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Study of the Process of Joint Transformation of Propane-Butane Fraction and *n*-Heptane over Modified Zeolites

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Abstract

High-silica ZSM-5-type zeolite with silica module of 40 was produced by hydrothermal synthesis using hexamethylenediamine as a structure-forming additive. Its belonging to the pentasyl family and crystallization degree were determined by IR spectroscopy and X-ray phase analysis. Metal-containing zeolite catalysts were prepared by mechanical mixing of zeolite with powders of nickel and zirconium with a medium particle size of 50 nm and those of rhenium with that of 770 nm in terms of 0.5 mass %. The specific surface area of samples and parameters of their porous structure were determined by BET according to low-temperature nitrogen adsorption, acidic characteristics – by temperature-programmed ammonia desorption. It was demonstrated that the introduction of metals into zeolite reduced its specific surface area, pore volume, and acidity. The catalytic activity of metal-containing zeolites was studied during the transformation of propane-butane fraction and *n*-heptane. It was found that during their joint transformation over unmodified zeolite, the yield of the liquid product and the content of isoalkanes therein were higher than in case of conversion of only n-heptane. The addition of metals to zeolite led to a decrease in the concentration of *n*-alkanes, arenes, and alkenes in the resulting liquid products over catalysts and to a simultaneous increase in the fraction of iso- and cycloalkanes therein. Modification of zeolite with rhenium and zirconium increased formation selectivity of isoalkanes, while the introduction of nickel – that of aromatic hydrocarbons. The resulting zeolites might be used as the main component of catalysts for the gentrification of the straight-run gasoline fraction of oil during its joint conversion with hydrocarbon gases.

Keywords: zeolite ZSM-5, metal powders, porosity, acidity, conversion, activity, selectivity, propane-butane fraction, *n*-heptane

INTRODUCTION

Joint processing of gaseous and liquid hydrocarbons opens up a new area in the production processes of motor fuels. The proposed resource-saving technology allows solving the crucial issue of rational use of hydrocarbon gases and is more promising compared to their direct processing due to a reduction in the rigidity of conditions and the involvement of lower alkanes in the process of obtaining hydrocarbons at intervals of boiling gasoline fraction. Herewith, progression intensity of side reactions of cracking and hydrogenolysis of aliphatic components of gasolines is reduced. At the same time, the selectivity of target reactions is increased. The presence of finely dispersed platinum and hydrogen pressure generation in the reaction zone are required for the joint transformation of gaseous and liquid hydrocarbons [1–6].

The purpose of the present work was the study of the process of joint transformation of propane-butane fraction (PBF) and *n*-heptane over zeolite catalysts of the pentasyl family not containing noble metals, at ambient pressure and without using hydrogen.

EXPERIMENTAL

To carry out research by hydrothermal synthesis, there was produced high-silica ZSM-5-type zeolite with silica module of 40. It belongs to the pentasil family and its crystallinity degree is 93 % as determined using IR spectroscopy and X-ray phase analysis methods. Zeolite modification was performed by dry mechanical mixing of metal and zeolite powders in KM-1 vibratory mill for 2 h followed by calcination of the resulting mixture at 550 °C for 4 h. Mechanical mixing method used to prepare catalysts has a number of advantages over traditional modification techniques (impregnation and ion exchange) due to instrumentation simplicity and lack of harmful drains. Nickel and zirconium powders with an average particle size of 50 nm obtained by the gas-phase technique and rhenium powder with a particle size of 770 nm produced by the electroexplosive method were used as modifying elements. Preparation methods of metal powders were described in a great deal of detail in [7]. The content of each modifying element in zeolite was 0.5 mass %. To carry out tests, the samples were pressed into tablets that were then ground up and a fraction of 0.5–1.0 mm was selected. Transition metals with the incompletely filled d shell (platinum, iron, nickel, vanadium, rhenium, *etc.*), that have distinct hydrogenating-dehydrating properties are most often used as modifying agents to oil processing catalysts. As demonstrated by us earlier [8], their addition to zeolite catalysts of processing of hydrocarbons as finely dispersed powders contributes to increasing catalytic activity and selectivity.

Determination of the specific surface area of catalysts and parameters of their porous structure was carried out by BET (Brunauer–Emmett–Teller) method using Sorbtometer M analyser of manufacture of Katakon CJSC (Novosibirsk). The specific surface area was computed according to nitrogen adsorption isotherms at −196 °C. Pore volume and pore size of samples were determined using the BJH (Barett–Joyner–Halenda) model by adsorption and desorption isotherms at relative pressure $P/P_0 = 0.99$.

Acidic properties of catalysts were explored by temperature-programmed ammonia desorption that allows determining acid site distribution according to strength and their number. The chromatographic option of temperature-programmed thermal desorption lies in the fact that a sample with a probe substance (ammonia) is subjected to heating at a rate of 10 °C/min in helium flow. Acid sites concentration corresponds to desorbed ammonium amount, while their strength – to temperature maxima in the desorption curve [9].

Zeolite catalysts were tested during the joint transformation of PBF and *n*-heptane, while initial ZSM-5 was additionally studied during *n*-heptane transformation. To assess catalytic activity of samples, *n*-heptane transformation degree and the yield of gaseous and liquid reaction products were determined, and also there was computed formation selectivity of isoalkanes and arenes. Tests of catalysts were carried out using the flow type setup in the 300–550 °C temperature range, with the volumetric feed rate of PBF of 100 h^{-1}, *n*-heptane – 2 h^{-1}, atmospheric pressure. The volume of the catalyst loaded into the reactor was 5 cm^3.

A sampling of gaseous and liquid reaction products for analysis was carried out after 1 h of catalyst operation at each process temperature. The composition of transformation products of initial raw materials was analyzed by GLC using Chromatek-Crystal 5000.2 chromatograph. To determine liquid phase composition, BP-1 PONA capillary column (100 m × 0.25 mm × 0.5 μm), and for gas phase composition – capillary GS-Gas-Pro (60 m × 0.32 mm) and packed Carbosieve S-II (4 m × 2 mm, 60/80 mesh) columns were used.

RESULTS AND DISCUSSION

The advantage of adsorption-catalytic processes lies in their selectivity that determines an opportunity for selective transformation of one or several components of raw materials and process regulation

TABLE 1

Structural characteristics of zeolite catalysts

Sample	Specific surface area, m2/g	Pore volume, cm^3/g	Micropore volume, cm^3/g	Average pore diameter, nm
ZSM-5	443	0.19	0.13	2.0
Ni/ZSM-5	336	0.17	0.11	2.0
Re/ZSM-5	416	0.17	0.07	1.7
Zr/ZSM-5	387	0.15	0.08	1.9

flexibility towards target product generation. In this regard, the most important characteristics of catalysts are the properties of their structure. Table 1 gives determination results of the specific surface area and porosity of the zeolite catalysts under study. The ZSM-5 zeolite has a high specific surface area, there is the maximum reduction of the latter during the addition of nickel powder, and the lowest one – upon modification of zeolite with rhenium. The specific volume of pores and micropore volume are also maximum for unmodified zeolite compared to metal-containing catalysts. Specific pore volume for modified Ni and Re zeolites is identical and several times lower for the Zr/ZSM-5 sample. Micropore volume decreases in the series: Ni/ZSM-5 > Zr/ZSM-5 > Re/ZSM-5. The average pore diameter is the same for initial and Ni-containing zeolites, slightly lower for zeolite with zirconium additive; even smaller pore diameter is typical for Re-containing zeolite. It is worth noting that changes in pore volume and diameter are not so significant and specific surface area is selected further as a reliable value to explain changes in the catalytic activity of metal-containing zeolites. Apparently, the observed changes are related to the different particle size of metals that contribute to a decrease in pore volume and diameter when distributing in the zeolite. Rhenium that has the largest particles increasingly affects these catalytic characteristics.

The catalytic activity of zeolites is also due to the presence of acid sites in their surface, therefore acidity is one of the main characteristics of catalysts. Table 2 gives the data regarding the acidic properties of the studied zeolite catalysts. Low-temperature acid sites of the initial zeolite and its modified forms vary considerably in strength characterized by the thermal desorption maximum in the TD spectrum. The initial zeolite has the maximum strength of low-temperature acid sites, and nickel or zirconium additive substantially decreases it. The concentration of the initial zeolite is maximum; it is somewhat lower for the Re-containing sample, mainly due to a decrease in the fraction of low-temperature sites. The addition of zirconium to zeolite, even more, lowers acid sites concentration, however, herewith, the concentration of low-temperature sites is comparable with that for Re/ZSM-5. The Ni-containing zeolite is characterised by the lowest number of acid sites of both types.

TABLE 2

Acidic characteristics of zeolite catalysts

Catalyst	Form T_{max}, °C		Acid sites concentration, μmol/g		
	T_I	T_{II}	C_I	C_{II}	C_Σ
ZSM-5	210	425	532	266	798
Ni/ZSM-5	170	425	471	199	670
Re/ZSM-5	205	420	492	263	755
Zr/ZSM-5	170	425	491	217	708

Note. T_I, T_{II} are temperatures of maxima of low- and high-temperature peaks in thermal desorption curves, respectively; C_I, C_{II}, and C_Σ are concentrations of weak and strong acid sites and their sum, respectively.

According to the strength of acid sites, ZSM-5 and Re/ZSM-5 catalyst are comparable: maxima of low-temperature ammonium desorption peaks for them correspond to 205–210 °C, and of high-temperature ones – 420–425 °C. For the studied catalysts, the number of weak acid sites is 1.9–2.4 times higher compared to the number of strong centres. It is worth noting that variation dependence of acid properties of the zeolite catalyst on the nature of the metal introduced into the zeolite consistently coincides with changes in its structural characteristics: the specific surface area, the strength and the concentration of acidic sites decrease in the series: ZSM-5 > Re/ZSM-5 > Zr/ZSM-5 > Ni/ZSM-5 (see Tables 1 and 2).

Table 3 gives the composition of the initial PBF and its transformation products over the unmodified zeolite. The apparent transformation of PBF begins at 400 °C and is mainly related to a decrease in the concentration of *n*-butane. At process temperature of 450 °C, transformations of propane and isobutane begin, and the concentration of *n*-butane in products is more than 10 % lower than in the initial gas. At 500 and 550 °C, propane and butanes are actively involved in catalytic transformations; their content in reaction products is significantly reduced. As process temperature increases, the concentration of hydrogen, methane, ethane, and lower olefins in the reaction products rises, which is related to an increase in rates of cracking reactions and the rate of proton separation and transfer in hydrocarbon species.

As it follows from the data of Tables 1 and 2, the introduction of metals into zeolite leads to changes in its structural and acidic characteristics, and therefore, its activity during the transformation of hydrocarbon raw materials. Table 4 presents the group composition of gaseous products of transformation of *n*-heptane and the PBF mixture with *n*-heptane over the catalysts under study. *n*-Alkanes, and in particular, propane prevail in the composition of the resulting gaseous products during *n*-heptane transformation over the ZSM-5. Among isoalkanes, there are isobutane and isopentane, while alkenes are presented by ethylene, propylene, and butylene. As process temperature increases, the yield of *n*-alkanes and alkenes increases, and the concentration of isoalkanes decreases. Joint transformation of PBF and *n*-heptane over the ZSM-5 insignificantly changes the qualitative and quantitative composition of the resulting gaseous products: the concentration of *n*-alkanes and alkenes increases, while the content of isoalkanes somewhat decreases compared to gaseous products obtained during

TABLE 3

Effect of process temperature on the composition of transformation products of PBF over the initial zeolite

Component	Content, %				
	Initial raw materials	Products			
		Process temperature, °C			
		400	450	500	550
Methane	–	0.8	6.3	12.5	23.6
Ethane	2.8	4.0	8.8	14.9	20.8
Ethylene	–	0.1	0.5	1.2	2.9
Propane	75.8	80.4	71.3	62.6	45.4
Propylene	–	0.2	0.5	1.2	2.0
Isobutane	5.2	5.5	5.0	2.3	1.0
n-Butane	16.2	7.6	6.0	3.2	1.5
Butenes	–	0.2	0.3	0.4	0.5
Isopentane	–	0.7	0.6	0.2	0.1
n-Pentane	–	0.4	0.3	0.2	0.1
Hydrogen	–	0.1	0.4	1.3	2.1

TABLE 4

Process temperature effect on the composition of gaseous products of transformation of *n*-heptane and its mixture with PBF over zeolite catalysts

Components	Content, %					
	Process temperature, °C					
	300	350	400	450	500	550
	ZSM-5 (raw materials: *n*-heptane)					
n-Alkanes C_1–C_5	68.1	70.7	77.8	83.2	84.2	85.8
Isoalkanes C_4–C_5	30.7	28.0	20.7	13.7	12.4	9.9
Alkenes C_2–C_4	1.2	1.3	1.5	3.1	3.4	4.3
	ZSM-5 (raw materials: PBF with *n*-heptane)					
n-Alkanes C_1–C_5	73.6	74.8	75.1	81.1	87.3	87.7
Isoalkanes C_4–C_5	24.5	23.1	22.3	15.2	7.9	5.2
Alkenes C_2–C_4	1.9	2.1	2.6	3.7	4.8	7.1
	Ni/ZSM-5 (raw materials: PBF with *n*-heptane)					
n-Alkanes C_1–C_5	73.2	74.3	79.5	83.6	85.5	86.8
Isoalkanes C_4–C_5	25.6	24.4	18.1	11.6	6.4	1.3
Alkenes C_2–C_4	1.2	1.3	2.4	4.8	8.1	11.9
	Re/ZSM-5 (raw materials: PBF with *n*-heptane)					
n-Alkanes C_1–C_5	71.3	74.2	75.4	82.8	83.1	88.1
Isoalkanes C_4–C_5	27.4	22.5	21.0	13.0	6.6	1.3
Alkenes C_2–C_4	1.3	3.3	3.6	4.2	10.3	10.6
	Zr/ZSM-5 (raw materials: PBF with *n*-heptane)					
n-Alkanes C_1–C_5	70.1	71.8	76.6	82.2	82.9	85.5
Isoalkanes C_4–C_5	28.4	26.3	21.3	14.4	6.5	3.3
Alkenes C_2–C_4	1.5	1.9	2.1	3.4	10.6	11.2

n-heptane conversion. The found regularities are mainly typical and for metal-containing samples, however, there are some differences. For example, at temperatures of 300 and 350 °C, less *n*-alkanes, alkenes and more isoalkanes are formed over modified zeolites than over the initial ZSM-5. During process temperature increase from 350 to 550 °C, the yield of *n*-alkanes formed over ZSM-5 and modified zeolites is comparable, but herewith, the yield of alkenes increases and that of isoalkanes over metal-containing samples decreases. This occurs especially intensely at 500–550 °C, when cracking and dehydration reactions begin to prevail with the involvement of metal active catalytic sites due to high process temperature. The composition of gaseous products obtained over the metal-containing samples differs insignificantly: slightly more isoalkanes are formed over the Zr/ZSM-5 catalyst, while in the presence of the Re/ZSM-5 sample, at temperatures above 450 °C, the content of methane and ethane increases in reaction products, and the propane concentration decreases. The metal component role is firstly to participate in dehydrogenation process of paraffin hydrocarbons of initial raw materials to olefins formation, secondly – in hydration reaction of intermediates. Thus, metal-containing zeolite catalysts accelerate the progression of reactions of two types, *via* dehydrogenation and hydrogenation. As a consequence, the rate-limiting step of the process (olefins formation) increases and the rate of formation of compaction products (coke) decreases.

Table 5 gives the group composition of liquid transformation products of *n*-heptane and its mixture with PBF over zeolite catalysts. It can be seen that during the addition of PBF to *n*-heptane, transformation degree of initial raw materials over ZSM-5 catalyst at 300–350 °C decreases, which is related to n-heptane dilution with gaseous hydrocarbons that do not undergo conversion at these temperatures. There is the close composition of transformation products of *n*-heptane and its mixture with PBF at temperatures of 400 °C and above. In the resulting catalysates, there are representatives of all classes of hydrocarbons, the content of which is largely determined by the reaction temperature. As the transformation temperature of *n*-heptane and its mixture with PBF in the resulting products rises, the concentration of *n*-alkanes decreases, mainly due to a decrease in *n*-heptane content. Furthermore, the concentration of arenes increases. The maximum amount of iso- and cycloalkanes are generated at 350 °C in case of using *n*-heptane as raw materials and also at 400 °C during the transformation of a mixture of PBF and *n*-heptane. The content of alkenes in catalysates is minor and changes in process temperature do not have a significant impact on this parameter. Thus, during using a mixture of PBF and *n*-heptane as raw materials in the 300–350 °C temperature range, the degree of its transformation over the ZSM-5 sample decreases compared to the conversion of only *n*-heptane. Furthermore, significantly less aromatic hydrocarbons are formed.

TABLE 5

Process temperature effect on the composition of liquid products of transformation of *n*-heptane and its mixture with PBF over zeolite catalysts

Components	Content, %					
	Process temperature, °C					
	300	350	400	450	500	550
ZSM-5 (raw materials: *n*-heptane)						
n-Alkanes C_1–C_5	87.2	47.3	19.2	18.5	14.5	13.1
Isoalkanes C_4–C_5	5.9	17.4	11.3	7.2	5.7	4.7
Arenes C_6–C_{12}	5.0	32.3	67.0	72.3	77.8	79.6
Cycloalkanes C_5–C_{10}	0.8	2.6	2.1	1.4	1.3	1.1
Alkenes C_4–C_{10}	1.1	0.4	0.4	0.6	0.7	1.5
ZSM-5 (raw materials: PBF with *n*-heptane)						
n-Alkanes C_3–C_{12}	90.3	86.2	41.2	12.3	12.0	11.6
Isoalkanes C_4–C_{10}	4.5	6.1	14.5	12.6	11.9	11.0
Arenes C_6–C_{12}	2.3	5.1	41.0	72.8	73.9	75.5
Cycloalkanes C_5–C_{10}	1.3	1.7	2.5	1.5	1.3	1.0
Alkenes C_4–C_{10}	1.6	0.9	0.8	0.8	0.9	0.9
Ni/ZSM-5 (raw materials: PBF with *n*-heptane)						
n-Alkanes C_3–C_{12}	58.2	13.8	9.2	2.6	2.0	1.7
Isoalkanes C_4–C_{10}	7.1	15.5	15.4	14.4	12.8	8.3
Arenes C_6–C_{12}	31.5	64.7	71.1	81.1	83.7	88.8
Cycloalkanes C_5–C_{10}	1.2	5.5	3.9	1.6	1.1	0.9
Alkenes C_4–C_{10}	0.6	0.5	0.4	0.3	0.4	0.3
Re/ZSM-5 (raw materials: PBF with *n*-heptane)						
n-Alkanes C_3–C_{12}	70.8	60.8	16.6	12.6	2.4	2.1
Isoalkanes C_4–C_{10}	16.2	16.1	15.8	15.0	14.9	13.3
Arenes C_6–C_{12}	7.8	18.9	64.7	70.1	80.9	83.1
Cycloalkanes C_5–C_{10}	3.0	2.4	2.3	1.8	1.5	1.2
Alkenes C_4–C_{10}	2.2	1.8	0.6	0.5	0.3	0.3
Zr/ZSM-5 (raw materials: PBF with *n*-heptane)						
n-Alkanes C_3–C_{12}	72.3	67.4	63.3	20.5	13.7	5.6
Isoalkanes C_4–C_{10}	14.5	13.1	12.7	12.5	12.3	12.1
Arenes C_6–C_{12}	8.4	15.5	20.3	64.0	71.4	80.3
Cycloalkanes C_5–C_{10}	2.7	2.5	2.3	2.2	1.8	1.2
Alkenes C_4–C_{10}	2.1	1.5	1.4	0.8	0.8	0.8

The addition of metal powders to zeolite leads to a decrease in the content of *n*-alkanes, arenes, and alkenes in liquid products formed over catalysts with a simultaneous increase in the fraction of iso- and cycloalkanes. As process temperature rises, the concentration of *n*-alkanes in catalysates decreases most intensely during using nickel-containing zeolite. The Re/ZSM-5 sample has the maximum isomerizing ability during the joint transformation of PBF and *n*-heptane; the maximum number of isoalkanes is formed over it at 300–350 °C. They are produced to a lesser extent over Zr/ZSM-5 and Ni/ZSM-5 catalysts, while there is the maximum yield of isoalkanes at 350–400 °C. Over metal-containing zeolites compared to the unmodified sample, more aromatic hydrocarbons are generated; their yield increases with process temperature increase. The maximum amount of aromatic compounds is obtained over the nickel-containing sample, while the minimum one – over the zirconium-containing catalyst. More cycloalkanes are formed over modified zeolites compared to the initial ZSM-5 and their yield decreases with process temperature increase. Less alkenes are also formed over metal-containing zeolites and depending on modifying element nature, their concentration decreases in the series: Zr/ZSM-5 > Re/ZSM-5 > Ni/ZSM-5.

Figure 1 demonstrates changes in the degree of conversion of *n*-heptane, catalysate yield, and formation selectivity of isoalkanes and arenes, *i.e.*, the main high-octane components, on transformation process temperature of *n*-heptane and its mixture with PBF over the unmodified ZSM-5 and metal-containing zeolites. The lowest degree of conversion of *n*-heptane at 300 °C is observed over the unmodified zeolite (see Fig. 1, *a*). A dramatic increase in the degree of conversion of *n*-heptane (to 70 %) is recorded at 350 °C, while in case of its mixture with PBF – only at 400 °C (76 %). The degree of conversion of *n*-heptane over all samples increases with process temperature increase. The former over the initial ZSM-5 at 550 °C is almost the same, both in case of its utilization individually (92 %) and as a mixture with PBF (90 %). The degree of conversion of *n*-heptane over metal-containing zeolites at the initial reaction temperature (300 °C) is significantly higher than in the source ZSM-5. Moreover, it is close for catalysts containing Re (38 %) и Zr (36 %) and somewhat higher for Ni/ZSM-5 (50 %). The Ni/ZSM-5 sample shows the maximum activity in the process under study. Thus, during the addition of PBF to *n*-heptane, the degree of conversion of *n*-heptane over the initial ZSM-5 decreases at all temperatures under study but especially significantly in the 300–450 °C range. Zeolite modification with metals leads to a significant increase in its activity during the transformation of hydrocarbon raw materials at 300–350 °C. There is also a higher degree of conversion of *n*-heptane over metal-containing zeolites at the final process temperature (550 °C).

At the initial reaction temperature (300 °C), liquid product yield during *n*-hexane transformation was 94 %, while in joint conversion with PBF – 97 % (see Fig. 1, *b*). With increasing process temperature, the yield of the liquid product decreases more dramatically compared to its transformation in the presence of PBF. For example, at 350 °C, the catalysate yield during the joint transformation of PBF and *n*-heptane over the unmodified zeolite was 78 %, while in the conversion of only *n*-heptane – 60 %. At a higher temperature of the process, the differences in transformation degree decease during using raw materials of different types, however, the total trend remains. For example, at 400 °C, liquid product yield over the ZSM-5 sample is higher by 13 %, while in the 450–550 °C range – only by 4 % than in *n*-heptane conversion. During joint transformation of PBF and *n*-heptane over Ni/ZSM-5 and Re/ZSM-5 catalysts at 300 °C, the amount of the resulting liquid product is less, and in the Zr/ZSM-5 probe, is almost the same, as in the initial ZSM-5. As with the unmodified sample, an increase in reaction temperature by 50 °C leads to a significant decrease in liquid product yield. With a further increase in process temperature, the yield of the catalysate formed over metal-containing zeolites is reduced less dramatically, as on the unmodified zeolite. Thus, during the joint transformation of PBF and *n*-heptane over the ZSM-5 sample the yield of the liquid product increases by 18 (350 °C), 13 (400 °C), and 4 % (300 and 450–550 °C) compared to the conversion of *n*-heptane only. Over modified

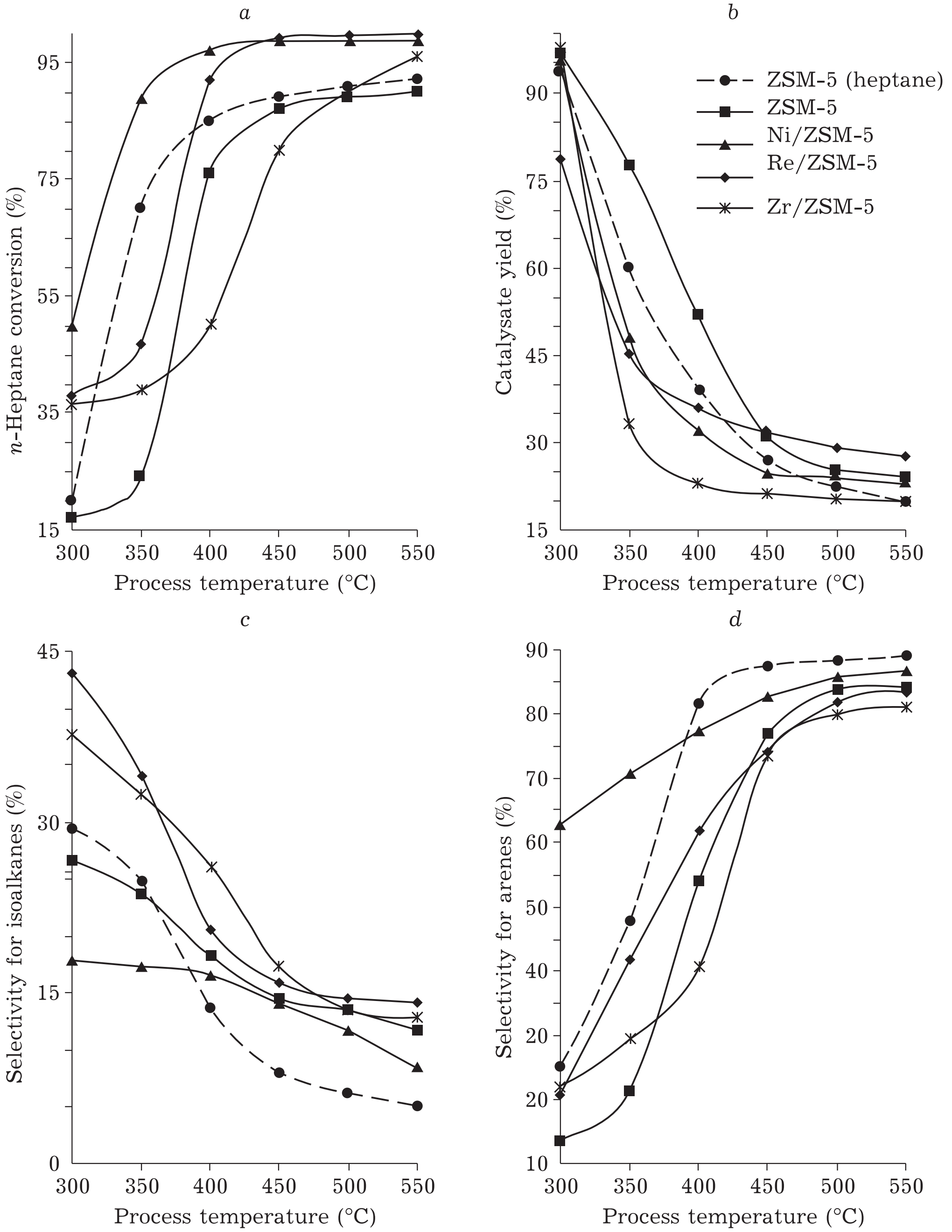

Fig. 1. Temperature effect of transformation of n-heptane and its mixture with PBF on *n*-heptane conversion degree (*a*), catalysate yield (*b*), and formation selectivity of isoalkanes (*c*) and arenes (*d*) over zeolite catalysts.

zeolites, the catalysate yield decreases, except for the Re/ZSM-5 sample, over which greater amounts of the liquid product are obtained at 450–550 °C.

Figure 1, *c* presents the data on changes in formation selectivity of isoalkanes with a rise in process temperature of the transformation of *n*-heptane (over ZSM-5) and its mixture with PBF over the catalysts under study. It can be seen that with temperature increase from 350 to 550 °C, formation selectivity of isoalkanes for the transformation of *n*-heptane over ZSM-5 is lower than the selectivity of their generation for the joint transformation of PBF and *n*-heptane. Moreover, the higher process temperature is, the more significant the differences in the degree of conversion become. Zeolite modification with rhenium and zirconium, unlike nickel, substantially increases formation selectivity of isoalkanes in the whole studied temperature range. At 300 °C, the maximum selectivity of formation of isoalkanes appears over the Re/ZSM-5 catalyst (43.1 %), in somewhat lower amounts, they are formed over the Zr/ZSM-5 sample (37.7 %).

At reaction temperature of 350 °C, these samples are almost comparable according to formation selectivity of isoalkanes: 34.1 and 32.5 % for Re- and Zr/ZSM-5, respectively. In the 350–500 °C temperature range, the Zr-containing zeolite is superior to the Re/ZSM-5 catalyst according to generation selectivity of isoalkanes, while at 550 °C, higher generation selecivity, *i.e.* 14.2 %, is typical for the latter. The lowest selectivity of isoalkane formation in the joint conversion of PBF and *n*-heptane is observed over the Ni/ZSM-5 sample. Thus, during joint transformation PBF and *n*-heptane over the source zeolite at 350–550 °C, formation selectivity of isoalkanes increases. It rises most significantly in case of the addition of rhenium and zirconium to zeolite, particularly, at the initial reaction temperature (by 11.2 and 16.6 % for Zr and Re/ZSM-5, respectively).

Figure 1, *d* demonstrates changes in the formation selectivity of aromatic hydrocarbons depending on the temperature of the transformation process of hydrocarbon raw materials of both types. With reaction temperature increase, formation selectivity of aromatic hydrocarbons increases over all catalysts. In case of *n*-heptane transformation at 300 and 350 °C, it is maximum for the Ni/ZSM-5 sample (63.0 and 70.8 %, respectively), while at temperatures above 400 °C, for the initial ZSM-5, the selectivity for arenes increases from 81.7 % at 400 °C to 89.3 % at 550 °C. The addition of PBF to *n*-heptane leads to a decrease in formation selectivity of aromatic hydrocarbons over the initial ZSM-5. Zeolite modification with rhenium and zirconium increases its aromatizing activity during the joint transformation of raw materials of both types at 300–350 °C, at 400 °C, the selectivity for arenes is already higher over Re/ZSM-5, and at higher temperatures, the unmodified zeolite is characterized by the higher aromatic activity. Thus, during the joint transformation of PBF and *n*-heptane over ZSM-5, formation selectivity of arenes is lower than during the use of *n*-heptane only. The Ni/ZSM-5 catalyst shows the greatest aromatizing activity during the joint conversion of raw hydrocarbon raw materials. Afterwards, Re/ZSM-5 and Zr/ZSM-5 samples follow.

CONCLUSION

The introduction of metal powders in zeolite lowers the specific surface area value, pore volume, and acidity of catalyst in the following series: ZSM-5 > Re/ZSM-5 > Zr/ZSM-5 > Ni/ZSM-5.

According to the qualitative and quantitative composition, gaseous products generated during the joint transformation of PBF and *n*-heptane are somewhat different from materials produced during *n*-heptane conversion: the content of *n*-alkanes and alkenes somewhat increases and the concentration of isoalkanes decreases.

In processing PBF and *n*-heptane over the initial ZSM-5, liquid product yield and isoalkanes content therein increase compared to the transformation of only *n*-heptane. The addition of metals to zeolite contributes to a decrease in the concentration of *n*-alkanes, arenes, and alkenes, and also to a simultaneous increase in the fraction of iso- and cycloalkanes in liquid products generated over catalysts during the joint conversion of raw materials of both types.

During the transformation of *n*-heptane over the initial ZSM-5, formation selectivity of isoalkanes is lower than that during the joint conversion of PBF and *n*-heptane. Zeolite modification with rhenium and zirconium significantly increases formation selectivity of isoalkanes, while the addition of nickel elevates the selectivity of formation of aromatic hydrocarbons.

The synthesized zeolites may be used as the main component of catalysts for the gentrification of both the straight-run gasoline fraction of oil and during its joint conversion with hydrocarbon gases.

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