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# Effect of Mechanical Treatment on Acidic and Catalytic Properties of Nickel-Containing Zeolite

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## Abstract

The mechanical treatment of zeolites in mills of various types is a promising modification method not requiring complex instrumentation and not yielding harmful waste water. In addition, dry mixing is the only method that allows introducing nanoscale metal powders into the zeolite structure without changing their properties. The proposed work prepared nickel-containing zeolite samples by the dry mechanical mixing of ZSM-5 zeolite with silicate modulus 40 and nickel powder with an average particle size of 50 nm per 0.5 mass %. They were exposed to mechanical treatment in a vibratory ball mill for 24–120 h. In order to retain properties of Ni nanopowder and avoid nickel oxidation, the resulting catalysts were not calcined. The degree of crystallinity of the initial zeolite and its mechanically treated modifications was determined by IR spectroscopy and X-ray structural analysis. Acidic properties of the catalysts were explored by ammonia thermoprogrammed desorption enabling to determine the distribution of acid sites according to strength, and also their number. Changing the catalytic activity and the selectivity of the initial zeolite and mechanically treated nickel-containing samples was explored in the model reaction of *n*-hexane transformation. As shown, the preliminary mechanical treatment of Ni/ZSM-5 reduces its crystallinity degree, and also acid sites strength and concentration. The variation of mechanical treatment time may directionally change the catalytic reaction pathway, as established. That allows an increase in the yield of the catalysate with improved environmental characteristics resulting from a decrease in the contents of *n*-alkanes, aromatic hydrocarbons, and alkenes, and also from a simultaneous increase in the fraction of iso- and cyclo-alkanes therein.

**Key words:** zeolite, ZSM-5, nanoscale nickel powder, mechanical treatment, crystallinity, acidity, conversion, activity, selectivity, isomerization, *n*-hexane

## INTRODUCTION

Mechanical treatment (MT) is an efficient method to modify zeolite-containing catalysts. It enables to change their physicochemical characteristics, reduce the activation energy of chemical reactions, and improve steric conditions for processes [1 and 2]. It has been earlier demonstrated that the preliminary mechanical activation of non-modified zeolite of the pentaxyl type [3], and also the preparation of metal-zeolite catalysts [4–10] derived therefrom by dry mechanical mixing with nanoscale powders (NSP) allow an increase in the yield of liquid products during the

transformation of straight-run gasoline fractions. The resulting catalysates have the required octane number and improved environmental characteristics, mainly due to a decreased number of the contents of aromatic hydrocarbons with carcinogenic properties therein. Hence, research on the combined effect of the addition of metal particles as NSP to zeolites and the impact of MT on their structure and catalytic activity upon hydrocarbon raw materials processing is of apparent scientific interest.

The purpose of this research was to explore acidic and catalytic properties of Ni/ZSM-5 derived by dry mechanical mixing pentaxyl zeolite

with nanoscale nickel powder exposed to subsequent mechanical treatment in the model reaction of *n*-hexane isomerisation.

## EXPERIMENTAL

The modification of the pentasil-type zeolite with a silicate modulus ( $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio) of 40 was carried out by the dry mechanical mixing of nickel NSP and zeolite in the KM-1 vibration ball mill for 2 h. Nickel nanopowder with an average particle size of 50 nm was obtained by the gas-phase method. The nickel content in zeolite was 0.5 mass %. The resulting nickel-containing sample to prevent NSP oxidation was not calcined.

The initial Ni/ZCM-5 catalyst was exposed to MT in the KM-1 vibration ball mill for 24, 48, 72, 96, and 120 h. In order to carry out tests, the resulting samples were pressed into tablets that were later ground. The 0.5–1.0 mm fraction was collected using sieves.

The crystallinity degree of the initial zeolite and mechanically treated nickel-containing samples were determined through IR spectroscopy and X-ray structural analysis. The IR spectra of zeolites were recorded using an FT-IR spectrometer with a Raman TermoElectron Nicolet 5700 modulus (USA) in the 2000–400  $\text{cm}^{-1}$  region; the FT-IR spectrometer was provided by Tomsk Regional Collective Use Center of the Tomsk scientific centre SB RAS (Tomsk Collective Use Centre SB RAS). X-ray structural analysis was performed using the D8 DISCOVER X-ray diffractometer from Bruker in the angle range  $2\theta = 10\text{--}70$  deg.

Acidic properties of the catalysts were explored by thermoprogrammed desorption (TPD) of ammonia enabling to determine acid site distribution according to strength, and also their number. The chromatographic variant of programmed thermal desorption consists in the fact that a sample with pre-adsorbed substance-probe (ammonia) molecules is exposed to heating at a linear rate of 10 deg/min under helium. The concentration of acid sites corresponds to the quantity of desorbed ammonia, whereas their strength – to temperature maxima in the desorption curve [11].

Zeolite catalysts were tested in the model reaction of *n*-hexane conversion widely used to determine their catalytic properties. The resulting relationships may be used to predict the progression of secondary processes of oil refining (isomerization, reforming, catalytic cracking, etc.) [12, 13]. In order to assess the catalytic activity of the

samples, the conversion degree of *n*-hexane, and the yields of gaseous and liquid reaction products were determined, and also the formation selectivity of isoalkanes was computed. The testing of catalysts was performed using a flow-through setup in the 280–360 °C range, at a volumetric feed rate of *n*-hexane of 2  $\text{h}^{-1}$  and atmospheric pressure. The volume of the catalyst loaded into the reactor was 5  $\text{cm}^3$ .

The sampling of liquid and gas reaction products was made after 1 h of catalyst operation at each temperature of the process. The composition of transformation products of the initial raw materials was analysed by GLC using a chromatograph CHROMATEK-CRYSTAL 5000.2. In order to determine liquid phase compositions, a BP-1 PONA capillary column (100 m  $\times$  0.25 mm  $\times$  0.5  $\mu\text{m}$ ), was used. On the contrary capillary GS-Gas-Pro (60 m  $\times$  0.32 mm) and packed Carbosieve S-II (4 m  $\times$  2 mm, 60/80 mesh) columns were employed for the gas phase.

## RESULTS AND DISCUSSION

Apart from the molecular sieve effect caused by pentasil structure peculiarities, the catalytic activity and the selectivity of zeolites are due to the presence of acid sites of various natures on their surface. Table 1 lists the crystallinity degree and acidic properties of the initial Ni/ZSM-5 and its mechanically treated modifications.

The crystallinity degree for the initial Ni/ZSM-5 is about 88 %; the MT of the zeolite during 24 and 48 h almost does not have an effect on this value, which attests to the strength of the crystal structure of a pentasil-type zeolite. When MT time is increased, the zeolite crystallinity is gradually reduced being equal to 78 % after 120 h.

Figure 1 demonstrates ammonia thermal desorption spectra for the initial Ni/ZSM-5 catalyst and Ni-containing samples after MT for 48 and 120 h.

All investigated samples are characterised by two types of ammonia desorption, such as the desorption range between 100 and 300 °C, and also a high-temperature one, between 300 and 600 °C. The mechanical treatment of zeolite for the first 48 h changes the strength of acid sites insignificantly, as evidenced by temperature maxima in thermal desorption curves, and the concentration of acid sites of both types that is calculated according to the surface areas under the curves. When treatment time is increased, temperature

TABLE 1

Degree of crystallinity and acid characteristics of zeolite catalysts

Catalysts	$\alpha$ , %	$T_{\max}$ of modification, °C		Acid sites concentration, $\mu\text{mol/g}$		
		$T_{\text{I}}$	$T_{\text{II}}$	$C_{\text{I}}$	$C_{\text{II}}$	$C_{\Sigma}$
Ni/ZSM-5	88	230	435	1058	391	1449
Ni/ZSM-5 (24 h MT)	87	230	435	1020	364	1384
Ni/ZSM-5 (48 h MT)	86	225	430	955	350	1305
Ni/ZSM-5 (72 h MT)	81	220	425	827	347	1174
Ni/ZSM-5 (96 h MT)	80	220	420	797	332	1129
Ni/ZSM-5 (120 h MT)	78	215	415	738	318	1056

Note.  $\alpha$ ,  $T_{\text{I}}$ ,  $T_{\text{II}}$ ,  $C_{\text{I}}$ ,  $C_{\text{II}}$ , and  $C_{\Sigma}$  are crystallinity degree, temperatures of low- and high-temperature peak maxima in thermal desorption curves, concentrations of weak and strong acid sites, and also their total amount, respectively.

peaks maxima are shifted to the low-temperature region and their intensity is decreased.

The issue regarding the nature of acid sites in zeolites has not been finally solved to date, however, there is the prevailing theory premised on the suggestion that acid sites with the desorption temperature of ammonia under 300 °C are referred to Lewis acid sites and above this point – to Bronsted ones. In most cases, Lewis acid sites are not completely coordinated aluminium atoms of the zeolite crystal lattice or transition metal cations introduced upon modification, whereas Bronsted acid sites are proton donating OH groups bound to lattice aluminium. When mechanical treatment time of Ni/ZSM-5 is higher than 48 h, its acidity is significantly reduced, as may be seen from a shift in maxima of thermal desorption peaks to the lower temperature region and a significant decrease in the concentration of weak and strong acid sites (see Fig. 1 and Table 1). The observed changes may be explained by first-

ly, a reduction in the number of active catalyst sites located in its volume resulting from the destruction of the zeolite crystal structure and secondly, by the formation of new active centres that are linked to the metal component and are inferior to zeolite acid sites according to strength, and thirdly, by steric hindrances of the accessibility of active sites due to blocking Ni by nanoparticles. The acquired data testify the effect of mechanical treatment time on the acidity of the nickel-containing zeolite. Acid sites strength of the mechanically treated zeolite is not changed for 24 h in case, whereas their number is slightly varied. The continuation of zeolite MT results in a more significant decrease in its acid properties.

Thus, the initial Ni/ZSM-5 catalyst has the highest strength and acid sites concentration. When catalyst MT is performed, their strength and number are substantially reduced; moreover, the longer MT is, the more intense is a decrease in acidity. Strong acid sites facilitate cracking and

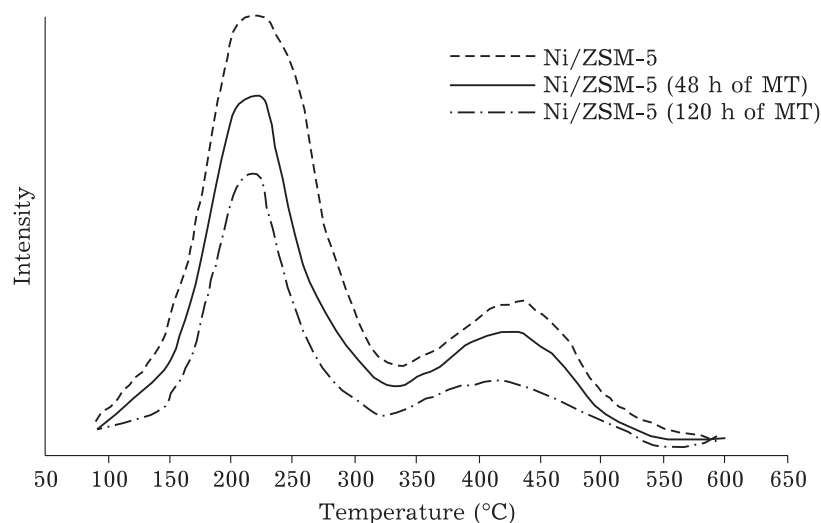


Fig. 1. Thermal desorption spectra of ammonia for nickel-containing zeolites.

TABLE 2

Effect of process temperature on the composition of gaseous products of *n*-hexane transformation over zeolite catalysts

Products, %	Process temperature, °C				
	280	300	320	340	360
<i>Ni/ZSM-5</i>					
C <sub>1</sub> -C <sub>5</sub> <i>n</i> -alkanes	75.1	76.9	78.7	80.5	80.1
C <sub>4</sub> -C <sub>5</sub> isoalkanes	24.2	22.4	20.6	18.7	19.0
C <sub>2</sub> -C <sub>4</sub> alkenes	0.7	0.7	0.7	0.8	0.9
<i>Ni/ZSM-5 (24 h MT)</i>					
C <sub>1</sub> -C <sub>5</sub> <i>n</i> -alkanes	67.0	68.2	71.1	76.0	80.0
C <sub>4</sub> -C <sub>5</sub> isoalkanes	32.4	30.5	28.2	23.2	19.1
C <sub>2</sub> -C <sub>4</sub> alkenes	0.6	0.5	0.7	0.8	0.9
<i>Ni/ZSM-5 (48 h MT)</i>					
C <sub>1</sub> -C <sub>5</sub> <i>n</i> -alkanes	65.7	66.6	70.2	74.5	79.9
C <sub>4</sub> -C <sub>5</sub> isoalkanes	33.8	32.9	29.1	24.8	19.2
C <sub>2</sub> -C <sub>4</sub> alkenes	0.5	0.5	0.7	0.7	0.9
<i>Ni/ZSM-5 (72 h MT)</i>					
C <sub>1</sub> -C <sub>5</sub> <i>n</i> -alkanes	63.7	65.5	68.4	73.6	78.5
C <sub>4</sub> -C <sub>5</sub> isoalkanes	35.9	34.0	30.9	25.6	20.6
C <sub>2</sub> -C <sub>4</sub> alkenes	0.4	0.5	0.7	0.8	0.9
<i>Ni/ZSM-5 (96 h MT)</i>					
C <sub>1</sub> -C <sub>5</sub> <i>n</i> -alkanes	61.9	63.8	67.7	73.2	78.4
C <sub>4</sub> -C <sub>5</sub> isoalkanes	37.7	35.7	31.5	26.0	20.7
C <sub>2</sub> -C <sub>4</sub> alkenes	0.4	0.5	0.8	0.8	0.9
<i>Ni/ZSM-5 (120 h MT)</i>					
C <sub>1</sub> -C <sub>5</sub> <i>n</i> -alkanes:	60.6	62.7	67.4	71.6	78.0
methane	0.1	0.1	0.2	0.2	0.3
ethane	0.3	0.4	0.5	0.8	1.3
propane	38.3	39.5	41.8	43.9	48.0
<i>n</i> -butane	17.6	18.3	20.1	21.5	22.9
<i>n</i> -pentane	4.3	4.4	4.8	5.2	5.5
C <sub>4</sub> -C <sub>5</sub> isoalkanes:	39.0	36.8	31.7	27.3	20.8
isobutane	33.4	31.6	27.7	23.4	18.3
isopentanes	5.6	5.2	4.0	3.9	2.5
C <sub>2</sub> -C <sub>4</sub> alkenes:	0.3	0.4	0.7	0.9	1.0
ethylene	0.1	0.1	0.2	0.2	0.3
propylene	0.1	0.2	0.3	0.4	0.4
butenes	0.1	0.1	0.2	0.3	0.3
Hydrogen	0.1	0.1	0.2	0.2	0.2

hydrocarbon aromatization reactions. Their strength and concentration are reduced after zeolite MT, which is likely to have an effect on the catalytic activity and selectivity of the zeolite catalyst upon hydrocarbon transformation.

Table 2 reports the group composition of gaseous products of *n*-hexane transformation that are formed over the initial Ni/ZSM-5 and mechanically treated samples for various times depending on process temperature. The detailed composition of hydrocarbon gases is given for Ni/ZSM-5 catalyst exposed to MT for 120 h.

During the conversion of *n*-hexane on the initial Ni/ZSM-5, the resulting gas products contain most of all *n*-alkanes, among which propane is prevailing. Isobutane and isopentanes are pre-

sent as a part of isoalkanes; alkenes are presented by ethylene, propylene, and butenes. When process temperature is increased, the yields of *n*-alkanes and alkenes are enhanced, whereas the concentration of isoalkanes is reduced. As a whole, the determined relationships of the effect of process temperature on the composition of gaseous products of *n*-hexane transformation over the initial Ni/ZSM-5 are mainly preserved for mechanically treated samples. Herewith, catalyst mechanical treatment facilitates the progression of the reaction under softer conditions: the rate of cracking reactions is decreased, resulting from which less *n*-alkanes are contained in the gaseous products and the yields of isohydrocarbons are increased. Thus, the resulting

TABLE 3

Effect of process temperature on liquid products composition and yield, and also on *n*-hexane conversion and formation selectivity of isoalkanes over zeolite catalysts

Products, %	Process temperature, °C				
	280	300	320	340	360
<i>Ni/ZSM-5</i>					
C <sub>3</sub> -C <sub>13</sub> <i>n</i> -alkanes	80.8	78.4	66.7	59.7	53.8
C <sub>4</sub> -C <sub>13</sub> isoalkanes	12.6	12.5	13.0	14.7	17.1
C <sub>6</sub> -C <sub>12</sub> arenes	4.8	7.0	17.8	22.5	25.0
C <sub>5</sub> -C <sub>10</sub> cycloalkanes	1.3	1.5	1.8	2.4	3.1
C <sub>4</sub> -C <sub>10</sub> alkenes	0.5	0.6	0.7	0.7	1.0
Conversion, %	30	40	55	64	70
Catalysate yield, %	95	77	50	43	38
Selectivity, %	42	31	24	24	24
<i>Ni/ZSM-5 (24 h MT)</i>					
C <sub>3</sub> -C <sub>13</sub> <i>n</i> -alkanes	81.3	79.8	67.0	60.9	54.3
C <sub>4</sub> -C <sub>13</sub> isoalkanes	13.1	13.3	13.5	14.4	18.1
C <sub>6</sub> -C <sub>12</sub> arenes	3.8	4.9	16.8	21.4	22.9
C <sub>5</sub> -C <sub>10</sub> cycloalkanes	1.3	1.3	1.9	2.5	3.8
C <sub>4</sub> -C <sub>10</sub> alkenes	0.5	0.7	0.8	0.8	0.9
<i>Ni/ZSM-5 (48 h MT)</i>					
C <sub>3</sub> -C <sub>13</sub> <i>n</i> -alkanes	80.7	78.7	68.8	60.1	56.4
C <sub>4</sub> -C <sub>13</sub> isoalkanes	14.3	14.5	15.7	19.0	19.1
C <sub>6</sub> -C <sub>12</sub> arenes	3.2	4.8	13.3	17.8	19.9
C <sub>5</sub> -C <sub>10</sub> cycloalkanes	1.1	1.2	1.3	2.2	3.7
C <sub>4</sub> -C <sub>10</sub> alkenes	0.7	0.8	0.9	0.9	0.9
Conversion, %	25	34	47	58	65
Catalysate yield, %	96	82	59	49	44
Selectivity, %	57	43	34	33	30
<i>Ni/ZSM-5 (72 h MT)</i>					
C <sub>3</sub> -C <sub>13</sub> <i>n</i> -alkanes	80.3	79.2	68.0	63.0	56.3
C <sub>4</sub> -C <sub>13</sub> isoalkanes	15.0	15.6	15.9	19.1	20.1
C <sub>6</sub> -C <sub>12</sub> arenes	3.0	3.1	13.9	15.0	18.9
C <sub>5</sub> -C <sub>10</sub> cycloalkanes	1.1	1.3	1.3	2.1	3.8
C <sub>4</sub> -C <sub>10</sub> alkenes	0.6	0.8	0.9	0.8	0.9
<i>Ni/ZSM-5 (96 h MT)</i>					
C <sub>3</sub> -C <sub>13</sub> <i>n</i> -alkanes	80.5	79.6	68.1	64.0	57.2
C <sub>4</sub> -C <sub>13</sub> isoalkanes	15.8	16.3	16.4	19.2	21.0
C <sub>6</sub> -C <sub>12</sub> arenes	2.0	2.3	13.3	14.2	17.0
C <sub>5</sub> -C <sub>10</sub> cycloalkanes	1.1	1.3	1.6	2.0	3.9
C <sub>4</sub> -C <sub>10</sub> alkenes	0.6	0.5	0.6	0.6	0.9
<i>Ni/ZSM-5 (120 h MT)</i>					
C <sub>3</sub> -C <sub>13</sub> <i>n</i> -alkanes	81.0	79.3	71.5	65.3	58.6
C <sub>4</sub> -C <sub>13</sub> isoalkanes	15.5	16.2	19.0	19.3	21.7
C <sub>6</sub> -C <sub>12</sub> arenes	1.8	2.2	6.5	12.3	15.3
C <sub>5</sub> -C <sub>10</sub> cycloalkanes	1.1	1.6	2.1	2.2	3.5
C <sub>4</sub> -C <sub>10</sub> alkenes	0.6	0.7	0.9	0.9	0.9
Conversion, %	20	25	40	51	58
Catalysate yield, %	98	86	68	60	56
Selectivity, %	78	65	48	38	37

gaseous hydrocarbons are mainly comprised of the propane-butane mixture. As demonstrated in [14], it may be processed into valuable chemicals. Herewith, zeolite-containing catalysts are used, including the procedure when they are added to the reaction mixture that contains liquid hydrocarbon raw materials.

Table 3 reports the group composition of liquid transformation products of *n*-hexane over the catalysts under examination.

Along with that, the effect of process temperature on their yields, *n*-hexane conversion, and formation selectivity of isoalkanes has been demonstrated. The resulting catalysates contain

representatives of all groups of hydrocarbons. Moreover, process temperature substantially affects the concentrations of the latter. When it is increased, the concentration of *n*-alkenes is decreased in the catalysates derived over the initial Ni/ZSM-5 and the samples exposed to MT. That takes place mainly due to a decrease in the content of the unreacted *n*-hexane and an increase in the concentration of aromatic hydrocarbons and cycloalkanes in minor quantities. Liquid products contain alkenes in small amounts; changing process temperature does not have a significant effect on the concentration of these species. When process temperature is increased, the yields of isoalkanes are decreased, as low process temperatures facilitate an increase in the rate of isomerization reactions. High hydrocarbon content at reduced arene concentration is likely to facilitate high environmental characteristics of the resulting gasolines when actual hydrocarbon raw materials, such as straight-run oil fractions, are processed. Low olefin concentration (about 1 %) would have a positive effect on the stability of the resulting liquid product.

The molecular mass distribution of hydrocarbons formed at reaction temperature of 340 °C for Ni/ZSM-5 catalyst after 120 h of MT looks as follows:

$C_3$ - $C_{13}$  *n*-alkanes:  $C_6 > C_5 > C_4 > C_7 > C_3 > C_8 > C_9 > C_{12} > C_{10} = C_{11} > C_{13}$  (the concentration of *n*-alkanes with a carbon atoms number of 6, 5, 4, and 7 is significant, and beginning with a quantity of carbon atoms of 3 in this series and hereinafter, according to a decrease, below 1 %);

$C_4$ - $C_{13}$  isoalkanes:  $C_6 > C_5 > C_4 > C_{10} > C_7 > C_8 > C_9 > C_{12} > C_{11} > C_{13}$  (isoalkane content, beginning with the carbon atoms number in the molecule of 8 and further in the presented series corresponds to a decrease in the yield of below 1 %);

aromatic hydrocarbons  $C_6$ - $C_{12}$ :  $C_8 > C_9 > C_7 > C_{10} > C_{11} > C_6 > C_{12}$  (the yield of some aromatic hydrocarbons with a a number of carbon atoms equal to 6, 11 and 12 is below 1 %);

$C_5$ - $C_{10}$  cycloalkanes:  $C_6 > C_7 > C_8 > C_9 > C_5 > C_{10}$  (the concentration of each cycloalkane with a carbon atoms number of 8, 9, 5 and 10 is below 1 %);

$C_4$ - $C_{10}$  alkenes:  $C_5 > C_4 > C_3 = C_7 > C_9 > C_8 > C_{10}$  (the total olefin concentration is not higher than 1 %).

Thus, transformation products of *n*-hexane are mainly presented by  $C_4$ - $C_7$  alkanes,  $C_4$ - $C_7$  and  $C_{10}$  isoalkanes,  $C_7$ - $C_{10}$  arenes, and  $C_6$ - $C_7$  cycloalkanes.

The given distribution of the products clearly displays the molecular sieve effect of zeolites of the pentasil family. The latter are characterised

by a low pore diameter limiting the formation of relatively large hydrocarbon species. Low unsaturated hydrocarbon content is a consequence of the progression of reactions that involve active metal sites of the hydrogenation reaction of the resulting hydrocarbon moieties.

Mechanical treatment time and process temperature do not have a significant effect on changing the presented molecular mass distribution within one group but facilitate a significant reduction in a ratio among different hydrocarbon groups. It can be noted that there are no such a significant reduction in the formation of isoalkanes and an increase in the yield of aromatic hydrocarbons in the mechanically treated samples compared to the initial catalyst.

The observable relationships are in a good agreement with structural changes and zeolite acidity under mechanical treatment. For example, the highest *n*-hexane conversion value is typical for the initial Ni/ZSM-5 catalyst that has the highest number of acid sites. The mechanical treatment of the nickel-containing zeolite facilitates a significant increase in the catalysate yield and isoalkane formation selectivity.

## CONCLUSION

The preliminary mechanical treatment of Ni/ZSM-5 zeolite as modification method results in the changed crystal structure, and also in decreased crystallinity degree and acidity of these species. The number of acid sites of the zeolite located in its volume is reduced and weaker acid sites linked to nickel metal are generated. A decrease in the number of strong acid sites that facilitate hydrocarbon cracking and aromatization reactions reduces the aromatising component and increases the isomerizing activity of the catalyst upon *n*-hexane conversion, and also results in the enhanced yield of the liquid product with improved environmental characteristics.

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