**ANNOTATION**

dissertations for the degree of Doctor of Philosophy (PhD), doctor of profile

specialty 6D073900 - Petrochemistry

**TEMIROVA AIMAN MAKSATOVNA**

 **«Production of aromatic hydrocarbons from propane-butane fractions on modified high-silica catalysts»**

**Relevance of the topic.** Alternative sources of raw materials are involved in the petrochemical and oil refining industry: gas condensates, natural and associated petroleum gases, refinery off-gases, in order to obtain motor fuels, lower olefins, arenes and other valuable products. A potential raw material for obtaining valuable petrochemical products is associated petroleum gas, which by its origin belongs to natural hydrocarbon gas. Along with associated petroleum gas, natural gas may become one of the main sources of raw materials for the production of organic compounds in the near future. The direct conversion of natural gas into liquid hydrocarbons is limited; practically all commercially implemented technologies for converting natural gas into chemical products have high CAPEX and OPEX costs due to its preliminary conversion into synthesis gas. In this regard, the cost of the final products obtained is much higher than that of analogues of petroleum origin.

A promising direction for the rational use of associated gas is the development of gas processing facilities at the sites of oil production, and processing in the presence of catalysts to obtain aromatic hydrocarbons. All this leads to the search and development of cheaper and highly efficient catalysts that do not contain noble metals, as well as fundamentally new conditions for the reforming reactions.

One such research is the development and application of new methods and technical solutions for catalytic systems based on zeolites. And increasing the activity and selectivity of catalysts for the conversion of natural gas components into highly aromatic products is the introduction of metals as modifiers and zeolites as carriers into the catalyst composition.

**Purpose of the work**

Development of effective catalysts based on high-silica zeolites modified with zinc, lanthanum, phosphorus; establishment of physical and chemical laws based on the study of the influence of the porous structure, acid characteristics and catalytic properties in the process of processing light alkanes to obtain aromatic hydrocarbons.

 **Tasks**

1. Information and analytical review of scientific, technical and patent literature and analysis of existing processes for aromatization of light petroleum feedstock and catalysts used;

 2. Synthesis of catalysts and their modification by introducing elements Zn, La and phosphorus into the structure;

 3. Physico-chemical study of the properties, microstructural and textural characteristics of catalysts based on high-silica zeolites modified with zinc, lanthanum, phosphorus elements and establishing the nature of active sites and the optimal composition of catalytic systems;

 4. Determination of the concentration and strength of acid sites of modified zeolites by the method of thermally programmed desorption of ammonia (TPD NH3);

 5. Study of the influence of technological parameters on the yield of target products obtained in the process of aromatization of lower alkanes on modified VKK; establishment of optimal process modes; chromatographic analysis of lower alkanes and aromatic hydrocarbons;

 6. Revealing the main regularities of the conversion of lower C1-C4 alkanes (propane-butane and propane-propylene fractions) on modified catalysts of various compositions based on zeolites and establishing the mechanism for the formation of cationic centers during aromatization.

 **Research methods**

 The paper presents the results of testing samples on a laboratory setup, in a flow-through quartz reactor with a stationary catalyst bed at atmospheric pressure and varying the reaction temperature from 400 to 600 °C. The properties of the developed catalysts were studied by a complex of physicochemical methods: transmission electron microscopy (TEM), scanning electron microscopy (SEM) - on an electron microscope EM-125, Uac = 75 kV and on an FEI QuantaInspect and Tescan MIRA3 LMU instrument (USA) using a standard sample preparation methods, X-ray phase analysis (XRF), Brunauer-Emmett-Teller method (BET), temperature-programmed ammonia desorption (TPD NH3); elemental analysis. IR spectra were recorded using a Nicolet IR200 IR-Fourier spectrometer in the range of 500-4000 cm-1. The reaction products were analyzed by gas chromatography (GC) "Khromatek-Kristall" and "Agilent" with a katharometer and a flame ionization detector.

In some cases, the synthesized products were characterized using an optical microscope MIN-8.

 **Scientific novelty and main results of the study**

For the first time, a series of catalysts were synthesized by impregnation according to moisture capacity and modified with active components, namely, the addition of the elements Zn, La and Р, 60 ZSM - 40 Al2O3, 3Zn-1La -60ZSM -36Al2O3, 3Zn-1La-3Р-60ZSM-33Al2O3, 3Zn-1La-3Р-60ZSM-10HY-23Al2O3, 3Zn-1La-3Р-60ZSM-10B(zeolite)-23Al2O3, 3Zn-1La-3Р-60ZSM-10MCM-40 -23Al2O3.

For the first time the modified catalysts were tested in the catalytic conversion of the propane-butane fraction into aromatic hydrocarbons; it was found that for the catalytic conversion of lower alkanes to aromatic hydrocarbons on modified hydrocarbons, the most optimal conditions are: T = 550°C, space velocity – 300 ч-1

Using a complex of physicochemical methods of analysis: scanning and transmission electron microscopy, IR spectroscopy, chromatography, BET method, ammonia TPD, the synthesized and modified zeolite catalysts were characterized:

The pore-textural characteristics of catalysts were studied for the first time by TEM and SEM; a change in the surface of the matrix is shown, due to the introduction of zinc, lanthanum and phosphorus particles into the structure, which leads to the appearance of new active centers; it was found that the smallest sizes of crystallites vary from 0.2 to 10.0-20.0 nm depending on the nature of the modifier metal. On the surface of catalysts, acid sites coexist with metal sites. The functioning of various types of centers in catalytic systems provides multifunctionality.

For the first time, using the TPD method of ammonia, it was found that the synthesized and modified zeolite-containing catalysts Zn-ZSM- Al2O3, Zn-La-ZSM- Al2O3, Zn-La-P-ZSM- Al2O3 have high catalytic activity and selectivity in the process of converting light gas into aromatic hydrocarbons ; The highest yield of aromatic hydrocarbons (40.3%) was obtained on the Zn-La-ZSM- Al2O3 catalyst at a temperature of 600ºС, with a degree of conversion of 98.4%.

 The adsorption and porous-textural properties were studied for the first time: the nitrogen adsorption capacity for all the studied catalysts before and after differs insignificantly and amounts to 0.03–0.08 cm3/g. The largest contribution to the total pore volume is made by the volume of micropores in the KTG-5 and KTG-6 catalysts, the value of which is somewhat larger than that of the others, and especially of the spent catalysts. Based on the test results, it was shown that the Zn-La-P-ZSM-XY- Al2O3 (KTG-4) catalyst based on ZSM-type crystalline zeolite with a mesoporous system has the highest activity and high operational stability. The maximum conversion on the catalyst was 81.4% with an aromatic yield of 52.6%.

 For the first time, based on the totality of the obtained research results, the following reaction mechanism was proposed: on the synthesized and modified catalysts, a multi-route process of converting lower alkanes occurs and reactions of a series-parallel nature are realized - dehydrocyclization, isomerization, alkylation, dehydrogenation.

 **Theoretical significance of the work**

 For the first time, catalysts modified with additions of zinc, lanthanum and phosphorus elements were obtained; catalytic, acidic, adsorption, porous-textural properties have been studied. The catalysts showed high efficiency in the conversion of lower alkanes (С3-С4). The main advantages of modified catalysts are environmental friendliness, chemical inertness, high chemical and thermal stability, selectivity, the possibility of changing properties by modification, duration of operation, manufacturability of use, and regeneration, i.e. recovery of activity by annealing coke.

**Practical significance of the study значимость исследования**

In recent years, due to the growth of energy consumption and high demand for motor fuel, there is a need to increase the processing of natural and associated petroleum gases, off-gases from refineries. A promising direction for the rational use of associated gas is processing in the presence of zeolite catalysts to obtain aromatic hydrocarbons.

In this regard, the results of this study, aimed at studying the catalytic and acidic properties of zeolite catalysts modified with active components, are important both from a scientific point of view, elucidating the nature of their active centers, and for the practical purpose of increasing the efficiency of the catalytic action of modified catalysts and enhancing the aromatization process. lower alkanes.

The development of new modified catalysts, as well as optimal technological conditions for the production of aromatic hydrocarbons in the process of catalytic conversion of light gases, is a practical contribution to petrochemistry, namely, to the processing of all types of natural and associated gases.

**The main provisions for defense:**

- synthesis of catalysts based on high-silica zeolites modified with additions of zinc, lanthanum, phosphorus elements allows to increase the yield of aromatic hydrocarbons during the processing of propane-butane fractions up to 43.6%;

- patterns of formation of active phases on a zeolite basis, the influence of the nature of modifying additives, changes in microstructural and textural characteristics (pore size, specific surface area), acidic and catalytic properties (from 21.23 to 37.00 \* 10-4 mol / g) during the conversion of gas mixtures;

- the most active and selective catalytic system from the investigated catalysts was determined and selected in the process of aromatization of light hydrocarbon feedstock (Zn-La-P-ZSM- Al2O3);

- substantiated and proposed a mechanism for the process of obtaining aromatic compounds from natural gases on synthesized high-silica zeolite catalysts modified with zinc, lanthanum and phosphorus.

**Main results of the work**

 1. Synthesis and study of catalysts based on silica zeolites of the ZSM-5 type, obtained by modifying the zeolite matrix with active components, namely, a system of Zn, La and P elements, in the reactions of the conversion of propane-butane and propane-propylene fractions into aromatic hydrocarbons was carried out. It is shown that the modification of the zeolite matrix leads to a significant increase in the activity of the ZSM-5 heterogeneous system and the selectivity of hydrocarbon conversion in aromatization reactions (67.6%);

 2. Modified zeolite-containing catalysts Zn-ZSM- Al2O3, Zn-La-ZSM- Al2O3, Zn-La-P-ZSM-Al2O3 have high catalytic activity and selectivity in the process of processing hydrocarbon gas into aromatic hydrocarbons; The highest yield of aromatic hydrocarbons (40.3%) was obtained on the Zn-La-ZSM- Al2O3 catalyst at a temperature of 600ºС, with a conversion rate of 98.4%.

 3. It has been established that the aromatizing ability of the created catalysts is determined by the silicate module in the zeolite, the nature and concentration of the modifying additive;

 4. Studies of the process of aromatization of propane-butane and propane-propylene fractions on catalysts have proposed an effective zeolite-containing catalyst modified with zinc, lanthanum and phosphorus - Zn-La-P-ZSM- Al2O3, which provides an optimal balance between the content in the product and the yield of target aromatic hydrocarbons (59.1% wt.).

 5. The dependence of the conversion and selectivity of the formation of the conversion products of propane-butane and propane-propylene fractions on modified zeolites on technological parameters: reaction temperature and space velocity of feedstock, catalyst operation time was revealed. It has been established that temperature is a decisive factor determining the depth and direction of the transformation of lower alkanes: with an increase in temperature, the degree of transformation of С1 – С4 increases due to an increase in the rate of cracking and dehydrogenation reactions;

 6. It has been established that the modified zeolite-containing catalysts have polyfunctional properties; the composition of acid sites can include metals in various degrees of oxidation, fixed both inside the zeolite cavities and on their outer side; the composition of the products of processing of light alkanes shows that the formation of aromatic hydrocarbons occurs in one a stage resulting from cracking, dehydrogenation, oligomerization, dehydrocyclization, alkylation reactions;

 7. The totality of the results of the study of catalytic systems based on a modified silica catalyst (ZSM-5) by various experimental and physicochemical methods made it possible to make an assumption about the mechanism of reactions of lower alkanes С1 – С4 at the gas-solid interface with the participation of active centers of different nature; on the studied catalysts, a multi-route process of lower alkanes conversion takes place and reactions of a series-parallel nature are realized: dehydrocyclization, isomerization, alkylation, dehydrogenation.

 8. Polyfunctional catalyst Zn-La-P-ZSM- Al2O3 is recommended for pilot tests at refineries in the process of processing propane-propylene fraction to obtain aromatic hydrocarbons.

**Compliance with the directions of scientific development or state programs.** The work was carried out in accordance with the research programs of the Al-Farabi Kazakh National University and the Institute of Fuel Catalysis and Electrochemistry named after. D.V. Sokolsky within the framework of Grant funding for fundamental and applied research of the Ministry of Education and Science of the Republic of Kazakhstan (2018-2021) .

 **Publications**

The data of the completed dissertation research have been published in domestic scientific publications and in foreign journals, as well as presented at international conferences and symposiums, which confirms their high scientific level. As a result of research on the topic of the dissertation work, 9 scientific articles were published in co-authorship, including 2 in the journals included in the Scopus database, 3 articles in the journal “Izvestia” of the National Academy of Sciences of the Republic of Kazakhstan, 1 article in the journal Oil and Gas, included in the list journals recommended by the Committee for Control in Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan and 3 reports at international scientific conferences and symposiums.

**List of publications:**

1. Tuktin B.T., Temirova A.M., Omarova A.A., Tenizbaeva A.S. Transformation of light alkanes into aromatic hydrocarbons on modified zeolite-containing catalysts.// Oil and gas. - 2019. - No. 3. –p.62-72

2. Tuktin B.T., Temirova A.M., Omarova A.A., Tenizbaeva A.S. Abstracts of the report on the topic "Conversion of gaseous hydrocarbons on modified zeolite-containing catalysts"//Chemical technologies of functional materials.- Novosibirsk.-2019.-p.334-337

3. Tuktin B.T., Temirova A.M., Saidilda G.T., Omarova A.A. Conversion of the propane-propylene fraction into aromatic hydrocarbons on modified zeolite catalysts.//Proceedings of the National Academy of Sciences of the Republic of Kazakhstan.-Series of Chemistry and Technology. -Almaty.-2020.-№1.-С.64-71

4. Tuktin B.T., Temirova A.M., Omarova A.A., Anisimov A.V. Aromatization of low molecular weight hydrocarbons on modified zeolite catalysts.//Chemical technology.-Moscow.-2020.No.21.-C 498.

5. Tuktin B.T., Temirova A.M., Omarova A.A., Saydilda G.T. Abstracts of the report on the topic "Aromatization of the propane-propylene fraction on modified zeolite catalysts".//Farabi Alema.-Almaty.-2020.-C 18.

6. B. T. Tuktin, A. M. Temirova, A. A. Omarova, Zh. K. Myltykbaeva , A. V. Anisimov//Aromatization of Low-Molecular-Weight Hydrocarbons on Modified Zeolite Catalysts// Theoretical Foundations of Chemical Engineering-V.55-N.5-P.1016-1021

7. Tuktin B.T., Tenizbaeva A.S., Temirova A.M., Saidilda G.T. Processing of n-alkanes and gasoline fractions on modified zeolite catalysts// Proceedings of the National Academy of Sciences of the Republic of Kazakhstan. - Series of Chemistry and Technology. - Almaty. -2021.- T.449 -№5-6. -p.75-83

8. A.M.Temirova., B.T.Tuktin, A.A.Omarova, E.A.Aubakirov, A.V.Anisimov Transformations of light hydrocarbons on modified zeolite catalysts//Chemical technology.-Moscow

9. Tuktin B.T., Temirova A.M., Saidilda G.T., Omarova A.A. Abstracts of the report on the theme "Processing of propane-butane fraction on modified zeolite catalysts"//Chemical technologies of functional materials. - Tomsk-2022.