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# Effect of Silicate Modulus and Modifying with Metals on the Acidic and Catalytic Properties of ZSM-5 Type Zeolite in the Isomerization of *n*-Octane

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## Abstract

High-silica pentasil zeolites with the silicate module from 20 to 200 were synthesized. Basing on them, catalysts have been prepared those contain nickel, zirconium and platinum introduced using various ways. An effect of the zeolite silicate modulus and modifying exerted on the acidity and activity of zeolite catalysts in the course of n-octane isomerization were studied. Optimal conditions for the isomerization of n-octane in the presence of catalysts under investigation have been determined.

Key words: zeolite, pentasil, ZSM-5, *n*-octane, isomerization, conversion, selectivity, modification, metal nanopowders

## INTRODUCTION

Efficient use of light hydrocarbons derived from crude oil and gas condensates is of particular interest for the oil refining and petrochemical industry. Their virgin gasoline fractions contain substantial amounts of alkanes with linear structure those have a low detonation resistance and therefore they cannot be used as a motor gasoline without further catalytic processing [1].

In the industrial isomerization processes there are generally three types of catalysts used: 1) platinum on chlorinated aluminum oxide, 2) platinum on mordenite and 3) superacid sulphatized zirconium [2]. The catalysts which are based on halogenated aluminum oxide and sulphatized zirconium oxide have a higher acidity level than catalytic systems based on zeolites, therefore the isomerization of  $C_5-C_6$  fraction occurs thereon at a temperature below 150 °C.

The disadvantages of halogen- or sulphurcontaining catalysts consist in the following features: 1) the modifier carryover in the course of operation, because of which constantly adding thereof is required to maintain a stable catalyst activity; 2) the use of strongly acidic catalysts leads to a rapid wear of the equipment; 3) industrial waste disposal being associated with environmental problems. This technology use is also provided by the presence of hydrogen in the reaction zone, whereas only a narrow fraction of  $C_5-C_6$  hydrocarbons is usually subjected to isomerization, which fraction represents valuable feedstock for the petrochemical industry.

Currently the possibility of using heteropolyacids [3], whereas various zeolites of different structural types [1, 4-8] as catalysts for the isomerization of normal alkanes is under active investigation.

Owing to the specific catalytic properties, basing on zeolites, including those modified with different metals one can create novel catalysts to develop energy-saving and environmentally friendly processes [1]. The catalytic activity of zeolite ZSM-5 in the conversion of alkanes with normal structure is caused by its acidity and molecular-sieve properties. It has high molecular-sieve selectivity with respect to normal paraffins and a high catalytic activity. The pore size inherent in a kind of zeolite belonging to pentasil family amounts to  $0.53 \times 0.56$  nm and  $0.51 \times 0.55$  nm, which hinders the formation and diffusion of highly branched molecules in the pores. At that, a molecular sieve effect begins to appear in the case of the isomerization of normal alkanes with the number of carbon atoms being greater than five [6].

In order to describe the isomerization of normal alkanes researchers offer different mechanisms depending on the type of catalyst used and on the reaction conditions. In general, the mechanism could be presented as it follows. On bifunctional isomerization catalysts those include zeolites there first occurs a dehydrogenation of n-paraffins at the active centre of the catalyst. Typically, it is presented by a modifier metal having a dehydrogenating function. Then, on the active acidic centers of the zeolite the olefin is converted into carbonium ion which is isomerised. Isomeric carbonium ions, giving a proton to the acidic active centre, are converted into olefins those are further hydrogenated on the corresponding active centers of a metal-containing zeolite catalyst. Thereby the rearrangement of intermediates on the acidic centers of the carrier is the slowest stage, which requires increasing the acidity of the carrier [2].

The acidic properties of high-silica zeolites (HSZ) such as ZSM-5 are determined by the value of its silicate modulus (M) thereof. Changing the  $SiO_2/Al_2O_3$  ratio for the original zeolite one could perform a targeted control of the acidity of the catalyst obtained on that base.

Thus, the development novel catalysts and the improvement of the existing catalysts for the isomerization of light hydrocarbon fractions in order to increase the octane number is urgent both from the standpoint of involving low-octane gasoline in the processing, and in connection with the global trend of reducing the content of aromatic hydrocarbons in motor fuel [1].

In addition, by now there is no clear understanding of the isomerization mechanism of paraffinic hydrocarbons on a zeolite-containing catalyst. It is known that the efficiency of the conversion process is determined by technological parameters, by molecular sieve effect of zeolite structure, by a relationship between the acidic (proton) and the hydrogenation-dehydrogenation functions of the catalyst under consideration [2].

The aim of this work consisted in studying the patterns of n-octane conversion into isoalkanes both with respect to the original zeolite of ZSM-5 type with different silicate module values, and with respect to the forms thereof modified in different ways.

#### EXPERIMENTAL

By means of hydrothermal synthesis from alkali alumina-silica gels we obtained high-silica zeolites with the silicate module equal to 20, 40, 60, 80, 100, 160 and 200.

The crystallization was performed in steel autoclaves at 175 °C for 4–6 days. After completing the crystallization, the zeolites were washed and dried at 100 °C for 24 h. In order to convert the zeolite into active H-form the samples were treated with 25 % NH<sub>4</sub>Cl aqueous solution, dried at 100 °C and calcined in air at 550 °C for 6 h.

High-silica zeolite was modified with metals by means of ion exchange and impregnation, and also by means of dry mechanical mixing with the appropriate nitrate salts and nanosized metal powders which were obtained using a gas-phase method. Estimated content of metal oxides in the zeolites was equal to 0.5 and 1.0 mass %. The average particle size of the metal nanopowders amounted to 50 nm.

By means of IR spectroscopy we determined the level of crystallinity for the zeolites synthesized and the fact that they belong to the family of pentasil. The IR spectra of the samples were obtained with the help of a Nicolet 5700 FT-IR spectrometer using KBr tablets (1.2 mg of zeolite per 300 mg of KBr), within the wave number region of 2000–400 cm<sup>-1</sup>.

The acidic properties of zeolite catalysts were investigated by means of thermally programmed ammonia desorption. With the help of the method one can determine the number of acidic centers and the strength distribution thereof. The chromatographic variant of the programmed thermal desorption consists in the fact that the sample of a catalyst with preliminary adsorbed probe substance molecules (ammonia) thereon is heated at the rate of  $10 \,^{\circ}C/$ min in a flow of helium. The concentration of acidic centers corresponds to the amount of desorbed ammonia, whereas the strength of the acidic centre is connected with the temperature maxima of the desorption peaks.

The catalytic activity of zeolite catalysts was determined in a model *n*-octane conversion reaction within the temperature range of 280–360 °C, at an atmospheric pressure, and the feeding flow rate equal to 1-6 h<sup>-1</sup> using a flow-through reactor with fixed-bed catalyst. The amount of the catalyst loaded into the reactor was equal to  $4 \text{ cm}^3$ , the size of its granules ranging within 0.5–1.0 mm. The duration of the process at each temperature did not exceed one hour, during which time the parameters of activity and selectivity for the action of the zeolite catalyst were not changed. The composition of *n*-octane conversion products formed

#### TABLE 2

Acidic characteristics of zeolites

### TABLE 1

Level of crystallinity inherent  $(\alpha)$  in high-silica zeolites

Silicate module (M)	α, %
20	90
40	100
60	95
80	89
100	86
160	84
200	83

on zeolite catalysts were analyzed using gas chromatography.

#### **RESULTS AND DISCUSSION**

According to IR spectroscopy, all the samples synthesized exhibit a set of absorption bands characteristic of zeolites with the structure of ZSM-5 type. The level of crystallinity is calculated as the ratio between the absor-

Zeolites (module values)	T <sub>max</sub> , °C		Concentration (C), $\mu$ mol/g		
-	$T_{\mathrm{I}}$	$T_{\rm II}$	$C_{\rm I}$	$C_{\rm II}$	C <sub>Σ</sub>
HSZ (M20)	185	450	637	332	969
HSZ (M40)	180	420	477	282	759
HSZ (M60)	180	415	336	203	539
HSZ (M80)	180	415	278	199	477
HSZ (M100)	180	410	273	187	460
HSZ (M160)	175	405	184	93	277
HSZ (M200)	170	395	177	82	259
HSZ (M40) + 0.5 % NiO (DM)	175	420	430	239	669
HSZ (M40) + 1.0 % NiO (DM)	185	420	409	168	577
HSZ (M40) + $0.5 \%$ NiO (IE)	185	425	369	188	557
HSZ (M40) + $1.0 \%$ NiO (IE)	180	420	365	149	514
HSZ (M40) $\pm$ 0.5 $\%$ NiO (impregnation)	185	425	421	156	577
HSZ (M40) $\pm$ 1.0 $\%$ NiO (impregnation)	180	420	427	157	584
HSZ (M40) $\pm$ 0.5 % Ni (NSP)	170	425	471	199	670
HSZ (M40) $\pm$ 1.0 % Ni (NSP)	175	420	463	204	667
HSZ (M40) + $0.5 \%$ Zr (NSP)	170	425	491	217	708
HSZ (M40) + 0.5 % Pt (NSP)	170	425	451	231	682

Notes. 1.  $T_{\rm I}$ ,  $T_{\rm II}$  – the temperatures of the peaks for the forms I and II. 2.  $C_{\rm I}$ ,  $C_{\rm II}$  and the  $C_{\Sigma}$  – the concentrations of acidic centres in the forms I, II, and the total value, respectively. 3. DM – dry mixing. 4. IE – ion exchange. 5. NSP – nanosized powder.

bance intensities of the absorption bands at 550 and 450 cm<sup>-1</sup>. The entire series of the samples is characterized by a fairly high level of crystallinity. So, for the zeolite with the silicate modulus M = 20, this value is equal to 90 %, whereas for the zeolite with M = 40 it amounts to 100 %. Further, with the growth of the zeolite silicate modulus up to M = 200 the crystallinity level is reduced to 83 % (Table 1).

Table 2 demonstrates the acidic properties of zeolites. It can be seen that the strength of acidic centers is reduced with increasing M from 20 to 200, which is indicated by shifting the maxima of the low temperature peaks at 185 to 170 °C and those of high temperature peaks from 450 to 395 °C. At that, the total number of acidic centers is reduced from 969 to 259  $\mu$ mol/g. This is connected with a decrease of the amount of Al<sup>3+</sup> cations in the zeolite crystal lattice; those are responsible for the formation of Lewis and Brönsted acidic centers.

As a basis for modifying, we have chosen zeolite with the silicate module equal to 40 which is characterized by the maximum level of crystallinity. As nickel, zirconium and platinum introduced into its structure in different ways the strength of acidic centers slightly decreases and their concentration decreases more significantly. To all appearance, this could be due to the fact that metal cations partially shade the aluminum atoms of the zeolite lattice responsible for the formation of acidic centers.

Nickel and platinum were chosen as modifying agents as metals having the dehydrogenating and hydrogenating properties, whereas zirconium oxide is used as the basis for industrial isomerization catalysts.

Figure 1 demonstrates the level of *n*-octane conversion on the zeolites with different silicate module values and nickel-containing catalysts prepared basing on the zeolite with M = 40, depending the process temperature.

It is seen that the maximum value is attained in the case of zeolite with M = 20, whereas with increasing the silicate modulus the level of noctane conversion is reduced (see Fig. 1, *a*). These data are in a good agreement with the acidic properties of zeolites (see Table 2). A higher content of strong acidic centres inherent in zeolites with a low silicate module promotes an intensive conversion of *n*-octane.



Fig. 1. Level of *n*-octane conversion on the zeolites with different silicate modulus values (*a*) and on Ni-containing zeolite with the modulus M = 40 (*b*) depending on the process temperature.

Within the temperature range of 280-320 °C the value of M exerts a significant effect on the activity of the zeolite, as evidenced by the differences in the values of *n*-octane conversion level. For example, at 280 °C the conversion was equal to 8 % for the zeolite with M = 80 and 45.2 % for the zeolite with M = 20. The most critically this is manifested when the process temperature is equal to 320 °C, which could be associated, to all appearance, with a simultaneous influence of the process temperature and the acidity of zeolites. As the temperature increases, the level of *n*-octane conversion increases significantly for all the zeolites, where-

as at 360 °C the differences in the magnitude thereof are already insignificant (see Fig. 1, a). Thus, at low temperature values, the conversion level of *n*-octane is markedly influenced by the composition of the zeolite catalyst. As the temperature of the reaction increases, an increasing contribution to the transformation of raw material is provided by the temperature factor, whereas the effect of the active centers of the zeolite exhibits weakening.

The modification of the zeolite with M = 40by nickel results in the fact that the level of noctane conversion can either increase or decrease, depending on the concentration and the method of introducing (see Fig. 1, b). So, at the temperature of 280 °C the maximum catalytic activity is demonstrated by the catalyst with nickel content of 1.0 %, obtained via dry mixing the zeolite with a salt of nickel. The lowest activity is exhibited by the zeolite sample containing 0.5~%of nickel nanopowder (the level of conversion being equal to 30.6 %). With increasing the temperature, the activity of the catalysts is changed. Within the range of 300–340 °C the sample with adding of 0.5 % of nanosized powder (NSP) is not inferior or even is superior with respect to all the modified catalysts in the activity in the process of n-octane conversion.

As compared with the original zeolite, the conversion rate of *n*-octane on this catalyst exhibit a 4-8 % increase. Although the acidity of the sample with adding 0.5 % of nickel NSP is significantly lower than the acidity of the original zeolite with M = 40, it exhibits a great activity in the catalytic process. This is, to all appearance, due to the fact that the catalyst contains a highly disperse nickel phase uniformly distributed on the surface of the zeolite catalyst.

Table 3 demonstrates an effect of temperature exerted on the composition of *n*-octane conversion products on the zeolite with M = 40. The gaseous reaction products are presented by  $C_1-C_4$ alkanes, among those propane, *n*-butane and isobutene are prevailing. With increasing the process temperature, the hydrocarbon composition of the resultant gas phase changes insignificantly.

The composition of catalyzate obtained at 280 °C contains mainly *n*-alkanes (76.0 %), 58.9 % of those represent unconverted *n*-octane. Among the normal hydrocarbons, there are alkanes with carbon number from 3 to 8

# TABLE 3

Effect of temperature on the composition of *n*-octane conversion products on the zeolite with M = 40 (flow rate 2 h<sup>-1</sup>), mass %

Products	Proce	Process temperature, $^\circ C$						
	280	300	320	340	360			
Gaseous:								
$C_1$ – $C_4$ alkanes	88.1	87.8	85.0	84.3	86.2			
$C_2$ – $C_4$ alkenes	0.7	0.8	0.4	0.3	0.3			
n-alkanes C <sub>5+</sub>	6.1	6.3	7.4	6.7	5.4			
isoalkanes $C_{5^+}$	5.1	5.1	7.2	8.7	8.1			
Liquid:								
$n$ -alkanes $C_{3+}$ :	76.0	63.7	42.3	29.5	19.2			
C <sub>3</sub>	0.4	0.3	0.9	0.5	0.5			
$C_4$	3.5	1.7	6.0	4.0	2.5			
$C_5$	7.9	4.1	8.5	7.8	3.3			
$C_6$	3.4	1.9	6.8	4.0	1.8			
C <sub>7</sub>	1.9	1.2	2.4	1.1	0.4			
C <sub>8</sub>	58.9	54.5	17.7	12.1	10.7			
isoalkanes $C_{4+}$ :	17.1	20.9	24.1	23.0	15.8			
$C_4$	1.8	2.8	3.0	1.9	1.5			
C <sub>5</sub>	5.0	5.3	5.8	6.5	4.2			
$C_6$	5.2	6.3	7.7	7.4	4.6			
C <sub>7</sub>	3.0	4.1	4.6	4.0	2.6			
C <sub>8</sub>	2.1	2.4	2.7	2.5	1.2			
$C_9$	-	-	0.3	0.3	1.0			
C <sub>12</sub>	-	-	-	0.4	0.7			
Arenes	2.6	9.7	26.4	43.3	62.3			
Cycloalkanes $C_{5^+}$	1.3	2.8	3.6	3.4	2.4			
Olefins $C_{5^+}$	3.0	2.9	3.6	0.8	0.3			

present those are distributed as  $C_3 < C_7 < C_4 \approx C_6$   $< C_5$  for the catalyzates obtained at different process temperature values. With increasing the reaction temperature, the yield of normal alkanes is significantly reduced resulting from the intensive conversion of *n*-octane. So, at 360 °C, the total content of *n*-alkanes amounts to 19.2 %, wherein 10.7 % fall at *n*-octane, *i. e.* at this temperature the level of *n*-octane conversion amounts up to 89.3 % (see Fig. 1, *a*).

With increasing the process temperature, the yield of isoalkanes has a maximum at 320 °C. At 280 °C,  $C_4-C_8$  isoalkanes are formed, at 320 °C the composition extends to  $C_9$ , whereas further increasing the temperature leads to the formation of branched-chain alkanes up to  $C_{12}$ . It should be noted that isoalkanes with the num-

ber of carbon atoms in the molecules equal to 10 and 11 were not detected in the liquid products obtained. The greatest number of isomeric structures, regardless of the temperature of the process, falls at the molecules containing six carbon atoms then in descending  $C_5$ ,  $C_7$ ,  $C_8$  and  $C_4$  are presented.

Increasing the temperature of the process results in an increase in the total yield of branched-chain hydrocarbons from 17.1 % at 280 °C to 24.1 % at 320 °C. Further, the concentration thereof is reduced to 23.1 and 15.8 %at 340 and 360 °C, respectively. The yield of individual isoalkanes almost in the same manner depends on the temperature of the process, as it is observed for the total yield: the maximum amount of  $C_4$ ,  $C_6$ ,  $C_7$  and  $C_8$  isoalkanes was obtained at a temperature of 320 °C, too, whereas only at 340 °C produced the greatest amount of  $C_5$  isoalkanes is formed. The higher the process temperature, the higher is the fraction of isostructural hydrocarbons with the number of carbon atoms equal to 9 and 12.

The process temperature significantly affects the formation of aromatic hydrocarbons. As the temperature increases from 280 to 360 °C, the concentration thereof in the liquid products increases from 2.6 to 62.3 %. The aromatic hydrocarbons are mainly presented by benzene, toluene, xylene and alkyl substituted benzenes.

In the course of *n*-octane conversion, a negligible amount of naphthenes and olefins, the yield of those has a maximum at the reaction temperature of 320 °C. At 280 °C, naphthenes with the number carbon atoms equal to 6 and 7 are formed, whereas the temperature increase results in the composition extending to  $C_{10}$  hydrocarbons. The olefins formed during the conversion of *n*-octane are presented by  $C_5$ – $C_8$  hydrocarbons.

On the original zeolite with different silicate module and on the samples modified with nickel there are products formed similar in composition. Depending on the temperature of the process there are the following patterns observed in changing the composition of *n*-octane transformation products at the reaction temperature values ranging within 280-320 °C, the main direction of *n*-octane transformation is presented by its isomerization, and alongside with the isomerization side reactions of cracking and disproportion ation occur. At the temperature values



Fig. 2. Selectivity level of isoalkane formation on zeolites with different silicate module (a) and on Ni-containing zeolites with M = 40 (b) depending on the process temperature.

of 280 and 300 °C the catalyzates obtained contain up to 70 % of *n*-octane, 20 % of isoalkanes and 10 % of aromatics; further there occurs increasing the fraction of aromatic hydrocarbons, whereas the isoalkane yield has a maximum at 300-320 °C. The maximum selectivity level of isoalkane formation is achieved at 300 °C on the zeolite with M = 40 amounts to 46.0 % (Fig. 2, *a*). With increasing the process temperature the influence of the M value upon the selectivity of isoalkane formation weakens, whereas at 360 °C it almost disappears.

The high-silica zeolite with the module equal to 40 demonstrated the greatest ability to isomerization in the course of n-octane conversion, were modified with nickel by means of different methods. The maximum selectivity of isoalkane formation is observed at the temperature of 280 °C (36.7 %) for the sample HSZ, containing 0.5 % of nickel NSP, whereas at 320 °C the maximum (37.5 %) is observed zeolite containing 1.0 % of nickel NSP (see Fig. 2, b). Zeolites with Ni NSP added somewhat inferior the original zeolite with module 40 in the selectivity of isoalkane formation, but in their presence the yield of liquid product is higher by 5-20 %.

Figure 3 demonstrates an effect of process temperature and feeding flow rate exerted on the level of *n*-octane conversion into isoalkanes and the selectivity of isoalkane formation in the presence of zeolite containing 0.5 % of nickel NSP. With increasing the feeding flow rate the level of conversion to *n*-octane decreases, since the contact time between the catalyst and raw material is reduced. At 280 °C the effect of feeding flow rate exerted on the level of *n*-octane conversion is most pronounced: at 1 h<sup>-1</sup> the level



Fig. 3. Level of *n*-octane conversion (*a*) and the selectivity of isoalkane formation (*b*) on the zeolite with M = 40, containing 0.5 % of nickel NSP, depending on the process temperature and feeding flow rate.

of *n*-octane conversion is equal to 69.8 %, whereas at 6  $h^{-1}$  this value amounts to only 18.5 %.

For all the values of feeding flow rate, increasing in the *n*-octane conversion level with increasing the reaction temperature is typical, except the feeding flow rate value equal to 1 h<sup>-</sup> <sup>1</sup> and the temperature values amounting to 280 and 300 °C. In this case, a higher level of noctane conversion at 280 °C could be caused, to all appearance, by a relatively long contact time of the feedstock with the active centers of the fresh catalyst and by growing the rate of its deactivation. This is indicated by a decrease of level of *n*-octane conversion at the temperature of 300 °C. With further increasing the process temperature, the influence of the contact time between the raw material and the catalyst and the influence of the catalyst acidity upon the conversion level exhibit weakening. At 360 °C the conversion level of *n*-octane is equal to 73 %only at a maximum feeding flow rate. For the other values of the flow rate, the mentioned value is almost the same (~97 %), i. e. the determining role in this case is played by the temperature of the process (see Fig. 3, a).

Unlike the conversion level, the selectivity of isoalkanes depending on feeding flow rate is much more complicated (see Fig. 3, b). Thus, at 280 °C for the flow rate of  $6 h^{-1}$  the selectivity of isoalkane formation is minimal (27.6 %), whereas at 360 °C the value is maximum (24.1 %). The highest selectivity with respect to isoalkanes is achieved at  $280 \ ^\circ C$  and  $2 \ h^{-1}$ (36.7 %), at 300 °C and 1 h<sup>-1</sup> (34.4 %). However, at the feeding flow rate of  $1 \text{ h}^{-1}$  increasing the reaction temperature results in decreasing the selectivity level of isoalkane formation due to the intensification of cracking and aromatization reactions. The least effect of the process temperature on the isoalkane formation selectivity is exerted at the feeding flow rate of noctane equal to  $4 h^{-1}$ , since the increase in the temperature of the process in this case "compensates" the increased load on the catalyst. The yield of gaseous products and aromatic hydrocarbons increases with decreasing the flow rate of *n*-octane. At the reaction temperature above 340 °C the selectivity of isoalkane formation is greatly reduced for all the values of the feeding flow rate of *n*-octane because of an abrupt increase in the level of conversion thereof.



Fig. 4. Level of *n*-octane conversion (*a*) and the selectivity level of isoalkane formation (*b*) depending on the process temperature on the zeolite with M = 40 modified with various metals.

High-silica zeolite having the silicate modulus M = 40 was subjected to the modification with the nanopowders of nickel, platinum and zirconium. Figure 4 demonstrates the level of *n*-octane conversion and the selectivity level with respect to forming the isoalkanes depending of the nature of the modifying metal. It can be seen that the minimum level of conversion is characteristic for zeolite containing 0.5 % of Pt NSP, whereas the maximum level is inherent in the nickel-containing zeolite (see Fig. 4, a). The highest selectivity with respect to the formation isostructured hydrocarbon within the temperature range of 280-300 °C is observed for the original zeolite, whereas at 320 °C and higher, the selectivity level is lower as compared to modified samples. The latter are characterized by a similar selectivity with respect to the formation of isoalkanes at the temperature values of 280-320 °C, whereas at T >320 °C the maximum selectivity of isoalkane

formation is demonstrated by Zr-containing zeolite (see Fig. 4, b).

#### CONCLUSIONS

With increasing the silicate modulus of highsilica zeolites and with modifying the zeolite by metals the strength and the concentration of acidic centers is reduced as the result of decreasing the number of aluminum atoms in the crystal lattice and their partial shielding.

The greatest activity in the isomerization of n-octane is demonstrated by the zeolites with silicate module values equal to 20 and 40; those are characterized by a maximum acidity level. An increase in the process temperature from 280 to 320 °C leads to an increase in the total yield of hydrocarbons with branched chain, whereas with the further increase in temperature, their concentration is reduced due to the intensification of cracking and aromatization reactions. The maximal amount of  $C_4$ ,  $C_6$ ,  $C_7$ , and C<sub>8</sub> isoalkanes is formed at the temperature of 320 °C, whereas the maximum yield of  $C_5$ isoalkanes is observed to form at 340 °C. With increasing the temperature, the fraction of isostructured hydrocarbons with the carbon atoms number of 9 and 12 in the catalyzate increases insignificantly.

For the modified samples, the selectivity level of forming the isoalkanes at the temperature values of 280–320 °C is less than that for the original zeolite. At higher temperature values the selectivity increases due to the enhancing the role of the metal active centers of metal-containing zeolites which exhibit the dehydrating and hydrogenating functions. The highest selectivity level with respect to isoalkanes is observed for the samples with adding the nanosized metal powders. To all appearance, this could be due to a more uniform distribution of fine-dispersed modifier metal particles on the surface of the zeolite.

The optimum process conditions for the isomerization of *n*-octane on zeolite-containing catalysts have been determined to be the following: the reaction temperature 300-340 °C, the feeding flow rate 2 h<sup>-1</sup>.

The data obtained could be used to refine the mechanism of the isomerization of normal alkanes contained in the virgin gasoline fractions, in the presence of zeolite catalysts.

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