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ABSTRACT

of the dissertation for the degree of Doctor of Science

DEVELOPMENT OF PROCESSES FOR OBTAINING ISOALKANES FROM C_4-C_8 PARAFFINS AND STYRENE FROM ETHYLBENZENE ON MODIFIED ZEOLITE AND METAL OXIDE CATALYSTS

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GENERAL CHARACTERISTICS OF THE WORK

Relevance of the topic and degree of elaboration. Catalytic transformations of hydrocarbons are usually accompanied by side reactions leading to the formation of undesirable products, such as carbon monoxide during the oxidative dehydrogenation of ethylbenzene (EB) to styrene (St) with the participation of CO_2 or gaseous products and the deactivation of catalysts, due to the accumulation of hydrocarbon deposits on them, when isomerization of n-alkanes. The elimination of the noted shortcomings associated with catalytic processes is an urgent problem in petrochemistry and oil refining. Innovative solutions to such problems can be the involvement of the resulting undesirable by-products of industrial processes in conjugated reactions of their disposal, without affecting the main process.

Styrene is an important monomer for the synthesis of polymeric materials based on it, the production of which is steadily increasing. The main industrial process for the production of St is direct, energy-intensive dehydrogenation of EB. Reducing the cost of production of St is possible by transferring the process from direct dehydrogenation of EB to oxidative one using CO_2 as an oxidizing agent. In this case, the formation of St will be accompanied by an equivalent consumption of “specially prepared” CO_2 and the formation of an appropriate amount of carbon monoxide requiring utilization.

The most important process of processing C_5-C_6 hydrocarbon mixtures into isomeric components of gasoline with high-octane characteristics is implemented using complex energy- and material-intensive technological schemes, including deisopentanization, deisohexanization columns in combination with the recycle of n-pentane and/or n-rentane and n-hexane. The stability of the isomerization process is achieved by using a high hydrogen pressure and introducing a hydrogenolyzing component (Pt, etc.) into the catalyst composition, which prevents the accumulation of high-molecular hydrocarbon deposits, but at the same time promotes the hydrocleavage of target isoalkanes. The presence of impurities of C_{7+} paraffins and/or aromatics in mixtures of C_5-C_6 hydrocarbons has a negative effect on the process. Despite the differences in the noted reactions and the conditions for their implementation, the noted drawbacks can be eliminated by involving the byproducts in conjugated reactions in a single reaction space. In the case of the oxidative conversion of EB to St with the participation of CO_2, such a coupled reaction can be the additional oxidation of carbon monoxide to dioxide by steam reforming. In the case of isomerization of a mixture of C_5–C_6 paraffins, it is possible to conjugate the formation and isomerization of bimolecular intermediates from gaseous products and paraffins with the hydrocracking of these intermediates to the target products. Carrying out such reactions is possible with the participation of composite catalytic systems, the components of which can be known catalysts of the main reaction and known catalysts of coupled reaction.

The development of such processes with the participation of composite catalytic systems is very promising, but practically insufficiently studied and requires systematic research. Establishing the foundations for the use of the noted coupled reactions for the implementation of such large-scale productions as the production of St or modern gasolines with a limited aromatic content is important not only for simplifying and intensifying these processes or eliminating their negative impact on the environment, but also for eliminating similar shortcomings in other petrochemical industries.

Object of research: ethylbenzene, carbon dioxide, oxygen (air), C_3-C_{6+} n-alkanes and their mixtures, gas gasoline and propane-butane fraction.

Subject of research: Coupling of EB oxidation in St with steam reforming of CO and conjugation of the transformation of a mixture of liquid and gaseous alkanes into branched bimolecular intermediates with their hydrodecomposition into C_5-C_6 paraffins, mainly of a branched structure, in the presence of composite catalytic systems.

Purpose and tasks of the work: Development of innovative conjugated processes including the conjugation of transformation of a mixture of gaseous and liquid C_{7+} paraffins to bimolecular intermediates and the hydrocleavage of these intermediates in the C_5 - C_6 components of high-octane gasolines at 140 - 200^{0}C and the conjugation of the oxidative conversion of EB to St wiht the vapor conversion of carbon monoxide in the presence of composite catalytic systems, components which are active in separate conjugated reactions.

To achieve this goal, the following tasks were solved:

- ✓ synthesized catalysts based on oxides of various metals and studied their activity in the reaction of oxidation and oxidative dehydrogenation of ethylbenzene to styrene at normal atmospheric pressure;
- ✓ regularities of oxidative conversion of ethylbenzene to styrene in the presence of O_2 and CO_2 have been studied;
- ✓ the conjugation of the conversion of ethylbenzene to styrene with the steam conversion of carbon monoxide was studied;
- ✓ the mechanism of conversion of ethylbenzene to styrene in the presence of both oxidizing agents was studied;
- ✓ synthesized composite catalysts based on sulfated zirconium dioxide and metal-modified zeolites and tested their isomerizing activity;
- ✓ individual isomerization of n-alkanes as a model reaction and joint isomerization of their mixture with butane were studied;
- ✓ the most efficient isomerization catalyst was chosen and the isomerization conversion of gas gasoline on this catalyst was studied;
- ✓ investigated the involvement of propane-butane fraction in the isomerization transformation of gas gasoline;
- ✓ the conjugation of the transformation of gaseous and liquid alkanes into bimolecular intermediates with the hydrodecomposition of these intermediates into C_5 - C_6 paraffins in the presence of composite catalysts was studied.

Research methods. Gas chromatographic analysis was used to analyze the composition of feedstock, products of oxidative transformation, and isomerization, and adsorption, TPR, TPD, TRXPA, EPR, and IR spectroscopy were used to study catalytic systems.

The main provisions of the protection:

- ✓ catalytic system MgO-ZrO_2 and Cr_2O_3/Al_2O_3 is a more active catalyst for the conversion of ethylbenzene to styrene;
- ✓ conversion of ethylbenzene in the presence of CO_2 makes it possible to obtain styrene with high selectivity;
- ✓ addition of copper to catalysts makes it possible to conjugate the steam reforming of carbon monoxide with the oxidative conversion of ethylbenzene to styrene in the presence of CO_2 and coupling the conversion of ethylbenzene to styrene with steam reforming of carbon monoxide makes it possible to simultaneously obtain two valuable products (styrene and hydrogen) in an environmentally friendly way;
- ✓ catalytic system consisting of sulfated zirconium dioxide and metal-modified zeolite allows n-alkanes isomerization at low temperatures with high selectivity;
- ✓ the conversion of n-alkanes and their mixtures on catalytic systems consisting of sulfated zirconium dioxide and metal-modified zeolite proceeds by conjugation of the formation of isostructural bimolecular intermediates with their hydrocleavage;
- ✓ joint processing of propane-butane mixture with natural gasoline on a catalytic system consisting of sulfated zirconium dioxide and metal-modified zeolite allows the use of these gases in the synthesis of high-octane fuel components.

Scientific novelty:

- ✓ the use of catalysts based on ZrO_2 makes it possible to reduce the temperature of conversion of ethylbenzene in styrene;
- ✓ it is possible to increase the intensity of the conversion of ethylbenzene in styrene by 4 times;

- ✓ conjugation of the conversion of ehtylbenzene in styrene with the steam reforming of carbon monoxide;
- ✓ conjugation of the isomerizing ability of sulfated zirconium dioxide with the hydrocracking ability of the metal-modified zeolite;
- ✓ with the use of a catalytic system consisting of sulfated zirconium dioxide and a metal-modified zeolite, it is possible to isomerize n-alkanes and their mixtures into high-octane isoalkanes;
- ✓ the possibility of single-stage conversion of gas gasoline into high-octane gasoline isocomponents has been established;
- ✓ involvement of associated petroleum gases in the production of high-octane fuel.

Theoretical and practical value:

- ✓ using the MgO-ZrO2 catalyst, the oxidation of ethylbenzene to styrene in the presence of oxygen can be carried out with a high yield and relatively low temperature;
- ✓ treatment with phosphoric acid stabilizes the activity of the catalyst $MgO\text{-}ZrO_2$ and the catalyst retains activity for a long time;
- ✓ conversion of ethylbenzene to styrene, conjuqated with steam conversion of carbon monoxide, allows to obtain environmentally friendly styrene and hydrogen;
- ✓ finding an effective catalyst and reaction conditions for the high selective isomerization of gaseous n-alkanes and gaseous gasoline on a catalytic system consisting of sulfated zirconium dioxide and metal-modified zeolite;
- ✓ involvement of accompanying oil gases in the production of liquid fuel components;
- ✓ creation of a mechanism of isomerization-disproportionation;
- ✓ revealing the relationship between the oxidative dehydrogenation of ethylbenzene to styrene and the mechanism of bifunctional isomerization of alkanes.

Publication. According to the dissertation work, 45 works were published, 19 of which are articles (8 without a co-author), and 26 of them are abstracts of reports of international and republican scientific conferences.

The results of the work were published in national and international journals: Processes of Petrochemistry and Oil Refining (Azerbaijan) - 5 articles; Chemical problems - 1 article (Azerbaijan); Applied Chemistry (Russia) - 3 articles; Oil refining and petrochemistry (Russia) -3 article; Azerbaijan Chemical Journal (Azerbaijan) - 2 articles; Oil and gas chemistry (Russia) - 1 article; Butlerov communications - (Russia) - 1 article, Catalysis in industry (Russia) - 1 article, International Journal of Scientific Engineering and Applied Science (India) - 1 article, Journal of Physical Chemistry and Biophysics (Spain) - 1 article.

Approbation. The main results of the dissertation were reported, discussed in the form of oral and poster presentations at international and republican conferences: “EcoMod 2015” (Boston, 2015); X International Conference "Mechanisms of Catalytic Reactions" (Svetlogorsk, Russia, 2016); V Russian conference (with international participation) Actual problems of petrochemistry. Dedicated to the memory of Academician V.N. Ipatiev.; V Russian scientific conference "Actual problems of petrochemistry" (Zvenigorod, 2016). ; IX Baku International Mammadaliyev Conference on Petrochemistry (Baku, 2016); III Russian Congress on Catalysis (Nizhny Novgorod, 2017); 3rd International Turkic World Conference on Sciences and Technologies (Baku, 2017); International scientific and technical conference "Petrochemical synthesis and catalysis in complex condensed systems", dedicated to the 100th anniversary of academician B.K. Zeynalov (Baku, 2017); Scientific Conference dedicated to the 110th anniversary of Academician M.Nagiev (Baku, 2018); IV International Turkic World Conference on Chemical Sciences and Technologies (Ukraine, Kiev 2018); III Scientific-Technological Symposium Catalytic Hydroprocessing in Oil Refining (Lyon, 2018); International Scientific and Practical Conference dedicated to the 110th anniversary of Academician V.S. Aliyev (Baku, 2018); IV All-Russian (with international partici-pation) scientific symposium (Ivanovo-Suzdal, 2019);); İnternational Conference on Actual Problems of Chemical Engineering (Baku, 2020); IV Scientific – Technological Symposium Catalytic Hydroprocessing in Oil Refining (Novosibirsk, 2021); IV Russian Congress on Catalysis "Roskataliz" (Kazan, 2021); IV Scientific – Technological Symposium Catalytic Hydroprocessing in Oil Refining (Novosibirsk, 2021); Republican scientific conference "Catalysts, olefin-based oils" dedicated to academician Nadir Mir-Ibrahim oglu Seyidov's 90th anniversary (Baku, 2022); “Synchrotron Radiation Techniques for Catalysts and Functional Materials” (Novosibirsk, 2022); 6-th International Turkic World Conference on Chemical Science and Technologies (Baku, 2022).

Place of creation of the dissertation work. The studies presented in this dissertation were carried out in the laboratory "Heterogeneous catalysis" of the Institute of Petrochemical Processes named after Y.H. Mammadalieva.

Personal contribution of the author. Statement of problems, collection and generalization of literature data, development and conduct of experiments, preparation of samples for their further study, systematization of results, preparation of articles and abstracts, as well as interpretation and generalization of data from physical and chemical analyzes were performed by the author.

The structure and scope of the dissertation. The dissertation work is presented on 294 pages of computer text and consists of an introduction - 9 pages (14967 symbols); 6 chapters: literature review – 63 pages (117811 symbols), experimental part - 20 pages (28 937 symbols), discussion of the obtained results (chapters 3 and 6) -157 pages (195112symbols); conclusions – 3 page (3814 symbols); the list of used literature consists of 290 bibliographic names. The dissertation includes 69 tables, 73 figures and 20 scheme. The total volume of the dissertation is 370730 symbols (without tables, figures, list of references).

In the introduction the relevance of the problem is substantiated, the purpose and objectives of the dissertation work, the scientific novelty and practical significance of these studies are defined.

The first chapter analyzes the current state of styrene production, existing problems in this area, literature data on solving these problems, the current state of n-alkanes isomerization, their use as a component of high-octane gasoline, isomerization catalysts.

The second chapter presents the methods for the synthesis of catalysts for the oxidative conversion of ethylbenzene to styrene and the isomerization of n-alkanes, their mixtures and gas gasoline, the methodology for conducting experiments.

The third chapter discusses the results of studying the oxidative dehydrogenation of ethylbenzene to styrene, the coupling of the steam conversion of carbon monoxide with the oxidative dehydrogenation of ethylbenzene to styrene, and the effect of water vapor on the process of oxidative dehydrogenation of ethylbenzene.

The fourth chapter discusses the results of studying the isomerization of n-alkanes on a catalytic system consisting of sulfated zirconium dioxide and metal-modified zeolite, and the influence of each of the catalyst components on this transformation. The results of studying the isomerization of qas gasoline on a composite catalytic system, the joint conversion of associated gases and natural gasoline are considered. The influence of the reaction conditions on the conversion of gas gasoline, the search for optimal process conditions, the selection of the optimal catalyst composition, and the results of studying the process on the most efficient catalyst are discussed.

In the fifth chapter the results of the physical-chemical study of catalysts are discussed.

The sixth chapter discusses the mechanisms of oxidative conversion of ethylbenzene to styrene over modified metal oxide catalysts and the isomerization of n-alkanes and their mixtures over composite catalysts, as well as the relationship between the mechanisms of these two important industrial processes.

GENERAL CONTENT OF THE WORK

Based on the main task of the dissertation work, catalysts were synthesized based on the deposition of MgO, ZrO_2 and Cr_2O_3 oxides on γ-aluminum oxide and their modification with ortho-phosphate acid and CuO. The regularities of oxidative convertion of ethylbenzene to styrene in the presence of O_2 and CO_2 on these catalysts have been studied. It has been found that the inclusion of ZrO_2 in the catalytic system reduces the process temperature, treatment with orthophosphate acid increases the stability of the catalyst, modification with copper makes it possible to conjugate the reaction of oxidative conversion of ethylbenzene to styrene with steam reforming of carbon monoxide. The developed catalytic systems make it possible to create an environmentally friendly method for the simultaneous production of styrene and H_2 with high selectivity.

In order to obtain isocomponents of high-octane gasoline from isomerization of n-alkanes and their mixture, also from gas gasoline and its mixture with propane-butane fraction were synthesized composite catalytic systems consisting of zirconium dioxide modified with sulfate anions and metal-modified (mainly cobalt) zeolites HMOR(17) and HZSM-5(23). The patterns of isomerization of n-alkanes and natural gasoline on these systems were studied. It is shown that the components of the catalytic system individually are not active in the low-temperature isomerization of alkanes and natural gasoline at atmospheric pressure of hydrogen, but their composite catalytic systems exhibit high isomerization activity. It has been established that the synthesized composite catalytic systems make it possible to involve associated petroleum gases in the process of synthesis of high-octane gasoline components. It is shown that these processes occur by conjuqation of the formation of a bimolecular isostructural intermediate and its hydrocraking. It was found that the transformation of alkanes and their mixture in the presence of composite catalytic systems occurs by conjugation of the formation and isomerization of bimolecular intermediates with their hydrocracking.

Catalysts and research methods. Researches were carried out with the presence of Me_xO_y/Al_2O_3 (Me–Mg, Zr, Cr) and Co(Ni)/HMOR (HZSM-5)-SO_4^{2-}/ZrO_2 catalytic systems. MgO/Al_2O_3,ZrO_2/Al_2O_3 and ZrO_2,MgO/Al_2O_3 catalysts were prepared by impregnation of the corresponding metal salt solution in water into γ-Al_2O_3, dried at 120-150^{0}C, calcined at 550^{0}C and subsequent thermal calcining.

ZrO_2,MgO/Al_2O_3 catalysts were prepared by two methods: sequential and co-impregnation methods.

A part of prepared ZrO_2,MgO/Al_2O_3 catalyst samples was treated with orthophosphoric acid. For this purpose, after keeping them in orthophosphate acid solution for 24 hours, the water phase was evaporated, the obtained extrudates were dried at 80-120 and 300^0C for 3 hours and calcined at 500-600^0C. The amount of phosphorus in the samples is 5% (based on P_2O_5).

Taking some of the synthesized 1.0%ZrO_2,2.0%MgO/Al_2O_3 sample, the ZrO_2,MgO /Al_2O_3+P_2O_5+CuO catalysts were prepared on its basis. The ZrO_2,MgO/Al_2O_3 sample is impregnated with copper 2-nitrate solution of a certain concentration and is treated with ammonium carbonate, dried, washed, filtered through filter paper and kept in orthophosphoric acid for 24 hours. It is then evaporated. The obtained mass is dried at 80-120 and 300^0C for three hours and calcined at 500-600^0C. In the finished sample, the amount of copper (according to CuO) is 1 wt.%, and that of phosphorus is 5 wt.% (according to P_2O_5).

In the synthesis of aluminochrome catalysts, industrial pasty aluminogel was used as the aluminum component, and the chromium component was synthesized using potassium bichromate. 30 wt.% of the finished sample is Cr_2O_3, and the rest is Al_2O_3. A portion of this sample is promoted with potassium carbonate. The amount of K_2CO_3 in the finished catalyst is 15% by mass. This catalyst (30%Cr_2O_3/ 15%K_2CO/Al_2O_3) was named as AXM-1. The rest of the sample was modified with copper and promoted with K_2CO_3. This catalyst (30%Cr_2O_3/1.5%CuO/15%K_2CO_3/Al_2O_3) was named AXM-2.

These catalysts are referred to as "model" catalysts to distinguish them from catalysts made from spent aluminochrome catalysts, which will be shown below.

The second series of aluminochrome catalysts was synthesized on the basis of the used aluminochrome catalysts used in the dehydrogenation of hydrocarbons by the “Sabic” company. Preliminary studies show that this catalyst, which has already been used in the dehydrogenation of hydrocarbons, does not show activity in the oxidative dehydrogenation of ethylbenzene. To free the catalyst from the carbon deposits accumulated on its surface, it is calcined in air at $650-700^0C$ for 3 hours and the temperature is lowered to room temperature. This sample is crushed in an agate mortar and treated with solid KOH solution with careful stirring (48 hours). As a result, the grains of the sample soften and the sediment becomes pasty. The sediment is filtered through a sieve, decanted with distilled water, dried in air for 24 hours, then passed through a 3 mm diameter filter, dried in air under an electric incandescent lamp (24 hours), cut into cylinders 5-6 mm high, placed in a cup at 80°C (3 hours), dry at 120°C (3 hours) and calcined at 700°C for 3 hours, increasing the temperature gradually (100°C/1.5 hours). This example is divided into three parts. The first part is treated with calcium carbonate solution. For this, after keeping the sample in this solution for 24 hours, it is evaporated and dried as described above. The amount of K_2CO_3 in the finished catalyst is 15% (C - 1).

The remaining two parts are placed in porcelain bowls and a previously prepared mic-2 nitrate solution is poured over them. The samples are evaporated after remaining in the solutions for 48 hours. The dried samples were treated with solid sodium bicarbonate solution, decanted with distilled water, dried at 80^0C (3 hours) and 120^0C (3 hours) and treated with K_2CO_3 as described above. In the modified samples, the amount of CuO is 1.0 and 1.5 wt.% of the catalyst mass (the catalysts are named C-2 and C-3, respectively), and the amount of K_2CO_3 promoter in both catalysts is 15 wt.%.

Isomerization of alkanes was studied on Co(Ni)/HMOR (HZSM-5 and or Al_2O_3)-SO_4^{2-}/ZrO_2 composite catalytic systems. Depending on the intended purpose, modification of primary zeolites was carried out by decationization, dealuminization, introduction of various metals by ion-impregnation method, and modification of zirconium dioxide was carried out by impregnation of a solution of sulfating substance with a certain concentration of -ions calculated on SO_3. The composition of the synthesized catalysts is given in the following table:

Table 1

Composition of synthesized composite catalytic systems

Catalyst	Composition
M-1	0.4%Co/HMOR
M-2	0.4%Co/HMOR/10%ZrO_2
M-3	HMOR/10%ZrO_2 - SO_4^{2-} (6%)
M-4	0.4%Co/HMOR/10%ZrO_2 - SO_4^{2-} (6%)
M-5	0.4% Ni/HMOR /10%ZrO_2 - SO_4^{2-} (6%)
A - 6	0.4%Co/Al_2O_3/10% ZrO_2-SO_4^{2-}(6%)
K- 2	0.4%Co/HZSM/10% ZrO_2-SO_4^{2-}(2%)
K - 4	0.4%Co/HZSM/10% ZrO_2-SO_4^{2-}(4%)
K- 6	0.4%Co/HZSM/10% ZrO_2-SO_4^{2-}(6%)
K - 8	0.4%Co/HZSM/10% ZrO_2-SO_4^{2-}(8%)

*all samples have 25% Al_2O_3

Ethylbenzene, O_2, CO_2, CO, water vapor, n-C_4H_{10}, n-C_5H_{12}, n-C_6H_{14}, n-C_7H_{16}, gas gasoline and propane-butane fraction were used as reactants.

The experiments were performed in a flow-type catalytic unit equipped with a quartz reactor with a stationary catalyst bed.

The reaction products were analyzed by gas chromatography.

Conversion, yield and selectivity were calculated based on the initial amount of the components in the reactant and remaining in the catalysate.

The textural properties of the catalysts were studied by benzene adsorption, and their physicochemical properties by TPD, TPR, X-ray phase analysis, infrared spectroscopy and electronpara-magnetic resonance methods.

Oxidative dehydrogenation of ethylbenzene to St on MgO/Al_2O_3, ZrO_2/Al_2O_3 and ZrO_2,MgO/Al_2O_3 catalysts. The primary aluminum oxide used in the preparation of cata-lysts is γ-Al_2O_3 with a specific surface area of 200 m^2/g. Experiments show that this oxide is not very active in the oxidation of EB.

The activity of the catalysts for the oxidative dehydrogenation of ethylbenzene to styrene increases due to the effect of Mg, Zr (basic) oxides.

Impregnation of up to 2% MgO on alumina practically does not affect its activity, increasing the amount of MgO from 2% to 4% leads to EB conversion of 61.2 and selectivity to styrene to 90% . A further increase in the amount of MgO leads to a decrease in both activity and selectivity.

In case of impregnation of ZrO_2 on aluminum oxide, with the increase of ZrO_2 content from 0.4% to 2.0%, the activity of the samples increases up to 63.5% (ZrO_2 content is 1.3%) and then decreases. The selectivity of the conversion of ethylbenzene to styrene also increases monotonically from 86.3% to 91.5% with increasing ZrO_2 content from 0.4% to 1.3% and then decreases.

It is of interest to study the activity of the catalysts synthesized by joint impregnation of MgO and ZrO_2 on γ-Al_2O_3 in the oxidative dehydrogenation of EB to St. The results of the oxidative dehydrogenation of EB to styrene in the presence of oxygen on MgO/Al_2O_3 catalysts modified with 0.4% ZrO_2 show that the introduction of ZrO_2 into the catalyst under conditions standard for aluminomagnesium catalysts (500^0C, table 2) changes their catalytic properties. This change is not unequivocal.

Table 2

Conversion of EB to styrene over ZrO_2,MgO/Al_2O_3 catalysts WSHV=0.5 h^{-1}; T = 500^0C; EB:air = 1:6 (mol/mol

MgO, %	ZrO_2, %	Conversion, %	St yield, mol %	ZrO_2, %	MgO %	Conversion, %	St yield, mol%
4.0	0.0	61.2	50.4	1.3	0.0	63.5	58.1
2.0	0.4	63.0	52.1	0.4	2.0	55.7	50.1
4.0	0.4	60.5	49.3	0.7	2.0	60.2	54.8
6.0	0.4	59.5	48.5	1.0	2.0	63.5	58.4
8.0	0.4	57.4	42.3	1.3	2.0	60.2	51.2
10	0.4	40.4	32.9	2.0	2.0	53.6	44.5

Comparing the catalytic properties of ZrO_2, MgO/Al_2O_3 catalysts with MgO/Al_2O_3, it can be seen that the activity of ZrO_2, MgO/Al_2O_3 samples depends only on the amount of MgO. When the amount of MgO in Al_2O_3 is increased to 2.0%, the introduction of ZrO_2 allows both the increase of the activity of the sample and the increase of the yield of St. A further increase in the amount of MgO decreases the activity of the catalyst. If we compare the conversion of EB and the yield of St at 500^0C, we can see that a small change in the activity of the sample (57.5% instead of 63.0%) has little effect on the selectivity of St formation (84 % and 82.6%).

Incorporation of 0.4 % ZrO_2 into MgO/Al_2O_3 samples with large amounts of MgO led to a sharper decrease in activity than into samples with small amounts of MgO. To clarify this fact, the effect of MgO inclusion in the ZrO_2/Al_2O_3 sample on the activity of this sample in the oxidation of EB to St was investigated (table 2).

It can be seen from table 2 that the inclusion of MgO in ZrO_2/Al_2O_3 samples does not have an unambiguous effect on the oxidation of EB to St. In contrast to the ZrO_2/Al_2O_3 samples, whose activities increase as the content of ZrO_2 increases up to 1.3%, the addition of 2.0% MgO leads to an increase in the activity of the ZrO_2/Al_2O_3 samples with only up to 1.0% ZrO_2. In samples with ZrO_2 content above 1%, addition of 2.0% MgO results in decreased activity.

Modification of ZrO_2/Al_2O_3 samples with MgO, as well as of MgO/Al_2O_3 samples with ZrO_2, allows lowering the reaction temperature to 475-480^0C. At this time, the target product selectivity increases to 94% (1.0% ZrO_2, 2.0% MgO /Al_2O_3).

Thus, the study of the effect of the sequence of inclusion of activating ZrO_2 and MgO components shows that the sequence of inclusion of these components does not significantly affect the catalytic properties of ZrO_2, MgO/Al_2O_3 samples in the conversion of EB to St. The activity of these samples is probably limited by the total amount of activating components and the ratio of their amounts to each other.

A characteristic feature of the formation of St is the development of the activity of the catalyst during the course of the reaction, which ends in about 1 hour. Another feature of the primary catalyst is that it is not stable in the studied reaction. As can be seen from Fig. 1a, the catalyst reaches the maximum yield of St and loses its activity after operating at this yield for some time (~1 h).

The effect of orthophosphoric acid modification on the activity of 1.0% ZrO_2, 2.0%MgO/Al_2O_3 catalyst was studied and the results are shown in figure 1 b. It was found that the maximum activity of the sample in the conversion of EB (63.5%) and the maximum yield of St (58.4%) (at 500^{0}C) did not change even after treatment with orthophosphoric acid. It can be seen from the figure that the modification with orthophosphoric acid does not eliminate the effect of the development of the activity of the sample, but only slightly accelerates this process (the initial yield of styrene is 52% instead of 44% at 15 minutes). The possible importance of the modification with orthophosphoric acid is the increase in the stability of the catalyst. The results depicted in figure 1 b show that the activity of

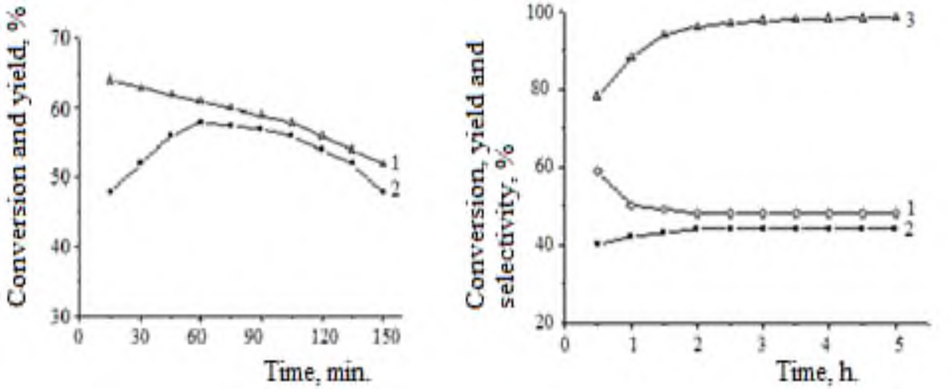
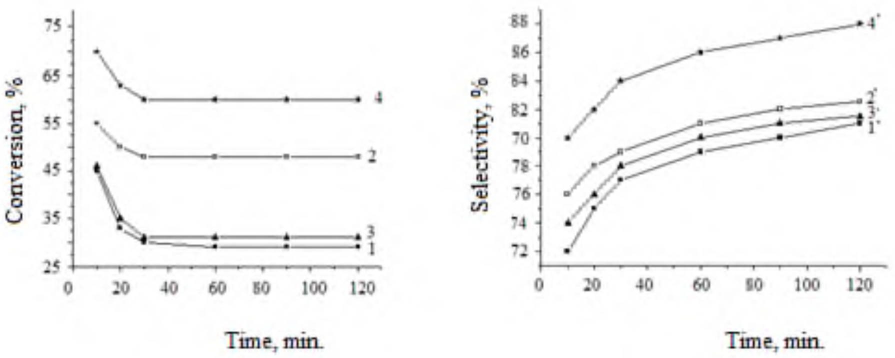


Figure 1. Dependence of the activity of 1.0%ZrO_2,2.0%MgO/Al_2O_3 (a) and 1.0% ZrO_2,2.0%MgO/Al_2O_3 + 5%P_2O_5 (b) catalysts in the oxidative dehydrogenation of EB to St from the duration of the experiment. WHSV = 0.5 h^{-1}, 480^{0}C, EB : air = 1 : 6 (mole ratio). 1-conversion, 2-yield, 3-selectivity.

the orthophosphoric acid-modified sample does not decrease even after 5 h of working over the development period, and the yield of St is distinguished by its high selectivity achieved after the visible development of the catalyst activity (2 h) (Fig.1b,curve 3).

Oxidative dehydrogenation of ethylbenzene to styrene over aluminochrome catalysts. The conversion of EB over model aluminochrome catalysts was first performed in the absence of oxygen. In this case, in order to maintain the hydrodynamic parameters of the process, air was replaced by inert gas (nitrogen), and the volume rate of liquid supply was 0.5 h^{-1}. At the beginning of the reaction, a certain time interval corresponding to the activation of the catalyst is observed. During this time, the activity of the catalyst reaches 30% and remains practically constant (fig. 2 a and b, curve 1 and 1′).



a) b)

Figure 2. Oxidative dehydrogenation of EB to styrene over model aluminochrome catalysts. T = 600^0C, WHSV = 2h^{-1}, EB : air = 5 : 1 (mol).

Cat. AXM-1: 1, 1`-direct dehydrogenation; 2,2`- oxidative dehydrogenation.

Cat. AXM-2: 3,3' – direct dehydrogenation; 4,4` oxidative dehydrogenation.

1, 2, 3 and 4 - conversion; 1', 2', 3' and 4' – selectivity.

The reaction products are benzene (14%), toluene (4%) and the target product styrene (80%). Other unanalyzed products (2-4%) are apparently destruction products.

Carrying out the reaction in the presence of an oxidizing agent - air oxygen (fig. 2. a and b, curves 2 and 2′) shows that the basic regularities of the conversion of EB to St practically do not change. This applies to both the activation time of the catalyst and the selectivity to styrene, which remains at 80%. In addition, the introduction of oxygen into the process increases the conversion of EB up to 20% under the same conditions. In this case, due to the effect of the oxidizer, the volume velocity increases by about 4 times (2 h^{-1} for the liquid), and thus the intensity of the process also increases.

Modification of the model catalyst with copper significantly affects the conversion of EB. Figure 2. a and b (curves 4 and 4′) show that modification with copper in the presence of oxygen led not only to an increase in the degree of conversion of EB, but also to an increase in selectivity (4 – 6%) of the target product St. It can be seen from the picture that the conversion of EB on a copper-modified aluminochrome catalyst in the absence of an oxidant is the same as the conversion on a copper-free aluminochrome catalyst. This shows that modification of the aluminochrome catalyst with copper does not affect its "pure" dehydrogenation ability. Thus, the increase in activity of the catalyst in the oxidative dehydrogenation reaction of EB on the aluminochrome catalyst after modification with copper and the shift of the reaction towards the production of styrene may be related to the increase in the ability of the catalyst to selectively oxidize the generated hydrogen.

Catalysts C-1, C-2 and C-3, developed on the basis of the aluminochrome catalyst of the “Sabic” company, do not differ from the model aluminochrome catalysts in the conversion of ethylbenzene to styrene in the presence of oxygen.

Oxidative dehydrogenation of EB to St in the presence of CO_2 over 1%ZrO_2,2.0%MgO/Al_2O_3 catalysts. The results of the study of the conversion of EB to styrene on zirconium-magnesium-aluminum oxide catalysts in the presence of CO_2 showed that the conversion of EB to St on these catalysts significantly depends on the ratio of CO_2 EB (mol/mol). By increa-sing this ratio to 4-5 on 1.0%MgO, 2.0%ZrO_2/Al_2O_3, the conversion of EB increases to 53-54%, and the selectivity St reaches 94%. On the 1.0%ZrO2, 2.0%MgO/Al_2O_3+5%P_2O_5 catalyst within the ratio of EB : CO_2 = 1 : 5 (mol/mol), the conversion of EB increases 2.5 times compared to conventional dehydrogenation, and the yielf of St rea-ches 46%. A further increase in the EB : CO_2 ratio from 5 to 10 does not significantly affect the conversion of EB and the yield of St. Modification with orthophosphoric acid does not significantly affect the conversion and selectivity of EB (conversion decreases by 3-4%, and selectivity decreases by 2%) (figure 3), and also increases the stability of the catalyst, as in the case of conversion in the presence of oxygen.

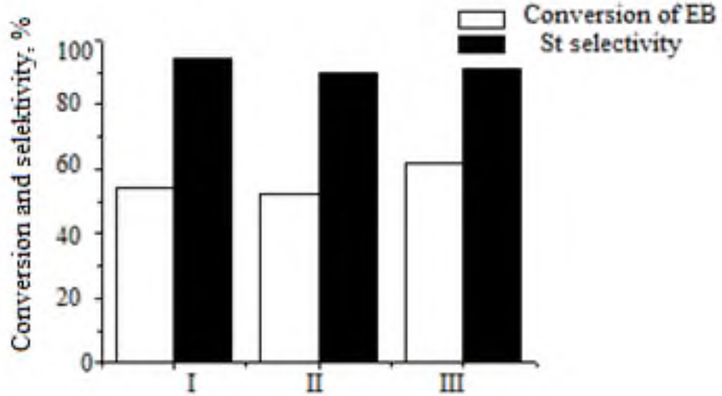


Figure 3. Conversion of EB to styrene in the presence of CO_2 over zirconium-magnesium-alumina catalysts.

T=500^0C; WHSV=1h^{-1}, GHSV=500h^{-1}; CO_2:EB=4:1 mol /mol. τ = 2 h.

I– 1.0%ZrO_2,2.0%MgO/Al_2O_3;

II-1.0% ZrO_2,2.0%MgO/Al_2O_3 + 5.0% P_2O_5 ;

III-1.0%MgO,2.0%ZrO_2/Al_2O_3 + 5.0% P_2O_5 +1%CuO

Promotion of 1.0%ZrO_2,2.0%MgO/Al_2O_3 catalyst treated with orthophosphoric acid with copper oxide leads to a further increase in the conversion of EB, already at the ratio of CO_2 : EB = 4 (mol/mol), the activity of the catalyst in the conversion of EB reaches 62% , but at this time the selectivity for St decreases slightly to 91% (figure 3).

Thus, under the influence of CO_2 on all three catalysts, the dehydrogenation of EB and the yield of St are increased compared to conventional dehydrogenation**.**

Oxidative dehydrogenation of EB to St in the presence of CO_2 over a model aluminochrome catalyst. In the conversion of EB to St, replacing oxygen with CO_2 sig-nificantly increases the selectivity to styrene. The results depicted in figure 4 show the effect of CO_2 on the conversion of EB to styrene over a model aluminochrome catalyst. The analysis of the reaction products shows that in addition to styrene, a small amount of benzene, toluene, and small molecular C_1-C_2 hydrocarbons are formed. The approximate composition (%) of these hydrocarbons corresponding to 90-92% selectivity according to St is as follows: CH_4 - 0.3; C_2 - 0.7; C_6H_6 - 2.2; C_7H_8 - 1.8. The increase in selectivity towards styrene is a consequence of the absence of further oxidation of EB, while the formation of additional hydrocarbon products indicates that hydrolysis has occurred.

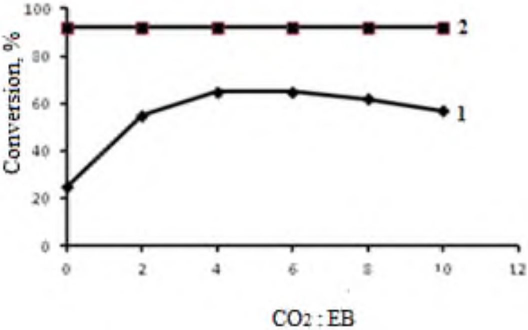


Figure 4. Effect of CO_2 on the oxidative dehydrogenation of EB to St on model AXM-2. T=580^0C; WHSV=$2h^{-1}$.
1 – conversion; 2 – selectivity.

The conversion of EB increases under the influence of CO_2.

However, the effect of CO_2 on the main reaction is complex. As the CO_2 : EB ratio increases from 0 to 4, the conversion of EB increases from 28 to 65%, and this value remains constant up to a ratio of CO_2 : EB = 6. Then, an increase in the CO2 : EB ratio leads to a decrease in the conversion of EB. The stability of the AXM-2 catalyst during conversion of the CO_2 : EB mixture is not high. The loss of catalyst activity is almost independent of the composition of the CO_2 : EB mixture used and drops below 30% in the 30th minute of the experiment. However, comparing the CO_2 : EB mixture conversion data of figure 4 with the N_2 : EB conversion (corresponding to the point CO_2:EB=0 in the figure), it can be seen that CO_2 has a promoting effect on the dehydrogenation of EB to St. At this time, CO is recorded in the conversion products, the output of which corresponds to the output of St, regardless of the CO_2 : EB ratio.

In the oxidative dehydrogenation of ethylbenzene to styrene in the presence of CO_2, the catalysts of C-1, C-2 and C-3, prepared on the basis of the aluminochrome catalyst of “Sabic” company behave like model aluminochrome catalysts and are not inferior to them in activity.

Catalytic activity of ZrO_2, MgO/Al_2O_3 catalysts in steam conversion of carbon monoxide. The study of the conversion of CO on the 1.0%ZrO_2,2.0% MgO/Al_2O_3 catalyst shows that this compound does not undergo convertion. However, upon contact with CO, the catalyst turns black. Such a change in the color of the catalyst (turning from white to black) indicates that it is coking. The deposition of coke on the catalyst indicates that the Bouduar reaction is taking place on it:

$$2CO \rightarrow C + CO_2 \qquad (1)$$

This reaction takes place in the active centers of the studied catalyst, and the coke formed surrounds such centers and deactivates the sample, preventing the further course of the reaction. Carrying out a similar process with a mixture of CO:H_2O, when the ratio of the components of the mixture is changed from 1 to 2.5, shows that at 400 to 500^0C steam conversion of carbon monoxide i.e. reaction (2):

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (2)$$

not gone. However, in addition, under these conditions, coking of the catalyst is observed, which can be explained by the departure of the Bouduar reaction. However, raising the temperature to 600^0C allows reaction (2) to proceed over the 1.0%ZrO_2,2.0%MgO/Al_2O_3 catalyst. The conversion of CO reaches 20% with the selective formation of H_2.

Modification of 1.0%ZrO_2,2.0%MgO/Al_2O_3 catalyst with orthophosphoric acid and copper significantly affects its activity. Thus, the comparison of the conversion of CO:H_2O mixture on 1.0%ZrO_2, 2.0%MgO/Al_2O_3 and 1.0%ZrO_2,2.0%MgO/Al_2O_3+5%P_2O_5+1%CuO catalysts shows that the results differ. If the conversion of CO over 1.0%ZrO_2,2.0%MgO/Al_2O_3+5%P_2O_5+1%CuO catalyst at 500^0C does not differ from the conversion over 1.0%ZrO_2,2.0%MgO /Al_2O_3, the introduction of H_2O molecules into the reaction at 500^0C, activates reaction (2) on 1.0%ZrO_2,2.0%MgO/Al_2O_3 +5%P_2O_5+1% CuO (table 3).

Depending on the composition of the H_2O:CO mixture, the conversion of CO can be raised above 40%, and as the ratio of H_2O : CO increases, the stability of the catalyst also increases (table 3).

Table 3

Effect of water vapor on carbon monoxide conversion on 1.0%ZrO_2,2.0%MgO/Al_2O_3 + 5%P_2O_5 +1%CuO catalyst

T = 500°C; GHSV = 500h^{-1}

H_2O:CO, mol	Conversion of CO,%	τ*,min	Yield of H_2, mol	(CO_2 +H_2) selectivity, %
0	trace	-	-	-
0.25	11	15	0.029	26
0.5	18	40	0.07	38
1.0	37	55	0.17	48
2.0	43	20	0.4	93
2.5	43	120	0.41	96

* stable working time of the catalyst

The addition of H_2 to the reaction mixture (H2O:CO=2.5 mol/mol) shows that the product of the reaction - hydrogen does not affect the conversion of CO, that is, it does not prevent the reaction from proceeding.

Catalytic activity of AXM-2 catalyst in steam conversion of carbon monoxide. Contact of CO with AXM-2 catalyst at 580^0C causes coking of the catalyst and formation of carbon dioxide. Thus, CO undergoes the Bouduar reaction (1) on AXM-2 and the catalyst is deactivated due to carbon deposition.

With the inclusion of water molecules in the reaction, that is, the contact of the AXM-2 catalyst with the $CO:H_2O$ mixture, changes the nature of CO transformation dramatically. In this case, depending on the ratio of the components of the mixture, the stability of the catalyst and the conversion of CO increase (table 4).

Table 4

The effect of H_2O on the conversion of CO on the model AXM-2 catalyst. T = 580°C; GHSV = $500h^{-1}$

H_2O : CO, mol	Conversion of CO,%	τ*,min	Yield of H_2, mol	$(CO_2 + H_2)$ selectivity, %
0	13	-	-	-
0.25	36	30	0.017	88
0.5	62	60	0.013	93
1.0	94	75	0.0205	97
2.0	>97	120	0.0215	98
2.5	>97	120	0.0217	100

* stable working time of the catalyst

Conjugation of conversion of EB to St with steam conversion of carbon monoxide on ZrO_2,MgO/Al_2O_3 catalysts. The results of the study of the conjugation of conversion of EB to St with the steam conversion of carbon monoxide on 1.0%ZrO_2,2.0%MgO/Al_2O_3 catalysts showed that carbon monoxide itself does not affect the conversion of EB. However, it should be noted that coking deactivates the catalyst due to the Bouduarr reaction. Coupling the conversion of EB with the water vapor conversion of carbon monoxide increases the conversion of EB and the yield of St. Analysis of starting materials and reaction products shows that the conversion of carbon monoxide is very small, up to 8%. This, in turn, shows that the studied reactions are somewhat dependent on each other. The increase in EB conversion and selectivity to St in the presence of H_2O:CO mixture is undoubtedly due to the shift of the reaction towards the production of products, which leads to the idea of effective removal of the formed hydrogen from the reaction zone. Taking into account the low oxidizing capacity of CO, it can be assumed that either CO_2, a product of steam conversion of carbon monoxide, or its intense hydridation to methane is the basis of the interaction (combination) of reactions. However, it was shown above that hydrogen does not affect the conversion of carbon monoxide with water vapor. Therefore, the effect of the matching process on the conversion of EB to St is negligible. Treatment of 1.0%ZrO_2,2.0%MgO/Al_2O_3 sample with orthophosphoric acid and promotion with CuO leads to increase of EB conversion and selectivity to St in the presence of H_2O:CO mixture. As can be seen from figure 5, as the conversion of carbon monoxide increases in this catalyst, the conversion of EB and the selectivity to St also increase. At the same time, it should be noted that treatment of the 1.0%ZrO2,2.0%MgO/Al_2O_3 sample with orthophosphoric acid reduces the development time of the catalyst activity. If we take into account that the development of activity of catalysts of the dehydrogelation process is explained by the formation of CP on the surface of the catalysts, then the effect of phosphoric acid can be limited only by accelerating the accumulation of CP, the formation of which occurs with the participation of acid centers. Therefore, the increase of the activity of the catalyst in the target reaction is not only due to the accumulation of disproportionation products of carbon monoxide, which is facilitated (activated) due to the modification of the catalyst with CP, but most probably due to the

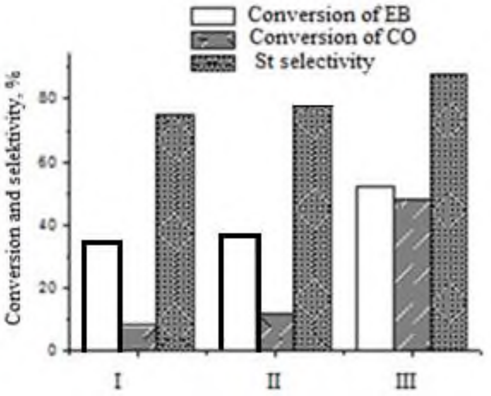


Figure 5. Conversion of EB to styrene in the presence of H_2O : CO. T=500^0C; $WHSV_{EB}$=0.5 h^{-1}, $GHSV_{H2O:CO}$ = 500 h^{-1}, H_2O:CO = 2.5.
I–1.0%ZrO_2,2.0%MgO/Al_2O_3;
II – 1.0%ZrO_2,2.0%MgO/Al_2O_3+5% P_2O_5;
III – 1.0%ZrO_2,2.0%MgO/Al_2O_3 + 1%CuO.

activation of the conversion of carbon monoxide with water vapor of CuO. Common to both cases is the accumulation of CO_2. Thus, CO_2, the product of the conversion reaction of carbon monoxide with water vapor, is a possible source of the observed change in the conversion of EB to St.

Conjugation of conversion of EB to St with steam conversion of carbon monoxide on AXM-2 catalysts. In the usual dehydrogenation of EB to St and its conversion to St in the presence of O_2, water vapor has a positive effect on the progress of the process of conversion of EB to styrene by accelerating the desorption of conversion products from the surface of the catalyst. At this time, water molecules do not affect the conversion process of EB itself. However, the investigation of the role of water in the conversion of EB to St in the presence of CO_2 shows that it also participates in rposes in addition to increasing the stability of the catalyst. The results of experiments conducted in this direction are given below.

A characteristic feature of the effect of H_2O on the conversion of the EB : CO_2= 1 : 5 mixture is the expected increase in the stability of the model AXM-2 catalyst. By increasing the H_2O : (EB: CO_2 = 1 : 5) ratio (mol) from 0.25 to 2.0, the operating stability of the catalyst increases monotonically. Increasing the density of water vapor to the following ratio H_2O:(EB:CO_2=1:5)=2.5 practically does not affect the stability of the process under the studied conditions (120 min.).

Analysis of the conversion products of EB gives results consistent with the above. However, the analysis of the conversion products of the EB:CO_2 mixture in the presence of H_2O shows that as the concentration of H_2O vapors increases, the output of CO decreases, while the output of hydrogen increases (figure 6). In general, the change in hydrogen yield is correlated with the change in EB conversion, and the molar sum of CO+H_2 corresponds quantitatively to the molar yield of styrene.

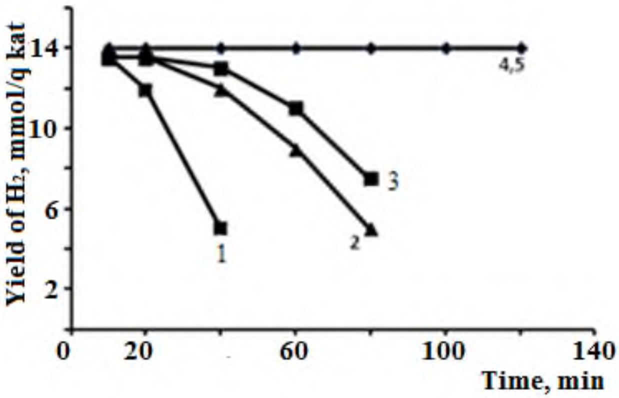


Figure 6. Effect of H_2O on the yield of H_2 in the conversion of EB:CO_2 (1:5 mol/mol) mixture to styrene on model AXM-2 catalyst. T = 580^0C; WHSV = 2 h^{-1}; selectivity 90-92%; H_2O : (EB : CO_2 = 1 : 5): 1- 0.25; 2 – 0.5; 3 – 1.0; 4 – 2.0; 5 – 2.5.

Thus, the practically absence of CO molecules, the correlation of the yield of hydrogen during the conversion of the mixture of EB and CO_2 with the process of conversion of EB to St indicates that a direct steam conversion reaction of carbon monoxide is taking place. Due to the presence of water vapors, the release of styrene, which is the target product of the reaction, is facilitated, and the passage of the Bouduar reaction, which enables the deactivation of the AXM-2 catalyst, is blocked.

Thus, the conversion of EB to St in the presence of CO_2 can be described by the following scheme, based on the ideas about the mechanism of steam conversion of carbon monoxide:

$$\left.\begin{array}{r}\mathrm{EB} \leftrightarrow \mathrm{St}+2\mathrm{H}_{\mathrm{ads}}\\ \mathrm{CO}_{2\mathrm{gas}} \leftrightarrow \mathrm{C}-\mathrm{O}-\mathrm{O}_{\mathrm{ads}}\end{array}\right\} \leftrightarrow \left.\begin{array}{c} St \\ \mathrm{Cu}(HCOO)OH\end{array}\right\} \leftrightarrow \begin{array}{c}\mathrm{H_2O}+\\ \mathrm{CO_{ads}}\end{array} \leftrightarrow CO_{\mathrm{gas}}$$

(3)

$$\left.\begin{array}{r}\mathrm{H_2\ (gas)} \leftrightarrow 2\mathrm{H}_{\mathrm{ads}}\\ \mathrm{CO_2(gas)} \leftrightarrow \mathrm{C}-\mathrm{O}-\mathrm{O}_{\mathrm{ads}}\end{array}\right\} \leftrightarrow \left. HCOO_{\mathrm{ads}} + \mathrm{H}_{\mathrm{ads}}\right\} \leftrightarrow \begin{array}{c}\mathrm{H_2O}\\ \mathrm{CO}\end{array}$$

(4)

The absence of CO in the reaction products shows that the reaction (4) in the conversion of EB to St on the AXM-2 catalyst is completely directed towards the formation of CO_2 and H_2 products.

According to the scheme (3), the reaction of dehydrogenation of EB to St proceeds independently, and is directed toward the obtainment of goal product due to the use of the released hydrogen in the reduction of CO_2. On the other hand, the absence of CO in the reaction products and the amount of hydrogen in these products corresponds to the yield of St shows that stage (4) in conditions close to the conditions of obtaining of St from EB in industry is directed towards the formation of steam conversion products of carbon monoxide. The connected nature of forward and reverse directions of steam conversion of carbon monoxide (SCCMO) activated by the AXM-2 catalyst allows considering CO_2 as a cyclic carrier of oxygen in the scheme of dehydrogenation of EB to St and conjugation of

SCCMO reactions.

Oxidative conversion of ethylbenzene is naturally accompanied by the formation and accumulation of oxidative condensation products (OCP), resulting in the development of low activity catalyst activity. It is believed that in the initial unstable stage of the process, St is formed in Lewis acid centers, then OCP is formed in the presence of these centers and oxygen. OCP is responsible for the oxidative dehydrogenation of EB. Accumulation of OCP until a monolayer is formed is the beginning of steady-state operation of the catalyst. A possible reason for the catalytic activity of OCP may be the geometric compatibility between EB and the centers located on the surface of OCP. As a result, there is a high concentration of carbon-oxygen centers responsible for the formation of St on the surface. Furthermore, the oxygen contained in the surface oxygenated groups is believed to be active enough to participate in the oxidative dehydrogenation of EB to St. Such a scheme does not involve EB forming any intermediate with oxygen. Therefore, the condensation products (CP) formed before the formation of OCP in oxidative conversion are the same as the CP formed during the direct dehydrogenation of EB. From this point of view, it can be assumed that similar forms of OCP are formed from the interaction of CO_2 with the previously formed CP as a result of the usual dehydrogenation of EB.

Thus, the following scheme of the formation of active centers in CP with the participation of O_2 and CO_2 in the conversion of EB to St can be proposed:

2▫□ + O2 →2▫ = O (5)
▫□+ CO2→[O…CO-▫] [O…CO… □▫] (6)

where □▫□ are carbon defects in CP; [O…CO-▫] [O…CO… □▫] shows the interaction of CO_2 with carbon centers (defects) in CP and its dissociation into oxygen atom and CO.

Isomerization-disproportionation conversion of n-alkanes on

composite catalysts.

Conversion of n-butane. From the preliminary study of the decationized forms of ZSM-5 type zeolite and synthetic mordenite, it was found that under the shown conditions, ZSM-5 type zeolites are almost inactive in the conversion of n-butane, while HMOR shows activity at 250-350^{0}C. During conversion, isobutane, propane, n- and isopentane are formed. By the 20th minute of the reaction, the yield of isobutane increases and reaches a maximum value (13.8% at 300^{0}C), and then decreases to 3.9% at the 60th minute. The maximum yield of propane, the main byproduct of the reaction, reaches 27% at the beginning of the reaction and then decreases to 12% within 60 minutes.

Isopentane and pentane yields remain at 2.5-2.8 and 1.0-1.5%, respectively, over 60 minutes. When the temperature is reduced to 250^{0}C, the yield of propane decreases more than the yield of isobutane, which leads to an increase in the selectivity in the direction of the isomerization reaction.

The inclusion of cobalt ions in the composition of mordenite (M-1) increases the activity of the sample. For example, the yield of isobutane at 300^{0}C is 16.3% in cobalt mordenite (M-1) (table 5).

While the yield of isobutane on HM, as already mentioned, reaches a maximum value at the 20th minute and decreases thereafter, the yield of isobutane on M-1 decreases only after the 40th minute of the reaction, which means that cobalt has a significant stabilizing effect on the process.

Dealumination of HMOR and its modification with zirconium dioxide allows to increase the yield of isobutane and lower the reaction temperature. The results show that adding 10% ZrO_2 to M-1 increases both butane conversion and isobutane yield (table 5).

The main products of n-butane conversion over mordenite-zirconium catalysts are propane, isobutane, isopentane. Small amounts of C_1-C_2 and n-pentane hydrocarbons are also formed.

Table 5

Conversion of n-butane on mordenite-based catalysts. GHSV = 150 h^{-1}, H_2 : n-C_4H_{10} = 2 : 1

Catalyst	T, ^0C	n-C_4H_{10} conversion, %	Yield, wt. %		
			C_3H_8	i- C_4H_{10}	i-C_5H_{12}
HM_{17}	300	46.9	27.2	15.5	2.8
	220	24.5	11.0	12.0	0.6
M-1	220	28.9	10.8	12.9	3.3
	300	55.2	34.8	16.3	2.6
M-2	190	12.7	1.6	9.1	1.6
	220	54.5	20.7	28.5	5.3
M-3	190	36.4	7.5	25.7	2.6
	200	46.1	11.7	27.7	4.6
	220	50.3	14.5	30.0	4.9
M-4	190	47.6	16.4	33.5	4.7

The inclusion of sulfate anions in the composition of the catalyst significantly changes its activity. In the temperature range of 190-220^{0}C, the conversion of n-butane is 36.4-50.3%, while the yield of i-butane is in the range of 25.7-30.0% (catalyst M-3). A noticeable increase in the activity of catalysts after sulfation is observed at 190^{0}C. Compared to M-2, the conversion of n-butane increases from 12.7% to 36.4%, and the yield of i-butane increases from 9.1% to 25.7%. When the temperature decreases, the yield of propane decreases, and due to this, the selectivity of the reaction increases (table 6).

The obtained results show that the presence of ZrO_2 and SO_4^{2-} in the M-4 catalyst allows the yield of i-butane to reach 33.5 mass % at the value of 47.6% conversion of n-butane at 190^{0}C, that is, the selectivity for the target product exceeds 70.4%.

A comparative analysis of the reaction products on different mordenite catalysts (table 5) shows that not only the conversion of n-butane, but also the distribution of the reaction products changes with the modification of zeolite. The formation of pentane and propane indicates that the process proceeds with the formation of active C_{8+} intermediates. Promotion of the catalyst with sulfate anions enables the accumulation of bimolecular intermediates, which leads to the selective formation of i-C_4H_{10} and the increase of the activity of the catalyst.

A similar transformation of n-butane is observed on the K-6 composite catalyst which was synthesized on the basis of HZSM-5 zeolite. A comparison of the activities of mordenite-based M-4 and HZSM-5-based K-6 catalysts shows that these catalysts are not strongly different from each other, and the optimal temperature of the isomerization reaction is 180^0C (table 6). Thus, the formation of a bimolecular intermediate takes place in the presence of SO_4^{2-}-ZrO_2.

Table 6

Conversion of n-butane on K-6 and M-4 catalysts. GHSV = 150 h^{-1}, H_2 : n-C_4H_{10} = 2 : 1

T, ^{0}C	K-6			M-4		
	Conversion, %	Selectivity, %		Conversion, %	Selectivity, %	
		i – C_4	C_3+C_5		i-C_4	C_3+C_5
160	34.0	68.1	31.9	39	67.5	32.5
180	38	72	28	47.6	70	30
200	46.0	51.5	48.5	54	52.8	47.2

Conversion of n-pentane. As with n-butane, the low-temperature isomerization of n-pentane was studied by stepwise study of the effect of the components of the synthesized composite catalysts on the conversion of n-pentane. As can be seen from table 7, the products of conversion

Table 7

Conversion of n-pentane on M-1. WHSV = $2h^{-1}$

$T, {}^0C$	Time, min	C_1-C_3	i-C_4	n-C_4	i-C_5	n-C_5	i-C_6	n-C_6
280	15	8.2	0.03	0.20	7	36.8	13.6	34
	30	11.2	0.5	0.4	12.7	42.1	13.2	33
	15*		1.5	1.6	13.4	21	10.1	52.4
300	15	32.1	1.1	0.5	11.6	29.8	10.7	14.2
	30	19.6	0.2	0.11	13.6	31.7	14.1	20.6
	15*	6.7	1.8	0.7	14.7	27.9	13.7	34.4

* In the presence of H_2

of n-pentane over M-1 in the absence of hydrogen are C_1-C_3 gases, n-C_4, i-C_4, i-C_5, n-C_6 and i-C_6 alkanes. The distribution of these products depends on temperature and reaction time. With increasing temperature, the amount of C_1-i-C_5 products increases, and at the same time, the amount of n-C_6 and i-C_6 decreases.

Adding hydrogen to the system has a significant effect on the composition of n-pentane conversion products. At 280^0C, the formation of C_1-C_3 gases stops completely, the conversion of n-C_5 and the yield of n-C_6 increase. When hydrogen is introduced into the system at 300^0C, the yield of C_1-C_3 gases decreases by 4.8 times, and the yield of isomeric products increases by 1.3 times. At the same time, the conversion of n-C_5 remains practically unchanged, while the yield of n-C_6 increases by 2.4 times. Thus, the introduction of hydrogen into the reaction system indicates that hydroisomerization is more efficient than conventional isomerization, and hydrogen is the co-reactant for n-pentane conversion.

The inclusion of ZrO_2 in the composition of the catalyst allows reducing the reaction temperature to 200^0C. With an increase in temperature, the yield of C_1-C_3 gases increases slightly and the selectivity according to isomers decreases.

The inclusion of sulfate anions in the catalytic system additionally increases its isomerization ability. In this case, the selectivity for isomers increases significantly and passes through the maximum at 180^0C. With increasing temperature, the conversion of n-pentane increases. At 200^0C, the amount of C_1-C_3 hydrocarbons increases sharply, which indicates an increase in hydrocracking.

Conversion of n-hexane. Mordenite catalyst (M-1) containing Co in the temperature range of 250–320^0C exhibits high activity in the isomerization of n-hexane. At the temperature of 320^0C and the volume velocity of n-hexane is $2h^{-1}$, the isoselectivity over M-1 is 97.4 mol.%, and the yield of isohexanes (including 2,2 dimethylbutane, 18.3 mol.%) is 73.5 mol.%.

The introduction of ZrO_2 into the M-1 catalyst significantly affects both the conversion of n-hexane and the yield of products. An increase in temperature from 200 to 250 ^{0}C has a noticeable effect on the distribution of reaction products. At 250^0C and below, the conversion products of n-hexane are both low and high molecular weight hydrocarbons. At the same time, the yield of isohexanes remains constant in the entire temperature range studied, while the yield of C_4 and C_5 hydrocarbons varies more complexly. An increase in temperature up to 290^0C leads to a decrease in the overall activity of the catalyst. It should be noted here that the yield of C_{7+} hydrocarbons decreases to 0.

From the data shown in table 8, it can be seen that sulfation significantly increases the isoselectivity. At the same temperature,the selectivity for isomers increases 6 times compared to M-2, the yield of cracking products decreases. Thus, catalysts with sulfated ZrO_2 allow isomerization reactions to be carried out with high selec-tivity

Table 8

Hexane conversion on M-4 catalyst. WHSV=2 h^{-1}, H_2:CH =3:1, $GHSV_{H2}$ = 350 h^{-1}

T, ^{0}C	Conversion, %	Selektivity, %			
		C_1	C_2 –n-C_5	i-C_4 –C_6	$\sum C_{7+}$
160	60	0.6	3.5	93.4	2.5
180	86	0.9	3.6	90.1	5.4
200	90	10	4.6	80	3.4

at lower temperatures that is thermodynamically acceptable for structural isomerization of n-paraffins.

The conversion of n-C_4H_{10}-n-C_6H_{14} alkane is accompanied by the formation of not only isomeric products, but also molecules with more and fewer carbon atoms in the chain than the original n-alkane. Such activity of the catalyst in the conversion of C_4-C_6 n-alkanes indicates a possible bimolecular mechanism of formation of intermediates and their hydrolysis.

Isomerization of n-heptane. In the next part of the experiments, the conversion of n-heptane over M-4 and K-6 catalysts was studied.

The study of the interaction of n-heptane with HMOR or HZSM-5, one of the components of these catalysts, showed that n-C_7H_{16} does not undergo transformation on these zeolites at temperatures below 280^0C. In contrast to these components, the M-4 and M-6 composite catalysts prepared on their basis show high activity in the conversion of n-hexane (table 9). As can be seen from the results, the regularity of conversion on both catalysts is the same and there is a slight difference in their isomerizing activities. In the temperature range of 140 – 300^0C, the main product of the conversion process on both catalysts is iso-heptane, and C_5 - C_6 paraffins are by-products. The first 20^0C increase in temperature is accompanied by a sharp increase in the yield of C_3 - C_4 alkanes and a dec rease in the yield of i-C_7 on both catalysts. During the subsequent increase in temperature, the yield of C_3-C_4 alkanes increases monotonically. At this time, a slight change in the yield of C_5-C_6 alkanes is observed. Based on the data given in table 10, it can be suggested that the formation of C_3-C_4 is the result of β-hydrolcleavage relatively to the triple carbon atom in the i-C_7H_{16} molecule, and the activation of n-C_7H_{16} is procced by the formation of the C_{7+} intermediate, the corresponding cycloalkyl transition and isomerization through the migration of the hydride ion, i.e., occurs according to the monomolecular mechanism of isomerization.

Table 9

Effect of temperature on the isomerization conversion of n-hep-

tane on M-4 and K-6. WHSV=2 h^{-1}, H_2:CH = 3:1.

T,^{0}C	Conversion, %	Yield, wt.%			Selectivity, %
		C_3-C_4*	C_5-C_6	i-C_7	i-C_7
M-4					
140	51.0	5.5	1.1	44.4	87
160	72.0	32.8	2.1	37.1	51.4
180	80.0	52.8	1.8	26.4	33
200	90.0	79.2	1.6	9.2	10.2
K-6					
140	43.0	4.5	5.3	33.2	77.2
160	64.0	29.2	6.5	28.3	44.2
180	72.0	36.7	7.3	28.0	38.9
200	93.0	80.5	2.5	10.0	10.8

*The amount of C_1-C_2 does not exceed 1%.

Thus, unlike n-C_4-n-C_6 alkanes, n-C_7H_{16} molecules do not form bimolecular intermediates

Conversion of gas and liquid n-alkanes mixture.

Co-conversion of n-butane and n-hexane on composite catalysts. The results of co-conversion of n-butane and n-hexane mixtu-re on M-4 catalyst are given in table 10.

The conversion products of n-butane:n-hexane mixture are C_4-C_6 isoalkanes, C_1-C_3 and n-C_5 alkanes. At this time, higher molecular weight C_{7+} hydrocarbons are also formed. The amount of normal alkanes in C_{7+} is not more than 5-8%. As the temperature increases from 120^{0}C to 170^{0}C, the isoproducts increase, while the formation of C_{7+} components decreases. As the temperature rises to 220, the share of i-C_4-C_6 components in the reaction products decreases, and the amount of low-molecular by-products increases. This indicates the transition from isomerization to hydrocracking.

Table 10

Conversion of n-C_4H_{10} and n-C_6H_{14} (1:1 mol) mixture on M-4

catalyst

T, ^0C	Conversion,* %		Selektivity, %				
	n-C_4H_{10}	nC_6H_{14}	C_1-C_3; n-C_5	i-C_4	i-C_5	i-C_6**	$\sum iC_{7+}$
120	18 (12)	32 (35)	6	5.8	38.4	19.8 (7.2)	30
170	60 (32)	65 (86)	9	8.8	42.3	21.9 (6.5)	18
320	88 (67)	92 (95)	37	2.8	34.8	15.4 (6.0)	10

* The individual conversion of n- C_4H_{10} and n- C_6H_{14} is given in parentheses

** The amount of 2,3-dimethyl butane in i-C_6H_{14} is given in parentheses

In particular, it should be noted that the conversion of n-butane, which is less active, increases under the influence of n-hexane, and the conversion of n-hexane is lower than its individual conversion. It is likely that butane, which is less active, occupies the centers that activate n-hexane.

The increase in the conversion of n-butane is primarily due to the formation of intermediates $[C_6H_{15+}]$ from n-hexane molecules and the involvement of these intermediates in the formation of a bimolecular intermediate:

$$C_6H_{14}+HA \leftrightarrow [C_6H_{15}]^+ \leftrightarrow [C_6H_{13}]^+ + C_4H_{10} \leftrightarrow$$

$$\leftrightarrow [C_{10}H_{23}]^+ \leftrightarrow [i\text{-}C_{10}H_{23}]^+$$

It follows from the obtained results that with the increase in temperature, destruction reactions involving the disproportionation of both the $[i\text{-}C_{10}H_{23}]^+$ derivative and the formed C_{7+} intermediate occur. Obtaining the necessary isomeric hydrocarbons - the high-octane components of gasoline - is possible by choosing the reaction conditions (feed rate, ratio of reactants, pressure, catalyst).

Conversion of n-butane:n-heptane mixture. During conversion of n-butane : n-heptane mixture on M-4, as a result of the interaction of the components of the mixture, a sharp decrease in the conversion of n-C_4H_{10} is observed, and a decrease in the conversion of n-C_7H_{16} is almost doubled compared to the individual conversion of these substances (table 11).

Table 11

Temperature dependence of conversion of n-C_4H_{10} : n-C_7H_{16} (1:1 mol:mol) mixture on M-4

T, ^{0}C	Conversion, %		Selektivity, %			
	nC_4H_{10}	nC_7H_{16}	C_3	C_4	C_5 –C_6	i-C_7
140	2.7	27.1(51)	2.2	-	56.2	41.6
160	4.6(39)	40.3(72)	8.2	-	44.9	46.9
180	7.5(47.6)	45.4(80)	13.6	-	36.8	49.6
200	-(54)	57.6(90)	28.3	30	23.6	17.9

Individual conversions of n- C_4H_{10} and n- C_7H_{16} are given in parentheses

Involvement of butane in the reaction leads to a significant increase in the amount of C_5-C_6 alkanes in the catalyst. Increasing the temperature from 140 to 180^{0}C causes a monotonous decrease in the yield of C_5-C_6-alkanes and an increase in the yield of iso-C_7 alkanes. In this temperature range, the yield of C_3 is significantly lower compared to the conversion of pure heptane. It should be noted that the share of butane in the formation of C_3 and C_5 alkanes is insignificant; C_3 is a breakdown product of C_7.

The absence of C_1-C_2 hydrocarbons in the reaction products and the presence of 2.7 to 7.5% primary butane suggests that the formation of C_5-C_6 alkanes is the result of the formation and hydrocracking of the bimolecular intermediate [C_4+C_7]. With an increase in temperature up to 200^{0}C, a sharp decrease in the formation of C_5-C_6 and i-C_7 reaction products is observed. In this case, the process is close in nature to the conversion of pure n-C_7H_{16}. The cut in consumption of butane and the sharp decrease in the yield of C_5-C_6 alkanes indicate a decrease in the contribution of the [C_4 + C_7] intermediate to the heptane conversion process. The reduction of heptane conversion from 90% to 57.6% in the presence of n-C_4H_{10} (table 11) indicates that n-butane competes for centers involved in hydrogen activation and thus prevents the hydrocracking of C_7 intermediates.

As in the conversion of the n-C_4H_{10} : n-C_6H_{14} mixture, the conversion of n-C_7H_{16} in the presence of K-6 decreases under the influence of n-C_4H_{10} (table 12). The temperature dependence of the

Table 12

Conversion of n-C_7H_{16} : n-C_4H_{10} (1:1) mixture on K-6

T, ^{0}C	Conversion, %		Selektivity, %			
	nC_4H_{10}	nC_7H_{16}	C_3	C_5 –C_6	i-C_7	C_8
140	21.5	28.2 (43)	21.0	54.2	24.8	-
160	30.6 (39)	41.0 (64)	28.2	40.6	28.6	2.6
180	43.4 (47.6)	36.7 (72)	19.0	36.6	39.9	4.5
200	5.0 (54)	23.5 (93)	46.9	30.3	22.8	-

conversion of n-C_7H_{16} becomes more complex. When the temperature is above 160^{0}C, the C_7H_{16} conversion decreases. A similar temperature dependence is observed for the yield of C_5-C6 conversion products of the butane-heptane mixture, all other conditions being equal. As the temperature increases, the yield of C_3 increases, but as can be seen from the data presented in table 12, in the range of 140-180^{0}C , the yield of i-C_7 products increases and the formation of higher molecular weight C_8 paraffins is observed.

Given the high yield of C_3, it is likely that the reaction products C_3 and C_8 are the result of the hydrocracking of the bimolecular [C_4 + C_7] intermediate. The absence of C_8 in the reaction products at 140^0C and the low yield in the temperature range of 160 -180^0C can be attributed to both their higher boiling point and high reactivity. The result of these effects is a monotonous increase in butane conversion in the 140-180^0C temperature range, despite a decrease in heptane conversion in the 4160-180^0C temperature range.

It should be noted that increasing the temperature to 200^0C changes the nature of the interaction between butane and heptane. A sharp decrease in the conversion of butane with an increase in temperature to 200^0C during the conversion of the mixture may be the result of a decrease in the probability of the formation of the bimolecular [C_4 + C_7] intermediate. The decrease in the conversion of heptane at 200^0C in the presence of butane indicates that the latter has the ability to prevent the hydrocraking of the former in the presence of anion-modified ZrO_2.

Thus, the composite catalytic systems, components of which are metal (Co, Ni)/H-zeolite (MOR or ZSM-5) and anion (SO_4^{2-})/ zirconium dioxide, have the ability to involve the gaseous C_{4-} and liquid C_7 paraffins in the process of isomerisation disproportionation through the formation and isomerization of bimolecular intermediates from these molecules and subsequent hydrocracking of this intermediates into C_5-C_6 alkanes with a high content of isocomponents.

Iisomerization of gas gasoline on composite catalytic systems. Isomerization of qas qasoline (GG) does not occur on individual components of composite catalytic systems. Co/H-zeolite is inactive at 140-200^0C K in this process, while SO_4^{2-}-ZrO_2 (SZ) loses its activety very quickly.

Iisomerization of gas gasoline on modified mordenite catalysts. Mordenite isomerization catalysts of n-alkanes are the most active medium-temperature zeolite isomerization catalysts. The use of such catalysts for gas gasoline isomerization showed that the C_{4-} and C_{7+}

components of gas gasoline is mainly converted to i-C_5, i-C_6 and n-C_5 on them. The introduction of transition metals, ZrO_2 and sulfate anions into these catalysts allows lowering the process temperature and increasing the isomerization activity of the catalytic system (table 13).

The results given in the table 13 show that the catalyst M-4 has the highest isomerizing activity among these catalysts. For it, the ratio of normal C_5 yield to i-C_5-i-C_6 yield is the lowest (n-C_5/i-C_5-C_6 = 0.02 - 0.08).

Table 13

Conversion of GG on M-1, M-2 and M-4 catalysts. H_2/CH = 1 : 3; WHSV = 2h^{-1}

T, ^{0}C	Conversion of C_{4-} and C_{7+}, %	Yield of nC_5, wt .%	Yield of iC_5-iC_6, wt. %	iC_5-iC_6 selectivity,%	nC_5/iC_5-iC_6
M-1					
300	39	11.3	11.4	51	1
320	32.2	10.2	8.6	46.5	1.2
M-2					
160	96	7.4	15.6	69	0.5
180	84.8	6.1	19.2	78.4	0.32
200	94.8	6.2	16.4	73.5	0.4
M-4					
180	49	0.8	18.1	97.8	0.02
200	49.7	2	17.1	92.4	0.08

When metal mordenite catalysts are used, the dehydro-hydrogenation function of the metal significantly affects the activity of the samples in the isomerization reaction of n-alkanes. In order to take into account the effect of the dehydrogenating component, a comparative experiment was carried out with the replacement of cobalt with nickel, which has high hydrogenating properties.

It should be noted that in all studied cases low-molecular C_{4-} alkanes are effectively involved in the process, while their initial amount in GG is 5.5%, the amount of these components in the catalysate is 1% and sometimes even lower.

The obtained results show that the main converted components in the conversion of GG in the above catalysts are C_{4-} and C_{7+} hydrocarbons, and the obtained products are mainly n-C_5, i-C_5 and i-C_6. Therefore, it can be concluded that during the conversion of GG, first C_{4-} and C_{7+} hydrocarbons form the bimo-lecular intermediate [C_{4-} - C_{7+}], and then this intermediate is divided into i-C_5 and n- C_6 or n-C_5 and i-C_6. Thus, high and low molecular weight components of GG are converted into medium molecular weight components. This averaging proceeds with superior formation of isomers on SZ-modified catalysts. Thus, if the ratio of n-C_5/i-C_5-C_6 for M-1 varies from 1 to 1.2, for M-2 and M-4 this ratio is small, that is, it varies from 0.06 to 0.5 (table 13). Thus, mordenitecontaining composite catalysts (CC) have the ability to convert n-alkanes and their mixture GG into C_5-C_6 alkanes with a high amount of structural isomers at low temperatures. Therefore, it is of interest to study the stability of these systems. The results of the research conducted in this direction (figure 7) show that the stability of the composite catalytic system depends on the modification of the zeolite component with a hydrogenating element and the temperature of the sample treatment with hydrogen.

Treatment with hydrogen in the range of 380–500^{0}C of M-3 catalyst, which does not contain a hydrogenating element, does not affect its stability (figure 7).

The inclusion of cobalt or nickel as a hydrogenating element in the zeolite component of the composite catalytic system has a different effect on the conversion of GG. If the introduction of nickel into the composite catalytic system allows to stabilize the performance of sample M-5 after pretreatment with hydrogen at 380^{0}C (figure 7), similar treatment does not affect cobalt-containing M-4. M-4 treated with hydrogen at 380^{0}C is similar in catalytic properties to M-3 without metal modification. However, increasing the hydrogen treatment temperature of M-4 up to 500^{0}C helps to increase the stability of the catalyst, but in this case its activity decreases (figure 7). Apparently, modification with these elements allows solving the problem of stable operation of CC. Studies show that the rate of CC deactivation is related to the rate of accumulation of bi- or polymolecular intermediates on the catalyst surface and is inversely proportional to their disproportionation by hydrocracking/hydrogenolysis.

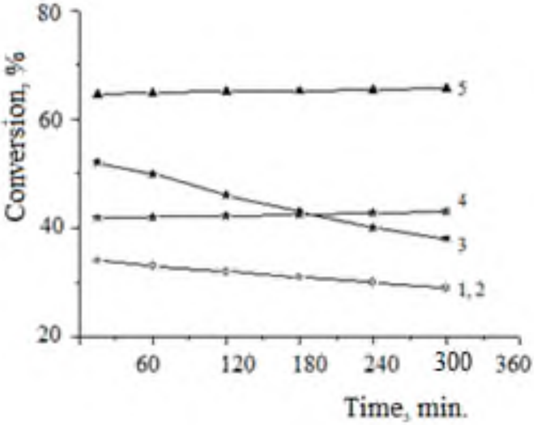


Figure 7. The influence of the hydrogen reduction temperature of the composite catalysts on their stability in the conversion of GG. 1–M-3(380^0C), 2-M-3(500^0C), 3-M-4 (380^0C), 4-M-4 M(500^0C), 5-M-5 (380^0C).

Gas gasoline conversion on HZSM-5 based composite catalysts. In order to investigate the effect of the nature of zeolite on the isomerizing activity of sulfated zirconium dioxide catalyst and to select a more effective low-temperature isomerizing catalyst, mordenite zeolite was replaced with HZSM-5 zeolite in the synthesized zeolite/SZ catalyst, and the activity of the obtained catalyst in the conversion of GG was studied. The results of this study are shown in table 14.

Table 14

Temperature dependence of gas gasoline conversion on K-6 catalyst. H_2/CH = 1:3; WSHV = 2h^{-1}, τ=30 min

T, ^{0}C	Conversion of C_{4-} and	Yield of n-C_5	Yield of isomers,	Selektivity of	n-C_5/i-C_5-C_6

	C_{7+} , %	, wt.%	wt.%	isomers, %	
180	74	7.2	16.6	69	0.44
200	75	9.1	15.6	66	0.51
220	79.6	12.4	12.6	50	1

The conversion pattern of GG over the HZSM-5-based K-6 catalyst is the same as over the mordenite-based catalyst. It was found that low and high molecular weight hydrocarbons of GG are converted into n-C_5, i-C_5 and i-C_6. Depending on the reaction time and temperature, the conversion of GG and the yield of individual products varies. As the temperature rises, the n-C_5/i-C_5-C_6 ratio approaches unity, the isomerizing activity of the catalyst decreases, and the hydrocracking ability increases (table 14).

Comparing the activities of M-4 and K-6 catalysts, which differ by zeolite component, it follows that the conversion of GG at 180^0C over the HZSM-5-based K-6 catalyst is 1.5 times higher than over the mordenite-based M-4 catalyst. In terms of isomer selectivity, M-4 is 1.5 times more active than K-6. Regarding the yield of n-C_5, the activity of K-6 is 7.2 times higher than that of M-4. This pattern is independent of temperature. In both catalysts, with increasing temperature, the isomer selectivity decreases and the yield of n-C_5 increases.

Considering that mordenite is a medium-temperature catalyst for the structural isomerization of n-alkanes, it can be concluded that there is a strong interaction between the metal zeolite and sulfated zirconium dioxide components of the synthesized catalysts: SZ lowers the operating temperature of the zeolite, and the metal-zeolite component increases the isomerization ability of SZ.

Conversion of GG over a modified alumina catalyst. Replacing the microporous metal/zeolite components of the composite catalytic system with mesoporous metal/Al_2O_3 shows that this catalyst has poor isomerization ability and its main feature is hydrocracking (table 15).

Table 15

Conversion of gas gasoline on the A-6 catalyst. H_2/CH = 1 : 3, WHSV = $2h^{-1}$

T, ^0C	Conversion of C_{4-} and C_{7+}, %	Yield of n-C_5 wt.%	Yield of isomers, wt.%	Selectivity of isomers, %	n-C_5/i-C_5-C_6
180	33	6.2	5	36	1.8
220	63	13.2	11.1	43	1.3

The lower isomerizing activity of the Al_2O_3-based catalyst compared to the zeolite-based catalysts once again proves the interaction between the components of the synthesized catalytic system. Indeed, zeolites, which are catalysts for the isomerization of n-alkanes at moderate temperatures, lead to higher activity and selectivity compared to Al_2O_3 due to their high acidity and microporosity properties.Changing the acid components in the catalysts also affects the hydrocracking properties in these systems.

The effect of the composition of the composite catalytic system on the conversion of GG. The influence of the mass ratio of the components of the composite catalytic system on its activity was studied on HZSM-5 based catalysts.

The influence of the amount of sulfate anions on the activity of the composite catalytic system was studied on K-2, K-4, K-6 and K-8 catalysts containing 2, 4, 6 and 8% SO_4^{2-} anions, respectively.

It was determined that the conversion of C_{4-} və C_{7+} components of GG over K-2, K-4, K-6 and K-8 increases with increasing temperature. However, as shown in figure 8, the conversion of C_{4-} və C_{7+} components of GG passes through the maximum with the increase of sulfate anions concentration. If the increase in the concentration of sulfate anions from 2 to 6% leads to an increase in the conversion of GG, when the concentration reaches 8%, the conversion decreases regardless of the temperature (180-220^{0}C).

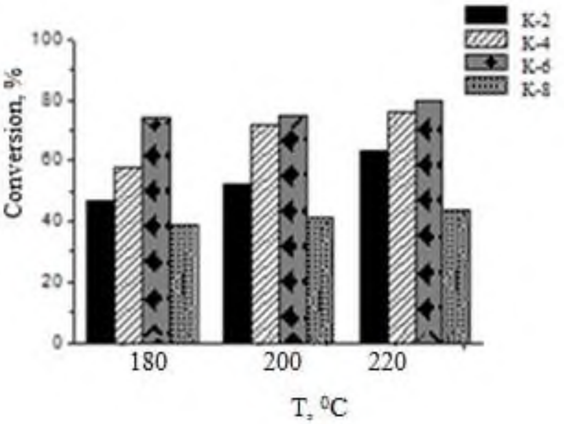


Figure 8. Conversion of C_{4-} and C_{7+} components of GG on K - 2, K - 4, K - 6 and K - 8. H_2/CH = 1 : 3, WHSV = 2h^{-1}.

The yield of isomers depends on both the amount of sulfate ions and the temperature. As the temperature increases, the isomer selectivity decreases in all catalysts. However, the izoselectivity of K-2, which is more selective in the range 180 - 200^{0}C, sharply decreases at 220^{0}C and is lower than the selectivity of K-4. At this temperature, K-4 catalyst containing 4% sulfate anions is more selective. The decrease in selectivity with the increase in the concentration of sulfate anions is apparently related to the increase in the hydrocracking activity of the samples. The ratio of the products of the isomerization and hydrocracking reactions depends on the residence time of the formed intermediate on the surface of the catalyst. If the acidity is not too strong, the residence time of these intermediates on the catalyst surface is short, they quickly convert into isomers, hydrogenated and leave the surface as isomers. When the acidity of the surface increases, the intermediates formed can remain on the surface for a longer time due to strong adsorption and undergo hydrocracking.

At 180 - 200^{0}C, the smallest n-C_5/i-C_5-C_6 ratio belongs to K- 2. This proves once again that the most selective catalyst is K-2 catalyst with 2% SO_4^{2-} anions. However, its selectivity is more sensitive to temperature and decreases faster with increasing temperature, and the conversion of QB and the yield of n-pentane over this catalyst are low. Catalyst K-6 lags behind K-4 and K-2 in terms of selectivity, but its selectivity is less sensitive to temperature, changing the temperature from 180 to 200^{0}C leads to a slight change in its isoselectivity. K-6 is more active than all other catalysts. Thus, K-6 catalyst is an effective catalyst for high conversion of GG and production of n-pentane, while K-2 catalyst is characterized by high isoselectivity.

Effect of reaction conditions on GG conversion

Effect of temperature. Based on the obtained results, the reaction temperature can be divided into two ranges: 140 - 180^{0}C and 200 - 250^{0}C (table 16). Intensive accumulation of C_5-C_6 isomers and consumption of C_{4-} - C_{7+} components are observed in the first temperature interval. This indicates that in the temperature range of 140 - 180^{0}C, hydroisomerization, which is one of the two main conversion pathways of the intermediates formed in the system, prevails.

Table 16

Temperature dependence of GG conversion on K-6. H_2/CH=1 : 3, WHSV = 2h^{-1}.

T, ^{0}C	$\sum C_{4-}$	iC_5	C_5	iC_6	C_6	iC_7	$\sum C_{7+}$
	Composition of raw materials , %						
	5.5	**25.2**	**19.2**	**18**	**8.4**	**5.4**	**18**
	Composition of catalysate, %						
140	4.5	28	20.3	20.2	6.3	4.2	16.5
160	1.8	34	24.4	21.6	2.8	3.6	11.8
180	1.0	37.5	26	22.6	2.6	4.5	5.8
200	0.4	26.6	32.2	19.8	2.7	7.9	10.4
220	1.0	26	31.0	19.4	1.5	9.0	12.2
250	2.0	25.4	27	20.0	2.0	10	14.0

In the second temperature interval, there is a marked decrease in the conversion of both C_{4-} and C_{7+}, and accumulation of i-C_7 occurs. The appearance of C_1-C_2 hydrocarbons in the products indicates the dominance of hydrocracking in the temperature range of 200 - 250^{0}C. The simultaneous change of C_{4-} and C_{7+} indicates their joint participation in the formation of intermediates that form the conversion products of GG.

The effect of the volume rate of GG. The results of these studies show that the conversion of C_{4-} and C_{7+} components of gas gasoline and the yield of i-C_5-C_6 alkanes increase with the increase in volume rate from 1h^{-1} to 3h^{-1} and have a maximum at 2h^{-1}. These indicators of the process decrease with the further increase of the volume rate. Thus, the most optimal volume rate for low-temperature isomerization of gas gasoline with the presence of synthesized composite catalytic systems is 2.0 h^{-1}.

Effect of H_2/CH ratio. It was determined that the change of the hydrogen/hydrocarbon ratio affects the composition of the catalysate during the contact of GG with the catalytic systems. The results of the study of the effect of this ratio on the composition of the catalysate are given in table 17. It has been shown that when the H_2/CH ratio changes from 1 to 3, the conversion of C_{4-} and C_{7+} components of GG, the yield of isoalkanes and n-C_5 increases monotonically. Starting from the H_2/CH =1:4 ratio, these indicators begin to decrease. A decrease in conversion means a decrease in the activity of the catalyst, which indicates that hydrogen prevents the deactivation of the catalyst, that is, removes the carbon deposits accumulated on the surface from the surface by hydrogenolysis. At H_2/CH ratios of 1:1 and 1:2, the conversion of C_{4-} components is low, and the conversion of C_{7+} components is high, indicating the participation of hydrogen in hydrocracking, and the high yield of isomers at the ratio of 1:3 indicates the participation of hydrogen in hydroisomerization. Thus, hydrogen participates in the process both as a reagent and as a carrier gas, and the process is more effective when the ratio of the amount of hydrogen to the amount of raw materials is 1: 3.

Table 17

Effect of H_2/CH ratio on gas gasoline conversion. K-6; T = 180^{0}C; WHSV = 2h^{-1}

H_2/CH	Composition of raw materials, wt.%						
	C_4-	iC_5	nC_5	iC_6	nC_6	iC_7	C_{7+}
	5.5	25.2	19.2	18	8.4	5.4	18.3
	Composition of catalysate, wt. %						
1:1	3.2	32	24	24.2	4.6	4.2	8.0
1:2	2.0	34	28	25.1	2.0	3.2	5.2
1:3	0.5	37.5	30	26.0	1.0	1.1	4.2
1:4	2.5	33	27.5	22.8	2.5	3.3	8.4
1:5	3	31	26.8	21.2	3.6	4.4	10

The role of conjugated formation, isomerization and hydrocracking of bimolecular intermediates in co-conversion of GG and propane-butane fraction. Taking into account the inclusion of C_{4-} alkanes in the process of formation of C_5-C_6 paraffins during the conversion of GG, it is possible to investigate the possibility of involving accompanying oil gases in the process of obtaining fuel (gasoline) in order to solve the problem of increasing the raw material sources of C_5-C_6 alkanes. The obtained results (table 18) show that even at a temperature of 160^{0}C, an intensive change in the composition of the GG : PBF (propane-butane fraction) (1:1) mixture occurs. PBF undergoes intensive consumption with complete absorption of C_4 components. At this time, up to 50% consumption of high-molecular components of QB is observed. In the conversion products of the mixture, the amount of i-C_5 - i-C_6 isomer components increases up to 27%, and the amount of n-C_5 increases 2 times.

Table 18

Effect of temperature on the conversion of mixture of gas gasoline and propane-butane fraction (1:1). K-6; WHSV=2h^{-1}, GHSV$_{PBF}$=

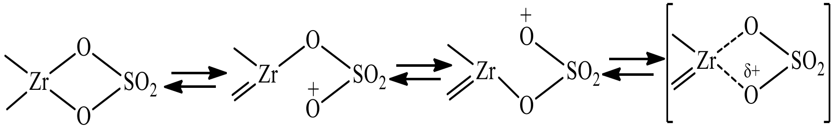
500h^{-1}

T, ^{0}C	C_2	C_3	iC_4	C_4	iC_5	C_5	iC_6	C_6	iC_7	C_{7+}
	Composition of the initial mixture (QB : PBF = 1 : 1), wt.%									
	5	17.8	9.9	16.7	15.1	12.3	8.1	3.7	2.4	9
	Composition of the catalysate, wt.%									
160	-	-	-	8.8	24.3	25.8	25.6	3	8	4.5
180	-	-	-	5.4	26.2	27.2	27.6	2.0	9.2	2.4
200	-	-	-	3.5	24	21.2	23.5	1.8	12.5	13.5

Taking into account the lack of appropriate activity in individual components of the catalysts of the composition, the products obtained as a result of the process, the hydrocracking activity of Co/H-zeolite, it can be concluded that the conversion of the GG and PBF mixture with the presence of C_{7+} and C_{4-} components occurs through conjugated formation, isomerization and hydrocracking of bimolecular [C_{4-} - C_{7+}] intermediates. The result of this transformation is the accumulation of C_5-C_6 hydrocarbons, that is, the molecular weight averaging of the hydrocarbons in the process. This process is conventionally called "syncretization" (from the Greek word "averaging"). The fact that the syncretization process takes place with the presence of gaseous alkanes indicates that it can be an effective process for the utilization of accompanying oil gases.

Dynamic scheme of isomerization-disproportionation conversion of a mixture of gaseous C_{4-} and liquid n-C_{6+} alkanes. The results of conversion of n-alkanes and their mixture in the presence of composite catalysts (CC) which components are sulfated zirconium dioxide and cobalt-modified H-zeolite (MOR or HZSM-5) show that the main product of the process is i-C_5-C_6 alkanes. Sometimes C_1-C_5 and C_{7+} alkanes are also formed at this time. These data indicate the formation of monomolecular and bimolecular intermediates and their subsequent isomerization or hydrocraking to the corresponding products. As the temperature rises, the yield of isomeric products decreases. The decrease in the yield of isomeric products and the increase in the selectivity for C_1 - C_5 hydrocarbons indicate that the hydrocracking activity of the catalyst increases with the increase in temperature.

Theconversion of alkanes over CC can be described by a multi-step scheme. The activation of alkane is related to its interaction with the active centers of CC. Such centers in CC can be Lewis acid centers consisting of electrophilic oxygen atoms, which can be formed as a result of dynamic equilibrium in the SO_4^{2-} - ZrO_2 system:

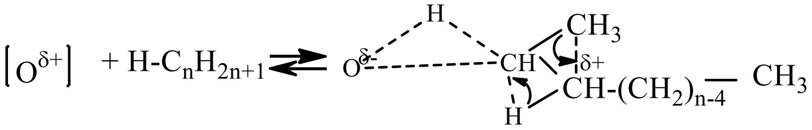


(7)

or

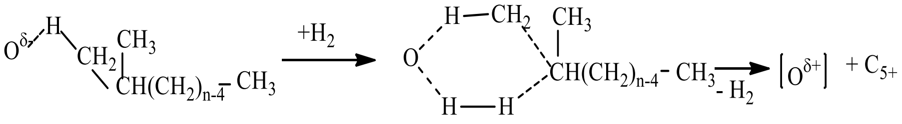
$$[O] \rightleftharpoons [O^{\delta+}]$$

The interaction of n-alkane with such centers leads to the formation of alkoxy groups that have a positive charge and their subsequent stabilization by the migration of the methyl group and the transfer of hydride ions, characteristic of their skeletal isomerization:



(8)

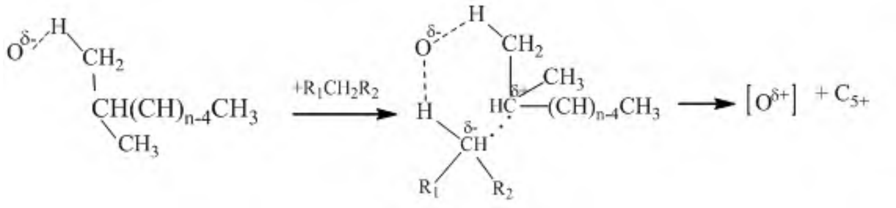
The interaction of the obtained monomolecular intermediates with hydrogen molecules enables the desorption of products according to scheme (9):



(9)

Hydrogen hydrogenates the C-C bond with the formation of low molecular mass products (β-splitting), and the share of this reaction increases with increasing temperature.

The conversion of a mixture of alkanes on CC follows a mechanism similar to the conversion mechanism of individual alkanes, in which H_2 is replaced by other lower molecular weight alkanes. The main products of the conversion of mixtures are C_5-C_6 alkanes (mainly isoalkanes), and by-products are C_1-C_3 hydrocarbons. In this case, high molecular weight C_{7+} hydrocarbons with isostructure are also formed. The presence of C_{7+} hydrocarbons and isomeric alkanes can be explained by the initial formation of bimolecular intermediates, their isomerization, and subsequent decomposition-disproportionation into low and high molecular hydrocarbons:



(10)

Scheme (10) with an intermediate cyclic state explains the co-conversion of n-alkanes. In this case, the interaction of hydrogen molecules with SZ according to scheme (9) is replaced by the second - low-molecular n-alkane molecules: low-molecular n-alkane molecules are already strongly polarized as a result of the shift of the positively charged hydrogen atom towards $O^{\delta-}$, the alkyl group with excess negative charge is attracted by the positively charged carbon atom of the intermediate formed by the primary alkane. The second low molecular weight alkane can compete with the high molecular weight primary alkane for interaction with SZ according to scheme (8) due to the bifunctional nature of the transformation. For example, as in the conversion of a mixture of n-butane and n-hexane. In this case, the presence of C_5 and propane in the conversion products of n-butane, and the decrease in the conversion of n-C_6H_{14} over CC confirm this possibility. However, highly reactive n-C_6H_{14} may show higher activity at this stage of the reaction. Blocking the interaction of hydrogen with SZ by n-butane leads to a change in the composition of the formed isomeric hexanes. The conversion products of n-hexane in the presence of n-C_4H_{10} are enriched with polyisomers, which easily undergo hydrocracking compared to normal and monoalkyl-substituted alkanes, formed in the absence of n-C_4H_{10} (table 10).

From the above, it can be concluded that the schemes proposed for the mechanisms of the oxidative conversion of ethylbenzene to styrene over metal-oxide catalysts and the isomerization of n-alkanes over a composite catalyst consisting of metal-modified zeolite and sulfated zirconium dioxide show that both of these processes goes with participation of oxygen. In addition, during these processes, the coupling of two reactions occurs in the system.

Thus, the main regularities of the conjugation of oxidative conversion of EB to St with steam conversion of carbon monoxide and the regularities of conjugation of formation and isomerization of bimolecular intermediates from C_4 gas and C_7 liquid paraffins with their hydrocracking have been determined. Such conjugated processes allow to utilisation of by-products in a single reaction system, to conduct processes in accordance with the requirements of "green chemistry", to simplify and intensify them.

RESULTS

1. It was determined that a catalyst (1%ZrO_2,2.0%MgO/Al_2O_3 +5% P_2O_5) with high activity and selectivity for oxidation of EB to St can be prepared by impregnating of MgO and ZrO_2 together on Al_2O_3 and promoting the obtained mass with H_3PO_4. Under the reaction conditions of WHSV=0.5h^{-1}, EB : air = 1:6 or EB : CO_2 = 1:5, 480^0C, in the presence of O_2, the conversion of EB and selectivity of St on this catalyst reaches 62 and 90%, and in the presence of CO_2, these indicators reach 54 and 94%, respectively [10, 11].

2. Using the synthesized $30\%Cr_2O_3/15\%K_2CO_3/Al_2O_3$ catalyst, it is possible to increase the volume rate of EB by 4 times. On this catalyst under the reaction conditions of WHSV=$2h^{-1}$, CO_2 : EB = 4, at 580^0C in the presence of CO_2 the EB conversion and St selectivity reach 64 and 95% , respectively [15].
3. The inclusion of copper in the synthesized catalysts increases their activity and selectivity. The conversion of EB in the presence of CO_2 over $1\%ZrO_2,2.0\%MgO/Al_2O_3+5\%P_2O_5+1\%$ CuO under reaction conditions of WHSV =$1h^{-1}$, GHSV =$500h^{-1}$, 500^0C is 62% and St selectivity is 96%. On $30\%Cr_2O_3/1.5\%CuO$ $/15\%K_2CO_3/Al_2O_3$ catalyst, under reaction conditions of 600^0C; WHSV=$2h^{-1}$; EB:CO_2=1:4 these indicators are 67 and 98%, respectively [3, 15].
4. The inclusion of copper in the composition of the synthesized catalysts allows the coupling of the oxidative dehydrogenation of EB to St with the steam conversion of carbon monoxide. The coupling of these reactions increases the conversion of EB to St. In this case, under the reaction conditions of 500^0C, WHSV=$0.5h^{-1}$, GSHV = $500h^{-1}$, the conversion of EB is 65%, the St selectivity is 92 % on $1.0\%ZrO_2,2.0\%MgO/Al_2O_3$ + $5\%P_2O_5+1\%CuO$ catalyst. On the $30\%Cr_2O_3/1.5\%CuO/15\%$ K_2CO_3/Al_2O_3 catalyst, at 580^0C, WHSV=$2h^{-1}$, the EB conversion and St selectivity are 68 and 92%, respectively [10, 11].
5. It was determined that the coupling of the oxidative dehydrogenation of EB to St in the presence of CO_2 with the steam conversion of carbon monoxide allows to create a simultaneous and environmentally harmless process of obtaining styrene and hydrogen [3].
6. The method of preparation of an effective catalyst for oxidative dehydrogenation of EB to St from used aluminochrome catalyst, which is a traditional dehydrogenation catalyst of hydrocarbons, was determined [14].
7. Composite catalytic systems containin of sulfated zirconium dioxide and metal modified zeolite allow to convert n-alkanes, their mixture, gas gasoline and mixture of propane-butane

fraction with gas gasoline into isocomponents with high selectivity at low temperatures. The components of this catalytic system are not individually active in the low-temperature isomerization of alkanes, and they only carry out this process together [9, 16].

8. It was determined that the conversion of gas gasoline and selectiviy for iso-C_5-C_6 alkanes is 74 and 69%, respectively on the most effective catalyst containing 0.4%Co/HZSM-5/10% ZrO_2-SO_4^{2-}(6%) under the reaction conditions of $WHSV_{GG}$= 2 h^{-1}, H_2/CH = 1 : 3, 180^0C [17].
9. Conversion of GG : PBF mixture (1 : 1) and isoselectivity are 84.2 and 44.4%, respectively on 0.4%Co/HZSM-5/10% ZrO_2-SO_4^{2-}(6%) catalyst under reaction conditions of $WHSV_{GG}$=2 h^{-1}, $GHSV_{PBF.}$=500h^{-1} and 180^0C [7].
10. In order to explain the obtained results, a bimolecular mechanism of isomerization with the presence of valence-unsaturated oxygen atoms of the catalyst was put forward. It was determined that the conversion of alkanes and their mixture, including gas gasoline and its mixture with the propane-butane fraction, on composite catalytic systems consisting of sulfated zirconium dioxide and metal-modified zeolite, proceeds through conjugation of formation and isomerization of bimolecular intermediates with their hydrocracking [18].
11. The connection between the mechanism of oxidative dehydrogenation of EB to St and the isomerization of alkanes was determined. Both of these processes take place in the presence of oxygen. In low-temperature isomerization, this is the electrophilic oxygen of the catalyst surface, and in high-temperature oxidative dehydrogenation, this is the nucleophilic oxygen - the reagent [18].

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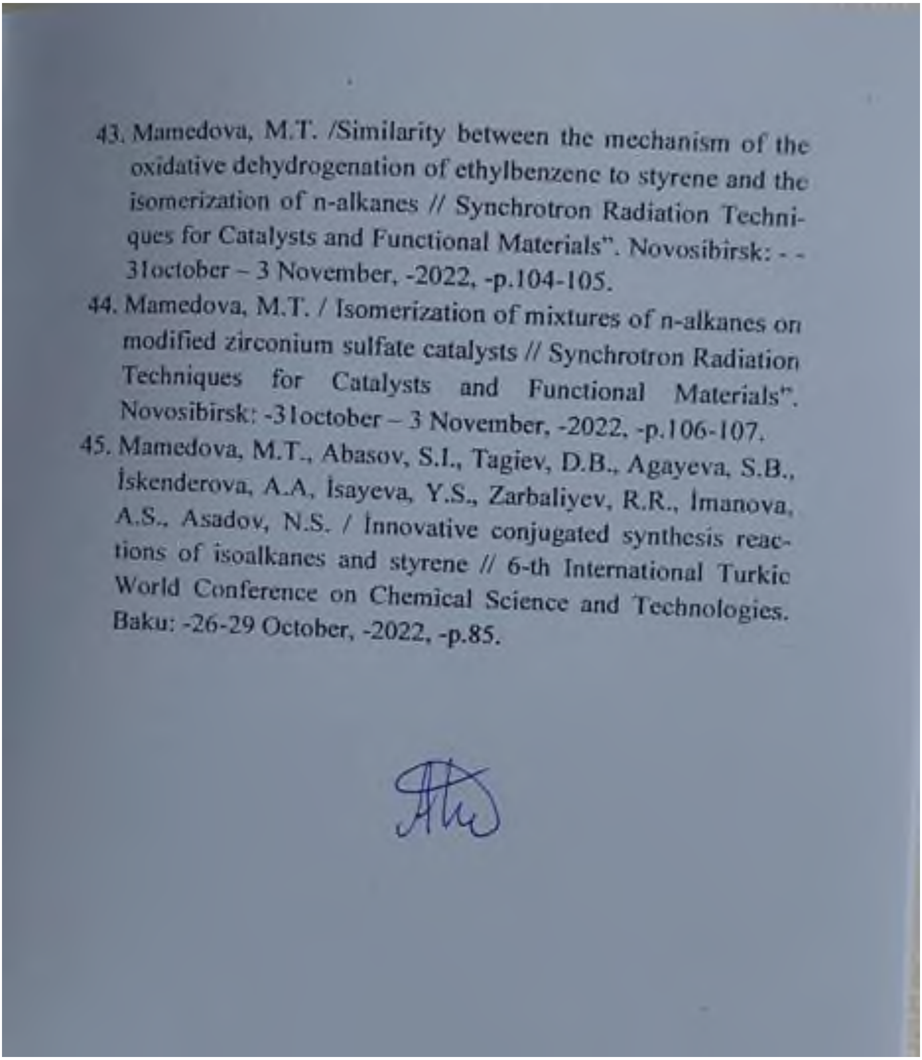

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