reactants.

Table 7

The product distribution conversion of methanol and DME
5 % HZSM-5 u 5 % P₂O₅ HZSM-5 (2) + 5 % R₂O₅ HY (1 : 1).
T = 375 °C; V = 350 h⁻¹; reactant : N₂ = 1 : 1 (vol.)

| Catalyst | 5 % P ₂ O ₅ HZSM-5 | | 5 % P ₂ O ₅ HZSM-5 (2) + 5 % P ₂ O ₅ HY | |
|-------------------|--|-----------------------------------|---|-----------------------------------|
| | CH ₃ OH | (CH ₃) ₂ O | CH ₃ OH | (CH ₃) ₂ O |
| Methane | 0.5 | Traces | - | traces |
| Ethylene | 14 | 11 | 24 | 12 |
| Ethane | 2 | 0.5 | 1.0 | 0.5 |
| Propylene | 34 | 21 | 40.2 | 23 |
| Propane | 1.0 | 1.2 | 1.5 | 1.2 |
| DME | 3.5 | - | - | - |
| ΣC ₄ = | 13 | 9 | 14.2 | 8.5 |
| ΣC ₄ + | 4 | 18.2 | 9.6 | 16.5 |
| ΣC ₅ + | 10 | 19.0 | 7.0 | 18.5 |
| Benzene | 0.8 | 0.8 | traces | 1.0 |
| ArH | 17.2 | 19.3 | 2.5 | 18.8 |



Graph 11. Effect of water vapor on the distribution of DME conversion products: 1, 2 – 5 % P₂O₅/HZSM-5; 3 – 5 % P₂O₅ HZSM-5 + 5 % P₂O₅/HY(1 : 1) T = 450 °C; V = 1h⁻¹

Indeed, as can be seen from the graph 11, the introduction of additional portions of water corresponding to the conversion of metha-

nol released, allows the composition to bring together product conversion of DME and methanol.

7. Dynamics and mechanism of formation of intermolecular C-C bonds involving methanol and methane

The above data show that the formation of C-C bonds between the molecules of methane or propane with benzene activated metal redox centers AMR catalysts containing elements VIII used particle group less than 2 nm. Therefore, MMC acidic components (mechanical mixture of catalysts) must activate oxidation-functionalized methane (methoxy formation) to the corresponding compounds, i.e. the formation of C-C bonds.

Character conversion of methanol, the oxidation of methane functionalized on zeolite catalysts are essentially depending on the type of zeolite which is prepared on the basis of the test sample (table 8) as a result of converting methanol to Y-zeolite sample (PM) is formed dehydration product methoxymethane–dimethyl ether (DME), which constitutes the main part of the converted reactant. Selectivity of DME (70-72 %) is not sufficiently high, but the amount of conversion of methanol and the resulting composition catalyze around timeslot PM test sample remains stable.

Table 8
The conversion of methanol on the sample PM;
T = 300 °C, V = 2 h⁻¹

| Time, min | Composition catalyze% CH ₂ | | | | |
|--------------|---------------------------------------|--|---|------|--------------------|
| | CH ₄ | $\sum_{\text{Olef}} \text{C}_2\text{-C}_4$ | $\sum_{\text{steam}} \text{C}_2\text{-C}_4$ | DME | CH ₃ OH |
| 15 | 1.7 | 14.8 | 5.7 | 56.5 | 21.3 |
| 120 | 1.6 | 16.5 | 4.5 | 55.7 | 21.5 |

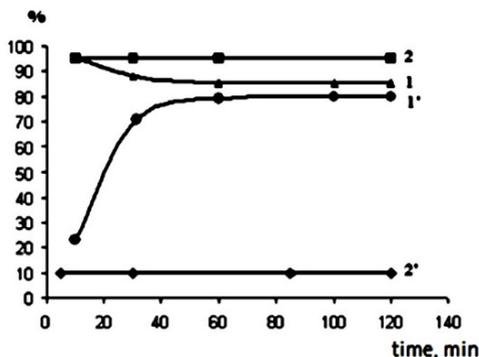
The conversion of methanol on pentasyl-containing sample (PM-1) is very different from its conversion on the PM sample. Product conversion of methanol on the sample PM-1 are aliphatic hydrocarbons consisting mainly of small amounts of CH₄, C₂-C₄ unsaturated and limiting C₃+ alkanes, also DME.

Methanol conversion during the first hours of PM-1 (graph 12) decreases slightly and then remains stable. Yield DME in the initial

30 minutes sharply rises and then remains at the same level.

Thus, PM-1 sample in the initial state exhibits high selectivity in the conversion of methanol to aliphatic hydrocarbons, with increasing duration of the experiment is sharply reduced due to increase selectivity symbolically DME. Marked differences in the conversion of methanol on the PM and PM-1 samples indicate that the selective conversion of methanol to DME proceeds at the contacts of an open surface, among which can be attributed to both Al_2O_3 , and wide porous zeolite Y, but the formation of hydrocarbons takes place at a narrow porous molecular sieves zeolite ZSM-5.

The introduction of phosphorus samples PM and PM-1 has a positive effect on the selectivity and stability of the contacts. The modified phosphoric acid PM-1R sample differs from the sample PM-1 higher activity, stability and increased yield of hydrocarbon products, while the yield of DME, although it remains stable, sharply reduced (to 10 %). The composition catalyze during the experiment remains practically constant. Modification PM phosphoric acid increases the selective conversion of methanol and DME yield.



Graph 12. The dependence of these converter methanol HZSM-5 catalysts of the duration experiments.

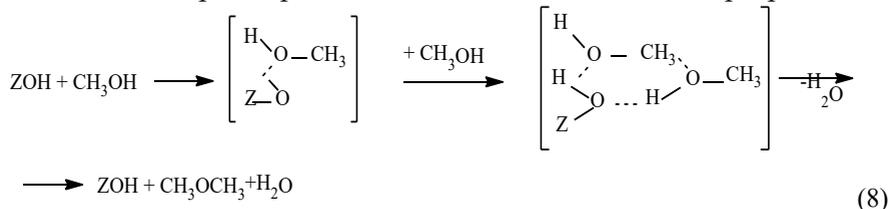
1, 1' – PM-1, 2, 2' – PM-1R; 1, 2 – CH_3OH conversion; 1', 2' – selectivity DME

A comparison of the results of methanol conversion on PM, PM-1 and PM-R and PM-1P samples modified with phosphoric acid shows that an increase in the stability and activity of these samples is accompanied by: a) increase in selectivity for DME on PM-P (up to

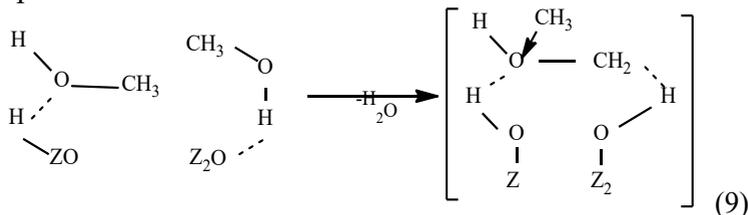
98 %); b) an increase in hydrocarbon selectivity at PM-1P. Based on these data, taking into account a decrease in the yield of hydrocarbons with increasing yield of DME (graph 12), it follows that the formation of hydrocarbons from methanol is preceded by the formation of DME.

Taking into account the literature data, it is assumed that 2 ZOH ZOZ + H₂O centers formed as a result of equilibrium zeolite dehydration are responsible for the formation of primary C-C bonds at methanol transformation. Modification of the PM sample with phosphoric acid increases DME activity and selectivity due to blocking ZOZ (Z₂O) groups and increasing hydroxyl groups in wide pores zeolite. In case of narrow porous pentasil PM-1 due to steric hindrance Z₂O centers located in the cavities of the micro pores may remain unavailable to react with phosphoric acid and therefore retain their activity in the formation of C-C bonds in methanol conversion.

The following mechanism of formation of dimethyl ether from methanol with participation of brandsted acid centers is proposed:



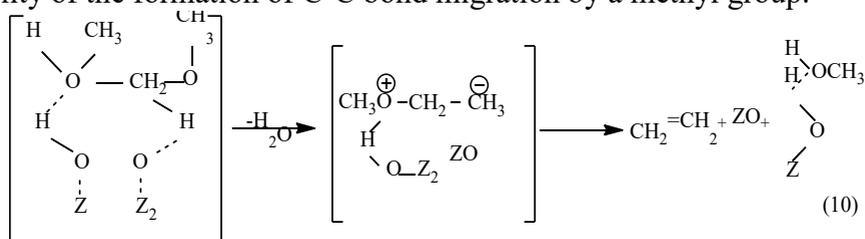
Formed on narrow porous pentasil DME with Z₂O, create a two-center bond with a deficit of electron density on one of the methyl groups:



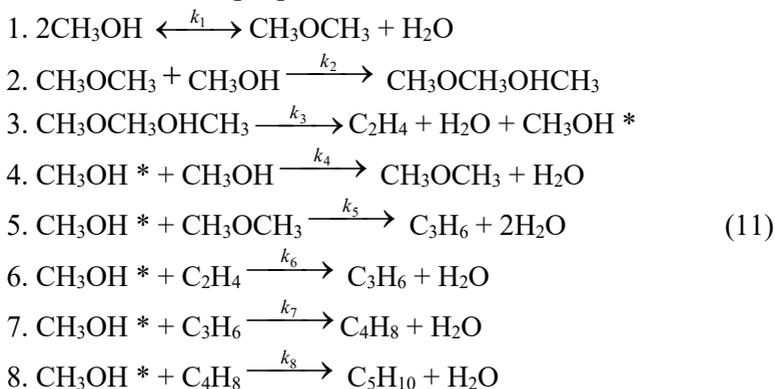
Attack of this group by hydroxyl group of the third molecule of methanol leads to formation of primary ethylene molecule.

Scheme (9) formally represents the isomerization of DME to ethanol. This conclusion is consistent with the idea that the formation of ethylene involves three molecules of methanol and proves the possi-

bility of the formation of C-C bond migration by a methyl group.



Taking into account the literature and obtained data on possible stages of methanol dehydration, the following scheme of the mechanism of products formation at the initial stages of methanol transformation reaction was proposed¹:



where CH_3OH^* – intermediate substances that are methanolonium ions sorbed at the brandsted acid centers.

Thus, a system of differential equations to describe the process kinetics on the basis of the proposed mechanism for the formation of products from intermediate substances, which are methoxy formulations sorbed at brandsted acid centers¹:

$$\begin{aligned}
 \frac{dC_1}{d\tau} &= -2(k_1C_1^2 - k_9C_2C_3) - k_2C_1C_2 - k_4C_1C_5 \\
 \frac{dC_2}{d\tau} &= 2(k_1C_1^2 - k_9C_2C_3) - k_2C_1C_2 + k_4C_1C_5 - k_5C_2C_5
 \end{aligned}$$

¹ Велиева Ф.М. Превращение метанола на цеолитных катализаторах. Сообщение 2. Кинетический анализ превращения метанола в углеводороды на НЦВК-содержащем контакте / Н.Н. Пириев, Р.Г. Ахмедова, Ф.А. Бабаева, Ф.М. Велиева, М.И.Рустамов // Процессы нефтехимии и нефтепереработки.– Москва: –2010, № 2(42), – с. 190-194.

$$\begin{aligned}
\frac{dC_3}{d\tau} &= 2(k_1C_1^2 - k_9C_2C_3) + k_3C_4 + k_5C_2C_5 + k_6C_5C_6 + k_7C_5C_7 + k_8C_5C_8 \\
\frac{dC_4}{d\tau} &= k_2C_1C_2 - k_3C_4 \\
\frac{dC_5}{d\tau} &= k_3C_4 - k_4C_1C_5 - k_5C_2C_5 - k_6C_5C_6 - k_7C_5C_6 \\
\frac{dC_6}{d\tau} &= k_3C_4 - k_6C_5C_6 \\
\frac{dC_7}{d\tau} &= k_6C_5C_6 - k_7C_5C_7 \\
\frac{dC_8}{d\tau} &= k_7C_5C_7 - k_8C_5C_8
\end{aligned} \tag{12}$$

where $C_1 - \text{CH}_3\text{OH}$; $C_2 - \text{CH}_3\text{OCH}_3$; $C_3 - \text{H}_2\text{O}$; $C_4 - \text{CH}_3\text{OCH}_3 \text{ OHCH}_3$; $C_5 - \text{CH}_3\text{OH}^*$ intermediate substances, which are methanolonium ions of methanol, sorbed on the brandsted acid centers; $C_6 - \text{C}_2\text{H}_4$; $C_7 - \text{C}_3\text{H}_6$; $C_8 - \text{C}_4\text{H}_8$

The kinetics of the conversion of methanol to hydrocarbons using the described two-phase model, which addresses the reactant concentration in the bulk gas flow and the pellet catalysts.

$$\begin{aligned}
k_1 &= 9,33 \cdot 10^7 \exp(-103650 / RT) \\
k_2 &= 3,88 \cdot 10^6 \exp(-93660 / RT) \\
k_3 &= 2,35 \cdot 10^6 \exp(-93370 / RT) \\
k_4 &= 1,76 \cdot 10^7 \exp(-102170 / RT) \\
k_5 &= 2,36 \cdot 10^5 \exp(-73050 / RT) \\
k_6 &= 1,09 \cdot 10^5 \exp(-65740 / RT) \\
k_7 &= 4,48 \cdot 10^3 \exp(-43670 / RT) \\
k_8 &= 2,35 \cdot 10^3 \exp(-43760 / RT) \\
k_9 &= 4,30 \cdot 10^2 \exp(-39050 / RT)
\end{aligned} \tag{13}$$

To solve the system of differential equations used the Matlab-7 program, with its built-in software module. Search was performed by the method of random steps by optimizing the parameters of the

equation (speed constant) to minimize the deviations of calculated values of speeds of experimental steps to achieve, resulting in the smallest value of their difference.

Evaluation of kinetic constants of equations obtained (Table 9) was performed by the modified method of random search with automatic selection step at a relative error of 10^{-4} - 10^{-5} .

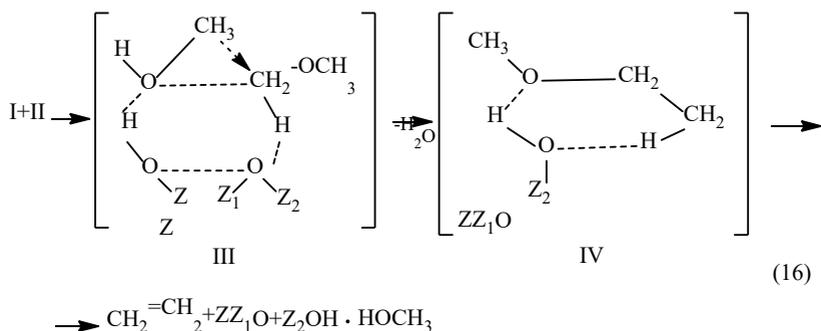
Table 9
Kinetic parameters of methanol conversion
on HZSM-5 containing contact

| $k_i \cdot 10^{-2},$ s^{-1} | T, K | | | k_0 | E, J / mole |
|----------------------------------|------|------|------|-------------------|-------------|
| | 570 | 630 | 650 | | |
| k_1 | 3.37 | 24.3 | 50.3 | $9.33 \cdot 10^7$ | 103650 |
| k_2 | 1.37 | 3.03 | 24.5 | $3.88 \cdot 10^6$ | 93660 |
| k_3 | 1.01 | 2.11 | 18.2 | $2.35 \cdot 10^6$ | 93370 |
| k_4 | 1.02 | 3.03 | 21.3 | $1.76 \cdot 10^7$ | 102170 |
| k_5 | 4.71 | 33.4 | 24.5 | $2.36 \cdot 10^5$ | 73050 |
| k_6 | 11.2 | 38.5 | 63.1 | $1.09 \cdot 10^5$ | 65740 |
| k_7 | 25.6 | 43.2 | 92.3 | $4.48 \cdot 10^3$ | 43670 |
| k_8 | 12.1 | 23.4 | 34.9 | $2.35 \cdot 10^3$ | 43760 |
| k_9 | 0.56 | 2.53 | 3.93 | $4.30 \cdot 10^2$ | 39050 |

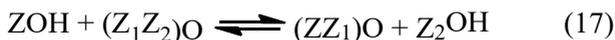
Evaluation of kinetic constants of equations obtained (Table 9) was performed by the modified method of random search with automatic selection step at a relative error of 10^{-4} - 10^{-5} .

Satisfactory consistency of experimental and computational data shows the adequacy of the model obtained. From the data in Table 9 shows that stages (6)-(8) with high values of speed constants of low molecular weight olefins formation do not have a limiting effect on the reaction course.

The transformation of methanol into primary ethylene is mainly influenced by stages (1)-(4) responsible for the formation of both DME (1) and formation and accumulation of methanolonium ion. It is difficult to form propylene as primary olefin on PM-1 and PM-1P samples. Stages (1)-(8) involve the interaction of two components, one of which (methanolonium ion) is in a sorbed state. The low value of pre-exponents k_5 shows that interaction with this DME formation



The redistribution of bonds in this complex with the release of a water molecule leads to the formation of a new complex (IV), which decomposes with the release of ethylene. The scheme draws attention to the fact that the formation of ethylene is accompanied by a transition to a. B.c. in b. L c.:



This change in surface properties is important for the implementation of catalytic processes and can certainly be the subject of further research. However, redistribution of bonds explains the possible stage of formation of the primary C-C bond, which is limiting in conversion methanol to hydrocarbons. Such a statement is based on the fact that dehydration of ethanol to ethylene, unlike methanol, flows easily on aluminum oxide and zeolite Y. The process on ZSM-5 according to scheme (16) agrees well with the known notions about the participation of three methanol molecules in the formation of ethylene and intermediate, similar in structure to methoxyethane. Therefore, the distances between a.B.c. (ZOH) and b.L.c. ($\text{Z}_1\text{Z}_2\text{O}$), limited by the dimensional parameters of zeolite micropores, contribute to the formation of activated III complexes in them. Moreover on the basis of the received data it is possible to draw a conclusion that with reduction of diameter of micropores from 1,32 (Y) to 0,55 nm (ZSM-5) probability of formation of such complex increases up to the limiting value (absence in DME products) and, consequently, predetermines structural sensitivity of primary ethylene formation at transformation of methanol and DME to structural type of zeolite. In this regard, it should also be noted that in the case of more narrow-

porous zeolites SAPO-34 and SAPO-17 (pore diameters 0.32-0.38 nm), the assumption of ethylene formation through ethanol (by means of two methanol molecules) can also be described by the scheme (13). However, in this case, due to the short distances between a.B.c. and b.L.c., in comparison with ZSM-5, the place of methanol (methoxony) in intermediations I and III is occupied by a water molecule (hydroxonium). The conversion of methanol on the H-ZSM-5 zeolite into higher hydrocarbons involves the successive formation of DME and primary ethylene. In contrast to methanol, the main products of which are low-molecular weight olefins, the transformation of DME is accompanied mainly by the formation of higher-molecular weight aliphatic hydrocarbons of the isostructure. During DME conversion, the additional water vapors introduced do not effect the yield of ethylene primary hydrocarbon, but influence only its subsequent oligomerization, reducing the yield of higher molecular weight hydrocarbons. At the same time it should be noted that water vapors, inhibiting oligomerization of formed low molecular weight olefins, do not influence primary ethylene alkylation. Therefore, by varying the ratio of DME (methanol) : H₂O can be purposefully regulated the yield of hydrocarbon products of their transformation.

Thus, the results of the research have shown that the modification of wide-porous type Y zeolites with phosphoric acid allows the process of methanol esterification at $V = 1072 \text{ h}^{-1}$ and due to this increases the productivity of methanol dehydration reaction in DME (at methanol conversion and DME yield, close to equilibrium). Analysis of the results obtained and literature data suggests that the formation of primary hydrocarbons is carried out with the participation of the Bronsted acid centers and the basis Lewis catalyst centers and depends on the distance between these centers. Therefore, this reaction can be considered a structurally sensitive reaction. With reduction of microporous diameter of zeolites from 0.55 (ZSM-5) to 0.38 nm (SAPO-34) at formation of primary ethylene one of methanol molecules is replaced by water molecule. This explains high yield of ethylene on SAPO-34 zeolites in comparison with ZSM-5, which is characterized by increased of propylene.

The analysis of kinetic regularities confirms the probability of the formation of primary ethylene from methanol involving three alcohol molecules through the intermediate substance, its methoxylation and decomposition to ethylene and methanoloxonium ion responsible for continuing the chain of further catalytic transformations of methanol.

8. Low temperature dehydroalkylation of benzene with propane

This section of the work is devoted to confirming the laws of methane activation with the formation of a primary C-C bond with its DHCH by involving the gas of alkane – propane in the formation of intermolecular C-C bonds. In such conditions the formation of a primary C-C bond molecules of methane, this hydrocarbon, in the main, is subjected to aromatization at 500 °C. With the participation of methane, propane at AMR forms C₄ alkanes, but with a very low yield. However, the formation of butanes indicates that propane is able to be activated to AMR systems at lower temperatures. In particular, to involve in the formation of C-C bond, benzene and lower temperatures were used. By selecting the catalysts for the conversion of propane it was shown that it is able to be activated at low temperatures only for a catalyst comprising a mechanical mixture, consisting of an active AMP catalyst in DHCH and an H-form zeolite (Y, MOR, ZSM-5).

9. Catalytic activation dehydroalkylation benzene propane to systems M, ReO_x/γ-Al₂O₃ + H-zeolite

Formation of products conversion of benzene-propane mixtures MMC (mechanical mixture of catalysts) is accompanied by the occurrence of three reactions: a) the alkylation of benzene; b) the propane dehydrogenation; c) the formation of alkylaromatic hydrocarbons (ArH). The course of these reactions depends on the contact conditions of the studied mixtures with MMC.

Conversion C₆H₆ : C₃H₈ mixtures at atmospheric pressure and low temperatures (< 200 °C) results in the formation. IPB (isopropyl

benzene). With increasing temperature, the product composition changes, so at 250 °C propylene is fixed, and above 300 °C formed an ArH (aromatic hydrocarbons). However, a further increase temperature to 400 °C leads to a decrease of benzene conversion. In the temperature range 400-450 °C IBT and propylene yield is reduced to zero, and the formation of ArH, as a result of the conversion of benzene, passed through a minimum increase again. These changes in the conversion of benzene and the yield of aromatic hydrocarbons are accompanied by the formation of low molecular weight alkanes C₁-C₂. These data indicate different mechanisms of ArH formation at temperatures below and above 400 °C. Comparing the laws of formation of isopropyl benzene, aromatic hydrocarbons at temperatures of 175-400°C it can be assumed that the ArH formed by series-parallel diagram, namely through as isomerization, and by converting the total intermediate. An increase in the yield of the ArH with a simultaneous decrease in the yield of IPB shows that the main contribution to the formation of the ArH is connected to the serial conversion of IBT. An increase in the yield of ArH with a simultaneous decrease in the output of IPB shows that the main contribution to the formation of ArH is associated with the successive conversion of IPB. It is shown that isopropyl benzene and propylene are the main products of the conversion of benzene-propane mixtures.

Table 10
Effect of temperature on the conversion of a mixture
of C₆H₆ : C₃H₈ (1 : 9 mol). On MMC- AMRC + HY; V = 500 h⁻¹

| T, °C | Conversion, % | | Product yield, % | | | | |
|-------|-------------------------------|-------------------------------|------------------|-------------------------------|--------|-----|--------------------------------|
| | C ₆ H ₆ | C ₃ H ₈ | IPB | C ₃ H ₆ | NPB | ArH | C ₁ -C ₂ |
| 200 | 4.8 | 0.6 | 1.4 | 0 | 0 | 0 | 0 |
| 250 | 11.4 | 2.0 | 3.1 | 0.6 | traces | 0 | 0 |
| 300 | 31.7 | 7.6 | 8.7 | 2.9 | 0.8 | 0 | 0 |
| 320 | 59.6 | 4.8 | 13.9 | 7.1 | 3.2 | 0.8 | 0 |
| 350 | 37.0 | 22.8 | 6.5 | 15.3 | 3.4 | 1.2 | 0 |
| 375 | 18.7 | 23.8 | 1.7 | 21.4 | 1.7 | 2.2 | 0 |
| 400 | 8.1 | 5.4 | traces | 3.5 | 0.4 | 1.5 | traces |
| 450 | 11.3 | 3.3 | 0 | 1.5 | traces | 1.5 | 2.2 |

The results show that regardless of the nature of the zeolite component of the MMC, carrier Bronsted acid centers, propylene begins to form at a temperature of 250 °C and its yield increases with temperature reaching a maximum value at 375 °C, i.e. the maximum values of benzene conversion, and yield IPB (320 °C), and propylene are different (Table 10).

Note that the type of zeolite affects the conversion and the yield (selectivity) product is converted mixture. Thus, at a temperature of 320 °C the conversion of benzene is reduced depending on the component type zeolite MMC as follows: Y > MOR > ZSM-5. At a temperature of 375 °C, this range is converted: ZSM-5 > MOR > Y. It should also be noted a slight difference between the total MMC activity studied. Replacement of the zeolite component changes the distribution of MMC C₆H₆/C₃H₈ mixture transformation products. Among the MMC zeolite components (Y, MOR, ZSM-5) yield of propylene and n-propyl benzene (NPB), increases, and also increases the temperature of formation ArH.

This a change corresponds to the usual conversion of aromatic hydrocarbons on used zeolites and is associated with their molecular sieve properties. Wherein, the ratios of the yield of IPB and propylene are limited by thermal control, and the formation of other (secondary) products given their dependence on the microporous structure of the zeolite, – kinetic. The latter is also connected with the IPB reactivity depending on the reaction conditions, so IPB yield decreases with increasing temperature due to dealkylation at acidic centers. Consequently, low-temperature dehydrogenation of propane is a result of the decay of the intermediate IPB (NPB), and benzene, plays the role of an astechiometric component.

10. The effect of reaction conditions on the conversion of benzene-propane mixtures on mechanical mixtures of catalysts

Results of studying the conversion of C₆H₆ : C₃H₈ mixtures MMC showed that only in the presence of benzene MMC has activity in a low temperature (≥ 180 °C) conversion of propane. The introduction of small amounts of benzene into propane (for example, 10

mol %) leads to its transformations and the formation of hydrogen, the molar value of which corresponds to the total molar conversion of propane. Eduction of hydrogen in the conversion of benzene-propane mixtures is a total reflection of the noted reactions. Conversion $C_6H_6 : C_3H_8$ mixtures depends on the pretreatment of the catalyst. Eduction hydrogen subjected to standard processing air MMC characterized by a period of activation. This activation period MMC is associated exclusively with the interaction of propane with AMR catalyst and, by analogy with methane, may be a consequence of the partial reduction of the metal component of MMC (table 11).

Table 11
The effect of the ratio of benzene conversion of propane and a mixture of $C_6H_6 : C_3H_8$. T = 250 °C, V = 500 h⁻¹

| Content, mol. % | | Conversion, % | | The product yield, % C | | |
|-----------------|----------|---------------|----------|------------------------|----------|-----|
| C_6H_6 | C_3H_8 | C_6H_6 | C_3H_8 | IPB | C_3H_6 | ArH |
| 125 | 100 | - | 0 | - | - | - |
| 250 | 90 | 12 | 1.9 | 3.6 | 0.5 | - |
| 500 | 75 | 14 | 7.2 | 6.2 | 0.7 | 2.2 |
| 750 | 50 | 23 | 7.7 | 6.4 | 0.4 | 2.6 |
| 1000 | 0 | 0 | - | - | - | - |

It is seen from Table 11, that the yield of conversion products $C_6H_6 : C_3H_8$ mixtures depends on their ratio. Changing the molar ratio of $C_6H_6 : C_3H_8$ from 1 : 9 to 1 : 1 leads to an increase in conversion of benzene and C_9 growth ArH composition.

Table 12
The effect of volume speed rate of reactants on the conversion of benzene-propane mixture at MMC-AMPK + HY; T = 250 °C

| V, h ⁻¹ | Conversion, % | | | Product Yield, % | | |
|--------------------|---------------|----------|-----|------------------|--------|-----|
| | C_6H_6 | C_3H_8 | IPB | C_3H_6 | NPB | ArH |
| 125 | 18.2 | 2.7 | 4.3 | 0.1 | 0.3 | 0.4 |
| 250 | 15.8 | 2.2 | 4.0 | 0.4 | 0.2 | 0.1 |
| 500 | 11.4 | 2.0 | 3.1 | 0.6 | traces | 0 |
| 750 | 10.2 | 2.9 | 2.8 | 1.4 | 0 | 0 |
| 1000 | 8.5 | 5.7 | 2.3 | 3.9 | 0 | 0 |

Varying the volume speed of from 125 to 1000 h⁻¹ changes as

the conversion of components of C₆H₆ : C₃H₈ mixture and distribution of the reaction products (table 12) – below than 500 h⁻¹ is increased yield IPB and formations NPB and ArH with slight amounts of propylene. Increasing the volume speed leads to a monotonic decrease of benzene conversion, while the conversion of propane in the range of V = 125-500 h⁻¹ is reduced, and then increases again with growth the volume speed of from 500 to 1000 h⁻¹.

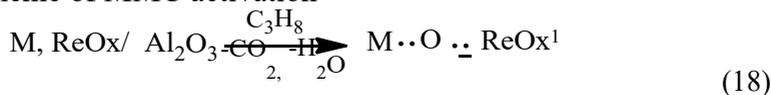
Varying the ratio of metal and acid MMC components leads to a change in the transformation products C₆H₆ : C₃H₈ mixtures.

The data show that the type of zeolite influences the conversion of individual components of the reaction mixture and the yield (selectivity) of the reaction products.

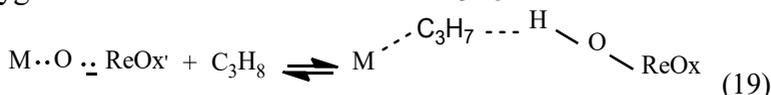
11. Cyclic proton transport between spatially separated centers

The results obtained show that at sufficiently low temperatures contacting benzol-propane mixture on the mechanical mixture of catalysts leads to the formation of products of two thermodynamically difficult reactions: dehydrogenation of propane and dehydroalkylation of benzol propane.

Taking into account the above mentioned facts: a) absence of activity in the reconstructed MMC samples; b) activation of propane only by the non-reconstructed metal-containing MMC component; c) presence of a catalyst activation period associated with partial recovery of the MMC metal component may suggest the following scheme of MMC activation



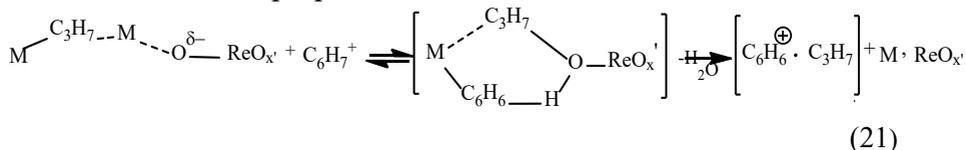
contributing to the formation of some active bridge form of bound oxygen involved in the activation of C₃H₈.



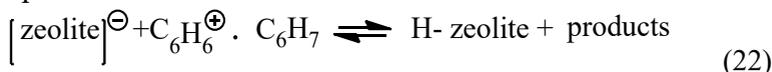
The interaction of benzene with the H-zeolite component of MMC promotes the formation of a stable benzolonium ion.



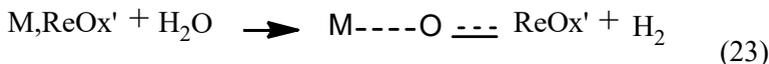
able to migrate to the metal-containing component of MMC and interact with activated propane.



The formed carbocation $[\text{C}_6\text{H}_6^{\oplus} \cdot \text{C}_3\text{H}_7]$ undergoes stabilization (with isomerization, depending on reaction conditions) on the zeolite component of MMC



Adjacent H_2O molecules, by analogy with DHCH methane, interact with reduced centers localized in AMR (MMC component).



The results of IR spectral study of APRC properties confirm the ability of the AMR component to reoxidation under the influence of molecules of formed water or due to hydroxyl groups of the carrier, which follows from the data of IS DR.

The noted thermodynamic restrictions are eliminated by reduction-oxidation stages (19) and (21) and cyclic proton transfer between MMC components by (20) and (23).

Thus, comparing the reactions of low-temperature DHA benzene with propane or propane dehydrogenation with the reaction of DHCH methane, it is possible to note an important similarity in their implementation, the stages pass through the formation of an alcoxy group. According to the data on methanol transformation to hydrocarbons, such a methoxy group is formed by separating one water molecule from two methanol molecules, i.e. the reaction is limited to the formation of an initial methoxy group associated with the catalyst, i.e. such preliminary stage due to functionalization of methane to methanol is realized at low temperature. Direct functionalization

of methane in one stage occurs with the participation of bound oxygen with the corresponding reactivity, but naturally requires higher temperatures. The presence of such oxygen in AMR and similar systems occurs under the influence of highly dispersed nanoparticles of group VIII b elements (smaller than 2 nm) on the applied rhenium oxide. It follows that the formation of primary C-C bond in all studied reactions flows through the formation of an alkoxy group bound with the catalyst and with the subsequent release of a water molecule, in combination with a second reactant.

The results obtained show the possibility of synthesis of catalysts for direct aromatization of methane with high activity (~ 30 %) and selectivity (~ 80 %), which allows to simultaneously obtain benzene and hydrogen, which are the most important intermediates for the synthesis of cyclohexane or isopropylbenzene, as well as for the synthesis of isopropylbenzene from benzene and propane. The results show that it is possible to effectively translate the MtSynfuels process into DMEtSynfuels. Moreover, the regularities of DHCH methane on AMR catalysts are unambiguously the basis for an alternative method of obtaining hydrogen and products of hydrogenation of benzene with the product of this reaction.

Comparative analysis of the results: methane dehydrocyclohexamerization, low-temperature propane alkylation and propane dehydration in the presence of benzene as well as the transformation of methanol or dimethyl ether into hydrocarbons allows to draw an important conclusion about the mechanism of formation of intermolecular C-C bond and assume that for the activation of methane and its low-molecular homologues need catalysts containing highly dispersed particles of elements of group VIII b (Ni, Co, Pt), with particle size not exceeding 2.0 nm, and polyvalent metal oxides, on which under the influence of the first, oxygen acquires reactive heterogeneity. Part of such oxygen is involved in the activation of methane and its gaseous homologues by their involvement in the process of primary formation of alkoxy formations and subsequent formation of C-C bond with the second molecule, accompanied by partial reduction of the oxide component and its subsequent reoxidation by the formed water molecules.

CONCLUSIONS

1. It was found for the first time that contacting methane with non-reduced bimetal-aluminum oxide catalysts containing a Group VIII element (Ni, Co or Pt) and a polyvalent metal oxide (Re or Cu) leads to its dehydrocyclohexamerization with the selective formation of benzene and an equimolecular amount of hydrogen upon conversion methane 24-30% [1, 4, 15, 22, 26, 27, 30-35, 54].
2. It has been shown that the activity of bimetal-aluminum oxide catalysts depends on the method of applying elements of group VIII group (Ni, Co or Pt), and high-temperature treatment of the carrier. On bimetal-aluminum-oxide catalysts that activate the conversion of methane and its low molecular weight homologs, metal particles (Ni, Co or Pt) localized by the adsorption method are in a highly dispersed state with a particle size of less than 2 nm [1, 2, 10,15, 21, 27, 44, 45, 49, 53].
3. It was found that in bimetal-aluminum oxide catalysts, oxygen contained in the oxide phase changes its reactivity under the influence of metal particles of group VIII b elements. The reactivity of oxygen contained in the oxide phase depends on the dispersion of the deposited metal particles and becomes reactive heterogeneity under the influence of pre-crystalline particles with a size of less 2 nm [1, 5, 10, 12, 16, 27, 29, 35, 44, 45, 49].
4. It was found that during methane dehydrocyclohexamerization on bimetal oxide contacts, their partial recovery occurs with the formation of active centers containing electrophilic oxygen, part of which is consumed to activate the target reaction, and the rest - prevents structural changes of the active phase, leading to irreversible destruction catalytic centers [1, 5, 22, 33, 34, 43].
5. Thermodynamic calculations found that at 650-700 °C the equilibrium yield of benzene with the participation of bound oxygen increases to 17 %, and under the influence of the formed carbon deposits – to 25 % compared with the direct conversion of methane 7-8 % [1,5].
6. It has been established that as a result of the reactant – catalyst

interaction, partial restoration and coating of the contact with carbon deposits occur. Limiting the time, the regeneration treatment of the deactivated during methane contact DHCH air, allowing not affect carbonaceous deposits, helps to eliminate the period of activation of the catalyst in subsequent regeneration cycles in the reaction [4, 10, 12, 21, 25].

7. It was found for the first time that on mechanical mixtures of catalysts consisting of bimetal-aluminum oxide catalysts M, Re/Al₂O₃, where (M = Ni, Co or Pt) and N-zeolite (Y, MOR or ZSM-5), low-temperature (≥ 180 °C)) alkylation of benzene with propane to form isopropylbenzene and the product of its dealkylation and isomerization. With the change in the ratio of C₆H₆ : C₃H₈ from 1: 9 to 1 : 1 at P = 0,1 MPa, T = 250 °C and V = 500 h⁻¹ a conversion of reactants changes from 12 to 23 % and from 1.9 to 7,7 %, respectively, and the selectivity for IPB from 100 to 71 % [3, 6, 7, 9, 11, 20, 36, 37, 44].
8. It was shown that the alkylation of benzene of propane on spatially separated centers of mechanical mixtures (bimetal alumina and H-zeolite) catalysts proceeds by cyclic transport of protons from acid centers on the metal reduction-oxidation and and back ions C₆H₇₊ and C₆H₆ C₃H₇₊.
9. It was found that, depending on the reaction conditions: the conversion of C₆H₆ :C₃H₈ = 1:9 to MMC (APRC+HY) at 320 °C is accompanied by a benzene conversion of 62.1 % and a selectivity for isopropylbenzene of 67.5%, and at 375 °C, propane conversion is 19.35 %, with propylene selectivity 80.3% [6,7, 20, 36, 37, 51].
10. It has been established that the implementation of processes at spatially separated active centers allows the use of industrially mastered catalysts as components of complex catalytic systems. An industrial cracking catalyst treated with phosphoric acid in a mechanical mixture with the catalyst converting the synthesis gas to methanol can quadruple the productivity of the selective production of dimethyl ether from synthesis gas through methanol [8, 14, 16- 18, 24, 28, 29, 47-50].
11. It was shown that the formation of the primary C-C bond (eth-

ylene) from methanol / DME is realized with the participation of the Brandsted and Lewis centers located in zeolite micropores diameter 0.32 (SAPO-34)-0.55 (HZSM-5) nm it is a structure-sensitive reaction [13, 23, 28, 40, 46- 50].

HIGHLIGHTS OF THESE SET OUT IN THE FOLLOWING PUBLICATIONS:

1. Абасов, С.И. Превращение метана на окисленных алюмоплатинорениевых катализаторах / С.И. Абасов, Ф.А. Бабаева, Б.А. Дадашев // Кинетика и катализ, Москва: – 1995, т.36, № 3, – с. 428-431.
2. Бабаева, Ф.А. Окислительное превращение метана на $\text{Co}/\text{Al}_2\text{O}_3$ катализаторе / Ф.А. Бабаева, С.И. Абасов // Азербайджанский химический журнал, Баку: – 2001, № 4, – с. 93-97.
3. Abasov, S.I. Low-temperature catalytic alkylation of benzene by propane / S.I. Abasov, F.A. Babayeva, D.B. Tagiyev, M.I. Rustamov // Applied Catalysis A: General. – 2003, № 251, – с. 267-274.
4. Babayeva, F.A. First stage of the oxidative mechanism of the catalytic dehydrocyclohexamerization of methane to benzene over mono-and bimetallalumina catalysts // Georgian Chemical Journal, – Georgia: – 2003,– v. 3, № 1, – p. 24-29.
5. Бабаева, Ф.А. Термодинамические и каталитические аспекты дегидроциклогексамеризации метана на гетерогенных системах // Грузинский химический журнал, – Тбилиси: – 2003, – т. 3, № 4, – с. 323-330.
6. Бабаева, Ф.А. Превращение бензол-пропановых смесей на каталитических системах $\text{Pt,ReO}_x/\text{Al}_2\text{O}_3$ / Ф.А. Бабаева, С.И. Абасов, А.Р. Насибова, А.А. Рашидова, Ф.М. Насирова // Грузинский химический журнал, – Тбилиси: – 2004,– т. 4, № 1, – с. 28-34.
7. Абасов, С.И. Влияние природы цеолита на низкотемпературные превращения C_6H_6 : C_3H_8 смесей на каталитических системах $\text{Pt,Re}/\text{Al}_2\text{O}_3$ + Н-цеолит / С.И. Абасов, Ф.А. Бабаева

- ва, А.Р. Насибова, А.А. Рашидова, Д.Б. Тагиев // Процессы нефтехимии и нефтепереработки, – Баку: – 2004, № 3(18), – с. 87-93.
8. Рустамов, М.И. Диметилловый эфир – новое экологически чистое топливо /М.И. Рустамов, Ф.А. Бабаева, Т.А. Мамедова, В.С. Гаджи-Касумов // Азербайджанское нефтяное хозяйство, – Баку: – 2008, № 8, – с. 76-80.
 9. Бабаева, Ф.А. Превращение метана на механической смеси катализаторов $M/Al_2O_3 + Pt, Re/Al_2O_3$ / Ф.А. Бабаева, Абасов С.И., Рустамов М.И. // Азербайджанский химический журнал, Баку: – 2008, № 1, – с. 27-31.
 10. Abasov, S.I. In situ characteristics of Pt- and Pt, Re/ Al_2O_3 Catalysts by IR Probe CO Molecules Adsorption / S.I. Abasov, F.A. Babayeva, M.I. Rustamov // Азербайджанский химический журнал, – Баку: – 2008, № 2, – с. 24-26.
 11. Бабаева, Ф.А. Превращение метан-пропановой смеси на моно- и биметалломооксидных катализаторах // Азербайджанский химический журнал, – Баку: –2008, № 3, – с. 207-210.
 12. Абасов, С.И., Роль циклической восстановительно-окислительной поверхностной реакции в активации алканов C_1-C_3 / С.И. Абасов, Ф.А. Бабаева, М.И. Рустамов // Грузинский химический журнал, – Тбилиси: – 2008, № 8(3), – с. 225-229.
 13. Пириев, Н.Н. Сопоставительное изучение превращений метанола на оксиде алюминия и цеолите Н-ЦВК / Н.Н. Пириев, Ф.А. Бабаева, М.И. Рустамов // Процессы нефтехимии и нефтепереработки, – Баку: – 2008, № 3-4(35-36), – с. 317-322.
 14. Пириев, Н.Н. Проблемы и перспективы процесса одностадийного синтеза диметилового эфира из синтез-газа / Н.Н. Пириев, Р.Г. Ахмедова, Ф.А. Бабаева, В.С. Гаджикасумов, М.И. Рустамов // Процессы нефтехимии и нефтепереработки, – Баку: – 2009, –т.10, № 3-4 (39-40), – с. 255-262.
 15. Бабаева, Ф.А. О каталитической активации низкомолекулярных алканов C_1-C_3 / Ф.А. Бабаева, С.И. Абасов, М.И. Ру-

- стамов // Катализ в химической и нефтехимической промышленности, – Москва: – 2009, № 6, – с. 23-27.
16. Rustamov, M.I. Dehydration of methanol on zeolite-containing catalysts / M.I. Rustamov, N.N. Piriev, F.A. Babaeva // Chemistry and Technology of Fuels and Oils, – Moscow: – 2010, V. 46, № 1, – p. 58-62.
 17. Пириев, Н.Н. Превращение метанола на цеолитных катализаторах. Сообщение 1. Влияние структуры цеолита на выходы диметилового эфира и углеводородов / Н.Н. Пириев, Р.Г. Ахмедова, Ф.А. Бабаева, М.И. Рустамов // Процессы нефтехимии и нефтепереработки, – Баку: – 2010, № 1 (41), – с. 97-102.
 18. Пириев, Н.Н. Превращение метанола на цеолитных катализаторах. Сообщение 2. Кинетический анализ превращения метанола в углеводороды на НЦВК-содержащем контакте/ Н.Н. Пириев, Ф.М. Велиева, Р.Г. Ахмедова, Ф.А. Бабаева, В.С. Гаджикасумов, М.И. Рустамов // Процессы нефтехимии и нефтепереработки, – Баку: – 2010, № 2(42), – с. 190-194.
 19. Пириев, Н.Н. Дегидрирование метанола в трехфазном реакторе на цеолитфосфатном катализаторе / Н.Н. Пириев, Ф.А. Бабаева, М.И. Рустамов // Kimya problemləri, – Баку: – 2010, № 3, – с. 428-432.
 20. Babayeva, F.A. Conversions of Mixtures of Propane and Benzene on Pt,Re/Al₂O₃ + H-Zeolite Systems / F.A. Babayeva, S.I. Abasov, M.I. Rustamov // Petroleum Chemistry, – Moscow: – 2010, –v. 50, № 1, – p. 42-46.
 21. Rustamov, M.I. The formation of metal-alumina-rhenium methane dehydrocyclohexamerization catalysts during the reactant-catalyst interaction / M.I. Rustamov, F.A. Babayeva, S.I. Abasov // Petroleum Chemistry, 2011, –v. 51, № 2, –p. 128-132.
 22. Бабаева Ф.А. Влияние элементов VIII Б группы на восстановление оксида рения в системе М (VIII б) ReO_x/Al₂O₃ и на активацию метана // Азербайджанский химический журнал, – Баку: – 2011, № 4, – с. 115-120.
 23. Бабаева, Ф.А. Альтернативные моторные топлива на базе метанола/ Ф.А. Бабаева, Б.Б. Кулиев, Э.Ф. Бабаева, С.И.

- Абасов, Х.Д. Ибрагимов // Процессы нефтехимии и нефтепереработки, – Баку: – 2011, –т. 12, № 3(47), – с. 203-208.
24. Бабаева, Ф.А. Разработка концептуальной технологической схемы процесса конверсии метанола в диметиловый эфир / Ф.А. Бабаева, Р.Г. Ахмедова, Э.Ф. Бабаева С.И. Абасов, Х.Д. Ибрагимов // Процессы нефтехимии и нефтепереработки, – Баку: – 2011, – т. 12, № 4 (48), – с. 280-286.
25. Бабаева, Ф.А. Влияние углеродистых отложений на неокислительное превращение метана в бензол с участием алюмо-никельрениевого катализатора // Азербайджанский химический журнал, – Баку; – 2012, № 1 – с. 112-116.
26. Бабаева, Ф.А. Современное состояние неокислительной каталитической конверсии метана в ароматические углеводороды // Процессы нефтехимии и нефтепереработки, – Баку: –2012, –т. 13, № 2, – с. 181-190.
27. Бабаева, Ф.А. Неокислительное превращение метана в бензол на Pt, $\text{ReO}_x/\text{Al}_2\text{O}_3$ катализаторах и факторы, ответственные за этот процесс / Ф.А. Бабаева, С.И. Абасов, Д.Б. Тагиев, М.И. Рустамов // Процессы нефтехимии и нефтепереработки, – Баку: – 2013, –т. 14, № 1(53), – с. 131-146.
28. Abasov, S.I. Conversion to hydrocarbons on modified zeolites y and ZSM-5 / S.I Abasov, F.A. Babayeva, B.B. Guliyev, N.N. Piriyev, M.I. Rustamov .Theoretical and Experimental Chemistry, – Russian: – 2013, –v. 49, № 1, – p. 55-59.
29. Абасов, С.И. Каталитическое превращение с участием пространственно-разделенных активных центров / С.И. Абасов, Е.С. Исаева, Ф.А. Бабаева, С.Б. Агаева, Х.Д.Ибрагимов, Д.Б.Тагиев, М.И.Рустамов // Журнал прикладной химии, – Санкт-Петербург: – 2015, –т. 88, вып. 5, – с. 744-752.
30. Abasov, S.I., Babayeva, F.A. The catalytic dehydrocyclohexamerization of methane to benzene and oxidation mechanism of its first stage // 3rd Wold Congress on Oxidative Catalysis, San Diego, California: September 21-26, 1997. –p. 1-2.
31. Abasov, S.I., Babayeva, F.A., Tagiyev, D.B., Rustamov, M.I. Methane Catalytic Activation in its Conversion to Benzene // 5th European Congress on Catalysis, Symposium 5, University of

- Limerick, Ireland, 2-7 September, 2001, – p. 19.
32. Abasov, S.I., Babayeva, F.A., Tagiyev, D.B., Rustamov, M.I. Initiation of unfavourable reactions by proton cyclic transfer over zeolite-containing catalysts // Proceedings of the 14th International Zeolite Conference, Cape Town, South Africa: – 25-30th April, 2004, – p. 2339-2346.
 33. Tagiyev, D.B., Babayeva, F.A., Abasov, S.I. Influence of supported Pt nanoparticles size on bound oxygen reactivity in the metal-oxide catalytic systems // EUROPACAT VIII Conference “From Theory To Industrial Practice”, Turku. Abo, – Finland: – 26-31 August, 2007, – p. 1-3.
 34. Abasov, S.I., Babayeva, F.A., Rustamov, M.I. Catalytic activation of unfavourable reactions by $M_n\text{ReO}_x/\text{Al}_2\text{O}_3$ catalysts // III International Conference “Catalysis: Fundamentals and Application” dedicated to the 100th anniversary of Academician Georgii K. Boreskov, Novosibirsk, Russia: July 4-8, 2007, –v II, p. 159-161.
 35. Бабаева, Ф.А., Абасов, С.И., Рустамов, М.И. О каталитической активации низкомолекулярных алканов C1-C3 / Тезисы докладов XVIII Менделеевского съезда по общей и прикладной химии, – Москва: 23-28 сентября, 2007, –т. 3, – с. 302.
 36. Рустамов, М.И., Бабаева, Ф.А., Абасов, С.И. Низкотемпературные превращения пропана в присутствии бензола на $\text{Pt}, \text{ReO}_x/\text{Al}_2\text{O}_3 + \text{H}$ -цеолитных системах // Материалы 5-ой Всероссийской цеолитной конференции «Цеолиты и мезопористые материалы: Достижения и перспективы», – Звенигород: 8-11 июня, 2008, – с. 158.
 37. Бабаева, Ф.А., Абасов, С.И., Рустамов, М.И. Роль металлических и кислотных центров в низкотемпературных превращениях бензол-пропановых смесях // Сборник трудов Республиканской конференции по нефтехимии и нефтепереработке, посвященной 100-летию В.С. Алиева, Процессы нефтехимии и нефтепереработки, – Баку: – 2008, № 3-4(35-36), – с. 194-195.
 38. Рустамов, М.И., Бабаева, Ф.А., Абасов, С.И. Конструирована-

- ние катализаторов активации низкомолекулярных алканов // Материалы VI Российской конференции «Научные основы приготовления и технологии катализаторов», – Новосибирск: 4-9 сентября, 2008, –т. 1, – с.103-104.
39. Рустамов, М.И., Бабаева, Ф.А., Абасов, С.И. Особенности дезактивации металлалюмоорениевых катализаторов активации низкомолекулярных алканов // Материалы V Российской конференции «Проблемы дезактивации катализаторов», – Новосибирск: 4-9 сентября, 2008, –т. 2, – с. 202-203.
40. Пириев, Н.Н., Бабаева, Ф.А., Рустамов, М.И. Влияние состава катализатора на превращение метанола в ДМЭ // Материалы IV Международной научно-технической конференции «Глубокая переработка нефтяных дисперсных систем», – Москва: – 2008, – с. 109-110.
41. Пириев, Н.Н., Ахмедова, Р.Г., Бабаева, Ф.А., Рустамов, М.И. Диметиловый эфир – новый энергоноситель // Материалы VII Бакинской Международной Мамедалиевской конференции по нефтехимии, посвященной 80-летию Института нефтехимических процессов НАН Азербайджана, – Баку: 29 сентября-2 октября, 2009, – с. 216-217.
42. Abasov, S.I., Babayeva, F.A., İsayeva, E.S., Maharramov, M.I., Ismailov, E.H., Rustamov, M.I. Dehydroalkylation of Benzene with Propane and Dehydrogenation of Propane over Me-ReOx/Al₂O₃ Contacts // VIII International Conference “Mechanisms of catalytic reactions”, dedicated to the 70th anniversary of the birth of prof. K.I. Zamaraev, Novosibirsk Russia: June 29-July 2, 2009, – p. 108-109.
43. Piriev, N.N., Ahmadova, R.G., Babayeva, F.A., Rustamov, M.I. Obtaining of synthetic fuel from methanol // International conference catalysis for renewable sources: fuel, energy, chemicals, – St. Petersburg, Tsars Village: June 28-July 2, 2010, – p. 132.
44. Рустамов, М.И., Бабаева, Ф.А., Абасов, С.И. Роль связанного кислорода в превращении метана в бензол и дегидроалкилирование бензола пропаном на биметалл-алюмооксидных катализаторах // Материалы IV семинара, посвященной памяти профессора Ю.И. Ермакова «Молекулярный дизайн катали-

- заторов и катализ в процессах переработки углеводов и полимеризации», Иркутск: 13-16 апреля, 2010, – с. 41-42.
45. Абасов, С.И., Бабаева, Ф.А., Рустамов, М.И. О варьировании реакционной способности кислорода в системе $M(Ni, Co, Pt)ReO_x-Al_2O_3$ // Материалы Российского Конгресса по катализу «РОСКАТАЛИЗ», – Новосибирск: 3-7 октября, 2011, – с. 118.
46. Абасов, С.И., Бабаева, Ф.А., Рустамов, М.И., Пириев, Н.Н., Ахмедова, Р.Г. Влияние воды на превращение ДМЭ в углеводороды различного строения // Тезисы докладов 6-ой Всероссийской цеолитной конференции. Цеолиты и мезопористые материалы: Достижения и перспективы, – Звенигород: – 14-16 июня, 2011, – с.162-163.
47. Абасов, С.И., Бабаева Ф.А., Рустамов М.И. Превращение метанола на модифицированных H_3PO_4 цеолитсодержащих катализаторах // Тезисы докладов 6-ой Всероссийской цеолитной конференции. Цеолиты и мезопористые материалы: Достижения и перспективы, – Звенигород: – 14-16 июня, 2011, – с. 167-168.
48. Babayeva, F.A., Guliyev, B.B., Ahmadova, R.H., Ismailov, E.H., Abasov, S.I. Ibrahimov, H.C., Rustamov, M.I. The mechanism of adsorbed methanol conversion over ZSM-5 type zeolite catalysts based on TG/DSC and GC/MS DATA / Materials of the VIII Baku International Mammadaliyev Conference on Petrochemistry, –Baku: 3-6 October, 2012, - p. 44-45.
49. Абасов, С.И., Бабаева, Ф.А., Агаева, С.Б. Ибрагимов, Х.Д., Рустамов М.И. Каталитические превращения с участием пространственно разделенных активных центров // Материалы II Российско-Азербайджанского симпозиума с международным участием «Катализ в решении проблем нефтехимии и нефтепереработки», – Санкт-Петербург: 17-19 сентября, 2013. – с. 28.
50. Бабаева, Ф.А., Ахмедова, Р.Г., Абасов, С.И. Конверсия метанола в диметилвый эфир на механической смеси катализаторов // Тезисы докладов VII Всероссийской цеолитной конференции «Цеолиты и мезопористые материалы: Дости-

- жения и перспективы», – Звенигород: 16-18 июня, 2015, – с. 212-213.
51. Abasov, S.I., Babayeva, F.A., Isayeva, E.S., Ağayeva, S.B., Starikov, R.V., Tagiyev, D.B. Catalytic Conversion of Low Molecular Alkanes with C-C Bonds Formation // XII European Congress on Catalysis: Balancing the use of fossil and renewable resources, Kazan (Russia): 30th August-4th September, 2015, – p. 218-219.
 52. Бабаева, Ф.А. Каталитическая активация метана на $M, ReO_x/Al_2O_3$ системах/ Azərbaycan Respublikası Təhsil Nazirliyi Gəncə Dövlət Universiteti “Muasir biologiya və kimyanın aktual problemləri” Elmi-Praktik Konfransının məruzələləri, – Gəncə: 05–06 may, 2015. – s.131-134.
 53. Abasov, S.I., Babayeva, F.A., Rustamov, M.I. The reactant-catalyst interaction at the methane nonoxidative aromatization over $Ni, ReO_x/Al_2O_3$ // “RR2017” International Conference “Renewable Plant Resources: Ghemistry, Technology, Medicine”, – Saint Petersburg: –18-22 September, 2017, – p. 88-89.
 54. Абасов, С.И. Способ получения бензола, Патент № 1811153, Российская Федерация / Абасов С.И., Бабаева Ф.А., Дадашев Б.А. – 1993.

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