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Effect of Alkaline Treatment on Physicochemical and Catalytic Properties of ZSM-5 Zeolite During Conversion of Straight-Run Gasoline Oil Fraction

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Abstract. Postsynthetic treatment of a ZSM-5 type zeolite with aqueous solutions of NaOH of various concentrations is carried out. Structural, acidic, and catalytic properties of the initial zeolite and treated samples are investigated in the course of conversion of straight-run gasoline fraction of oil. The main operational characteristics of the obtained high-octane gasolines are determined. The dynamics of deactivation of the initial ZSM-5 zeolite and the sample subjected to alkaline treatment is reported and the structure of coke deposits is studied. It is found out that alkaline treatment of zeolites leads to a decrease in their crystallinity, specific surface area and specific mesopore volume, while the average pore diameter increases. Also a decrease in the concentration of acid sites with an increase in their strength is observed. As a result of changes in the properties of zeolites, the performance and stability of the catalysts obtained on their basis increase, which contributes to the improvement of the quality of gasoline formed over these catalysts during the conversion of straight-run gasoline fraction of oil.

Keywords: ZSM-5 zeolite, gasoline, alkaline treatment, structure, acidity, activity, stability, catalyst performance, coke.

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Влияние щелочной обработки на физико-химические и каталитические свойства цеолита типа ZSM-5 в процессе превращения прямогонной бензиновой фракции нефти

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Аннотация. Проведена постсинтетическая обработка цеолита типа ZSM-5 водными растворами NaOH различной концентрации. Исследованы структурные, кислотные и каталитические свойства исходного цеолита и обработанных образцов в процессе превращения прямогонной бензиновой фракции нефти. Определены основные эксплуатационные характеристики полученных высокооктановых бензинов. Приведена динамика дезактивации исходного цеолита ZSM-5 и образца, подвергнутого щелочной обработке, изучена структура коксовых отложений. Установлено, что щелочная обработка цеолитов приводит к снижению их кристалличности, величины удельной поверхности и удельного объема мезопор, увеличению среднего диаметра пор, уменьшению концентрации кислотных центров и увеличению их силы. В результате происходящих изменений свойств цеолитов повышается производительность и стабильность работы катализаторов, полученных на их основе, а также улучшается качество бензинов, образующихся на них в процессе превращения прямогонной бензиновой фракции нефти.

Ключевые слова: цеолит ZSM-5, бензин, щелочная обработка, структура, кислотность, активность, стабильность, производительность катализатора, кокс.

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Авторы заявляют, что у них нет известных конкурирующих финансовых интересов или личных отношений, которые могли бы повлиять на работу, описанную в этой статье.

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Introduction

One of the possible ways to improve the catalytic properties of artificial zeolites of the ZSM-5 type is their post-synthetic modification with alkalis, which makes it possible to change both the strength and number of acid sites and the porous structure [1–8]. The impact of alkali on the zeolite at a certain temperature promotes the formation of pores of a larger diameter, which increases the accessibility of zeolite active sites located inside its volume. The treatment of the initial ZSM-5 zeolite with alkali leads to the interaction of structurally bound silicon oxide in its crystal lattice with an alkali solution and to the subsequent removal of part of silicon from the zeolite lattice and its transition to the solution [1, 2]. It is possible to remove silicon atoms from the zeolite framework at the optimum $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio, which for ZSM-5 zeolite lies within the range of 25–50 [3]. The intensity of silicon removal from the zeolite framework depends on the type and concentration of alkali used for its treatment and on the temperature and duration of treatment. The main factor determining the degree of zeolite destruction during alkaline treatment is the concentration of the alkali solution [6, 7]. The treatment of zeolite with sodium hydroxide makes it possible to significantly increase the surface area of the zeolite and create pores of larger diameter [5].

Despite the fact that ZSM-5 zeolites are successfully used to obtain high-octane gasolines from straight-run gasoline fractions of oils and gas condensates [9–14], no literature data are available on the potential use of zeolites that have undergone preliminary alkaline treatment in this process.

The purpose of this work was to study the effect of the concentration of an aqueous solution of sodium hydroxide during the treatment of ZSM-5 type zeolite on its physicochemical and catalytic properties in the course of obtaining high-octane gasoline from straight-run gasoline oil fraction.

Materials and Methods

Preparation of zeolite catalysts

A ZSM-5 type zeolite with a silicate modulus of 40 (the silicate modulus of the zeolite is characterized by the $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio) was obtained by hydrothermal synthesis from alkali aluminosilica gels using hexamethylenediamine as a structure-forming additive [14]. The resulted zeolite powder was treated with 0.1, 0.3, and 0.5 M NaOH solutions with vigorous stirring in a water bath at 90 °C for 2 h. After treatment, the zeolite was filtered off and washed with distilled water until neutral pH was obtained, then it was dried for 5 h at 100 °C and calcined at 550 °C for 4 h. Powdered samples were pressed into tablets and crushed, then the 0.5–1.0 mm fraction was withdrawn for catalytic testing.

Determination of structural characteristics of catalysts

The phase composition and crystallinity of the initial zeolite and samples subjected to alkaline treatment were determined by IR spectroscopy [15] and X-ray phase analysis [16]. The IR spectra of

zeolites were obtained using a Nicolet 5700 IR Fourier spectrometer (Thermo Electron Corp., USA) in the range 2000–400 cm^{-1} in air. The FTIR spectrometer was provided by the Tomsk Regional Center for Collective Use of the Tomsk Scientific Center of the Siberian Branch of the Russian Academy of Sciences (Tom CCU TSC RAS). The phase composition of the catalysts was studied by X-ray diffractometry using a D 8 DISCOVER diffractometer (Bruker, Germany).

The specific surface area of the catalysts was determined by the Brunauer-Emmett-Teller (BET) method from low-temperature ($-196\text{ }^{\circ}\text{C}$) nitrogen adsorption data obtained using an automatic gas adsorption analyzer Sorbtometer M (ZAO 'KATAKON', Russia).

Determination of acidic properties of zeolite catalysts

The acidic properties of the catalysts were studied by the method of temperature-programmed desorption (TPD) of ammonia, which makes it possible to determine the number of acid sites and their distribution by strength. The technique for performing thermal desorption measurements was proposed by [17].

Determination of the catalytic activity of zeolite catalysts

The catalytic activity of the initial zeolite and alkali-treated samples was determined in a flow unit with a fixed catalyst bed in the course of upgrading the straight-run gasoline fraction of oil. The volume of the catalyst loaded into the reactor was 4 cm^3 . The process was carried out at atmospheric pressure, a temperature of 340–400 $^{\circ}\text{C}$ with a step of 20 $^{\circ}\text{C}$, and a feedstock feed space velocity of 2 h^{-1} . To determine the activity of zeolite catalysts at different process temperatures, samples of the formed products were taken for analysis after 1 h of their operation.

Chromatographic analysis of feedstock and reaction products

Analysis of the feed composition and its conversion products was carried out by gas-liquid chromatography (GLC) using a Khromatek-Kristall 5000.2 chromatograph (GK 'New Technologies', Russia). To determine the composition of the liquid phase, a BP-1 PONA capillary column (100 m x 0.25 mm x 0.5 μm) was used, while the gas phase was determined using a capillary GS-Gas-Pro column (60 m x 0.32 mm) and packed Carbosieve S-II column (4m x 2 mm). The hydrocarbon composition was calculated by the method of internal normalization, the octane numbers of the feedstock and the resulted gasolines were determined by the calculation method based on chromatographic data according to the procedure described by [18].

Determination of catalyst deactivation dynamics and coke characteristics

The dynamics of deactivation of the initial ZSM-5 zeolite and alkali-treated sample was determined in a fixed-bed flow reactor at atmospheric pressure, a temperature of 380 $^{\circ}\text{C}$, and a weight space velocity of 2 h^{-1} for 30 h of continuous catalyst operation. Samples of the resulted reaction products were taken for analysis after 1, 15, and 30 hours of catalyst operation.

The *properties* of coke deposits formed on the surface of the catalysts under study during the conversion of the straight-run gasoline fraction of oil were determined by the method of differential thermal analysis using a Q-1500 D derivatograph of the Paulik–Paulik–Erdey system (MOM, Hungary).

Results and Discussions

Effect of alkali treatment on the structural properties of zeolite catalysts

Table 1 shows the crystallinity and structural characteristics of the initial ZSM-5 zeolite and alkali treated ZSM-5 based samples. The post-synthetic alkaline treatment of zeolite leads to a decrease in its specific surface area and specific pore volume due to a decrease in the mesopore volume and an increase in the average pore diameter. The observed changes are due to partial destruction of the zeolite crystal lattice under the action of alkaline solutions and to the removal of silicon and aluminum cations from zeolite framework. An increase in the pore diameter of zeolite will probably improve the accessibility of its active sites for the molecules of feedstock and favor a decrease in the rate of its deactivation by carbon condensation products.

Table 1. Structural characteristics of zeolite catalysts.

Catalyst	α , %	S_{BET} , m ² /g	S_{meso} , m ² /g	S_{micro} , m ² /g	V_{tot} , cm ³ /g	V_{meso} , cm ³ /g	V_{micro} , cm ³ /g	D , nm
ZSM-5	96	339	198	141	0.17	0.09	0.08	1.99
ZSM-5 treated with 0.1 M NaOH	94	328	157	171	0.14	0.07	0.07	1.99
ZSM-5 treated with 0.3 M NaOH	86	325	155	170	0.14	0.07	0.07	2.02
ZSM-5 treated with 0.5 M NaOH	84	273	117	156	0.14	0.06	0.08	2.03

Note. α is the crystallinity of the zeolite; S_{BET} is the specific surface area of the zeolite, measured by the BET method; S_{meso} , S_{micro} – specific surface of meso- and micropores; V_{tot} is the total specific pore volume; V_{meso} , V_{micro} – specific volume of meso- and micropores; D is the average pore diameter.

Effect of alkaline treatment on the acidic properties of zeolite catalysts

Along with the structural characteristics responsible for the molecular sieve effect of zeolite catalysts, another important property of zeolites is their acidity [3]. Table 2 shows data on the changes in the acidic properties of ZSM-5 zeolite with the concentration of the alkali solution used for its treatment. Thermal desorption spectra of all samples show two peaks: the first is a low-temperature peak lying within the ammonia desorption region from 100 to 300 °C and the second one is a high-temperature peak lying within the ammonia desorption region from 300 to 600 °C. The strength of acid sites of both types is characterized by peak maxima. They increase with an increase in the

Table 2. Acidic characteristics of zeolite catalysts.

Catalyst	T_{max} peaks, °C		Concentration of acid sites, $\mu\text{mol/g}$		
	T_I	T_{II}	C_I	C_{II}	C_{Σ}
ZSM-5	175	360	618	318	936
ZSM-5 treated with 0.1 M NaOH	175	390	578	311	889
ZSM-5 treated with 0.3 M NaOH	185	405	531	308	839
ZSM-5 treated with 0.5 M NaOH	210	415	446	277	723

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

concentration of the alkaline solution used to treat ZSM-5 zeolite, while the number of acid sites, on the contrary, decreases.

Changes in the structural group composition, yield, and octane numbers of the obtained gasolines, as well as in the productivity of catalysts with the process temperature

The major components of the gaseous reaction products are normal C₁-C₅ alkanes, where propane is more than half. The post-synthetic alkaline treatment of the zeolite catalyst has practically no effect on the qualitative and quantitative composition of gaseous products. Only a slight increase in the concentration of isoalkanes and alkenes formed over the treated samples is observed compared to the initial zeolite.

Table 3 shows the group hydrocarbon composition of the feedstock and the obtained catalyzates, their yields, octane numbers, and the calculated productivity of the catalysts. The qualitative compositions of liquid products obtained over the initial zeolite and treated samples are similar. An increase in the process temperature leads to a decrease in the amount of all groups of hydrocarbons contained in the obtained catalyzates, with the exception of aromatic compounds. According to current requirements for motor gasolines, the concentration of aromatic hydrocarbons in them is strictly limited, so it should not exceed 35 % by volume, where benzene should not exceed 1 % by volume. The content of olefins is also limited, so they should not exceed 18 % by volume and the octane number by the research method should be at least 80 points [19]. The catalyzates obtained at 340–360 °C over the initial ZSM-5 zeolite and those obtained at 340–380 °C over the samples treated with an alkali solution meet these specifications. However, with an increase in the reaction temperature, a decrease in the yield of the catalyzate is observed. Its composition also changes

Table 3. Composition and yield of liquid products of the conversion of straight-run gasoline fraction of oil over zeolite catalysts and their productivity.

Catalyst	Process performance	Feedstock	Process temperature, °C			
			340	360	380	400
1	2	3	4	5	6	7
ZSM-5	C ₃ -C ₁₂ n-alkanes	40.1	13.5	10.5	9.8	8.2
	C ₄ -C ₁₀ isoalkanes	26.8	32.3	30.6	29.2	28.1
	C ₆ -C ₁₂ arenes	7.3	29.7	34.8	39.7	48.9
	C ₅ -C ₁₀ cycloalkanes	25.8	22.6	22.2	19.5	13.0
	Octane number	68	90	91	94	97
	Yield of catalyzate, %	–	80	78	70	65
	Productivity, octane-ton		7200	7098	6580	6305
ZSM-5 treated with 0.1 M NaOH	C ₃ -C ₁₂ n-alkanes		18.4	16.2	14.0	11.2
	C ₄ -C ₁₀ isoalkanes		32.8	31.9	31.1	30.1
	C ₆ -C ₁₂ arenes		25.5	29.3	33.0	42.6
	C ₅ -C ₁₀ cycloalkanes		21.4	20.8	20.3	14.6
	C ₄ -C ₁₀ alkenes		1.9	1.8	1.6	1.5
	Octane number		87	88	91	95
	Yield of catalyzate, %		84	81	72	66
	Productivity, octane-ton		7308	7128	6552	6270

Continuation of the Table 3

1	2	3	4	5	6	7
ZSM-5 treated with 0.3 M NaOH	C ₃ -C ₁₂ n-alkanes		18.9	18.2	13.5	13.1
	C ₄ -C ₁₀ isoalkanes		33.7	33.5	32.4	30.3
	C ₆ -C ₁₂ arenes		24.2	25.9	32.2	38.7
	C ₅ -C ₁₀ cycloalkanes		21.3	20.7	20.4	16.4
	C ₄ -C ₁₀ alkenes		1.9	1.7	1.5	1.5
	Octane number		86	87	90	93
	Yield of catalyzate, %		87	85	76	68
Productivity, octane-ton		7482	7395	6840	6324	
ZSM-5 treated with 0.5 M NaOH	C ₃ -C ₁₂ n-alkanes		19.2	18.6	16.9	14.6
	C ₄ -C ₁₀ isoalkanes		33.7	33.4	33.0	31.4
	C ₆ -C ₁₂ arenes		21.3	25.2	28.5	36.1
	C ₅ -C ₁₀ cycloalkanes		24.2	21.2	20.0	16.3
	C ₄ -C ₁₀ alkenes		1.6	1.6	1.6	1.6
	Octane number		84	86	88	93
	Yield of catalyzate, %		89	86	77	68
Productivity, octane-ton		7486	7396	6776	6324	

leading to an increase in the octane number. The gasolines obtained over the initial ZSM-5 zeolite have the highest octane ratings. After alkaline treatment of the zeolite, the concentration of acid sites decreases. As a result, the catalytic activity in cracking and aromatization reactions resulting in the formation of gaseous and aromatic hydrocarbons also decreases, while the yield of liquid products increases. The productivity of every alkali-treated catalyst exceeds the productivity of the initial ZSM-5 zeolite, while the characteristics of the catalysts obtained over the samples after treatment with 0.3 and 0.5 M NaOH solutions are similar.

*Changes in the fractional composition
of the obtained gasolines versus the process temperature*

The fractional composition of gasoline must meet the requirements of Standard Specifications for five temperature characteristics: beginning of distillation at initial boiling point, distillation of 10, 50, and 90 vol%, and final distillation at the end boiling point [19]. With an increase in the temperature of the conversion of straight-run gasoline fraction over zeolite catalysts, an extension of the fractional composition of the formed catalyzates is observed, i.e. the temperature of the distillation beginning decreases and the temperature of the end of boiling increases. The fractional composition of resulted gasolines correspond to that of summer fuel (except for the end point of boiling).

Structure of coke deposited on zeolite catalysts

Table 4 presents the results of the differential thermal analysis of the initial ZSM-5 zeolite sample and the sample treated with a 0.3 M alkali solution, which were operated during the conversion of the straight-run gasoline fraction of oil at 380 °C for 30 h. From the data presented in Table 4, we can conclude that the untreated zeolite contains significantly more water and highly condensed products compared to the alkali-treated sample. A large peak with a maximum at 200 °C is observed on the DTG curve for the alkali-treated sample. This peak means removal of water and a large amount of C₈₊

Table 4. Data of differential thermal analysis of zeolite-containing catalysts after 30 h of their operation in the course of conversion of straight-run gasoline fraction of oil.

Catalyst	Temperature of removal of water and various hydrocarbons			
	water	C ₈₊ hydrocarbons of kerosene and diesel fractions	polyaromatic hydrocarbons	highly condensed products
	up to 200 °C	200–340 °C	340–465 °C	465–670 °C
Mass change, %				
ZSM-5	2.86 % (DTA and TG endo-effect at 126 °C)	2.24 % (DTA endo-effect at 250 °C, DTA exo-effect at 310 °C*, DTG exo-effect at 250 °C)	0.64 % (exo-effect at 420 °C)	9.10 % (exo-effect at 566 °C, DTG at 573 °C)
ZSM-5 treated with 0.3 M NaOH	2.19 % (DTA and TG endo-effect at 126 °C)	3.94 % (DTA endo-effect at 200 °C, DTG at 200 °C)	0.98 % (exo-effect at 420 °C)	6.90 % (exo-effect at 565 °C, DTG at 573 °C)

Note. *The endothermic DTA effect at 250 °C and exothermic DTA effect at 310 °C are explained by the fact that C₈₊ hydrocarbons are removed from the catalyst surface at the temperature up to 290 °C. This process proceeds with heat absorption (endo-effect at 250 °C). Their further removal becomes exothermic (exo-effect at 310 °C) because of autoignition of hydrocarbons.

hydrocarbons of the kerosene and diesel fractions. The DTA curve shows no exo-effect in the region of 310 °C, but in contrast to the initial ZSM-5 zeolite, the exo-effect is clearly manifested at 422 °C, which can be explained by the burnout of higher molecular weight hydrocarbons [20]. For the initial zeolite ZSM-5, the total amount of products removed in the range from 340 to 670 °C was 9.74 %, where 9.10 % are highly condensed compounds. For the alkali-treated sample, these values were 7.88 and 6.90 %, respectively. Thus, alkaline pre-treatment of the zeolite leads to a decrease in the formation of highly condensed products, which allows easier regeneration of the coked catalyst.

Conclusion

Post-synthetic alkaline treatment of ZSM-5 zeolite reduces its crystallinity, specific surface area and specific mesopore volume, increases the pore diameter, reduces the concentration of acid sites and also increases their strength. Alkaline treatment of zeolites improves the structural-group and fractional composition of high-octane gasolines obtained over them. Alkaline-treated zeolite catalysts, compared to the initial ZSM-5 zeolite, exhibit higher performance and stability in the course of the straight-run gasoline oil fraction conversion.

CRedit authorship contribution statement

Ludmila Velichkina: Conceptualization, Methodology, Investigation, Data curation, Writing-Original draft preparation. Yakov Barbashin: Investigation. Alexander Vosmerikov: Validation.

References

1. Sadowska K., Góra-Marek K., Drozdek M., Kuśtrowski P., Datka J., Martinez-Triguero J., Rey F. Desilication of highly siliceous zeolite ZSM-5 with NaOH and NaOH/tetrabutylamine

hydroxide. *Microporous and Mesoporous Materials* 2013. 168, 195–205. <https://doi.org/10.1016/j.micromeso.2012.09.033>.

2. Ghavipour M., Behbahani R. M., Moradi G. R., Soleimanimehr A. Methanol dehydration over alkali-modified H-ZSM-5; effect of temperature and water dilution on products distribution. *Fuel* 2013. 113, 310–317. <http://dx.doi.org/10.1016/j.fuel.2013.05.089>.

3. Zhao L., Gao J., Xu C., Shen B. Alkali-treatment of ZSM-5 zeolites with different SiO₂/Al₂O₃ ratios and light olefin production by heavy oil cracking. *Fuel and Energy Abstracts* 2011. 92(3), 414–420. <https://doi.org/10.1016/j.fuproc.2010.10.003>.

4. Su L., Liu L., Zhuang J., Wang H. Creating mesopores in ZSM-5 zeolite by alkali treatment: a new way to enhance the catalytic performance of methane dehydroaromatization on Mo/HZSM-5 catalysts. *Catalysis Letters* 2003. 91(3–4), 155–167. <https://doi.org/10.1023/B:CATL.0000007149.48132.5a>.

5. Groen J.C., Moulijn J.A., Pérez-Ramírez J. Desilication: on the controlled generation of mesoporosity in MFI zeolites. *Journal of Materials Chemistry* 2006. 16, 2121–2131. <https://doi.org/10.1039/B517510K>.

6. Ivanova I.I., Kasyanov I.A., Maerle A.A., Zaikovskii V.I. Mechanistic study of zeolites recrystallization into micro-mesoporous materials. *Microporous Mesoporous Materials* 2014. 189, 163–172. <https://doi.org/10.1016/j.micromeso.2013.11.001>.

7. Bjoergen M., Joensen F., Holm M. S., Olsbye U., Lillerud K. P., Svelle S. Methanol to gasoline over zeolite H-ZSM-5: Improved catalyst performance by treatment with NaOH. *Applied Catalysis A: General* 2008. 345(1), 43–50. <https://doi.org/10.1016/j.apcata.2008.04.020>.

8. Shahid A., Lopez-Orozco S., Marthala V.R., Hartmann M., Schwieger W. Direct oxidation of benzene to phenol over hierarchical ZSM-5 zeolites prepared by sequential post synthesis modification. *Microporous Mesoporous Materials* 2017. 237, 151–159. <https://doi.org/10.1016/j.micromeso.2016.09.012>.

9. Stepanov V.G., Snytnikova G.P., Ione K. G. Influence of Heat/Steam Treatment of Pentasil Zeolite on Zeoforming Results for Mixture of C₆-C₈ Hydrocarbons. *Chemistry and Technology of Fuels and Oils* 1992. 28(3), 163–167. <https://doi.org/10.1007/BF00727006>.

10. Klimov O.V., Kikhtyanin O.V., Aksenov D.G., Kodenev E.G., Echevskii G.V., Garifzyanov G.G., Garifzyanova G.G., Yarullin M.R. Manufacture of Motor Fuels on IK-30-BIMT. *Catalyst Chemistry and Technology of Fuels and Oils* 2005. 41(5), 357–361. <https://doi.org/10.1007/s10553-005-0080-x>.

11. Ponomareva O.A., Kasyanov I.A., Knyazeva E.E., Konnov S. V., Ivanova I.I. Effect of the degree of zeolite recrystallization into micro-mesoporous materials on their catalytic properties in petroleum refining and petroleum chemistry processes. *Petroleum Chemistry* 2016. 56, 819–826. <https://doi.org/10.1134/S0965544116090188>.

12. Sharifi K., Halladj R., Royae S. J. An overview on the effects of metal promoters and acidity of ZSM-5 in performance of the aromatization of liquid hydrocarbons. *Reviews on Advanced Materials Science* 2020. 5, 188–206. <https://doi.org/10.1515/rams-2020-0037>.

13. Kirgina M., Belinskaya N., Altynov A., Bogdanov I., Temirbolat A. Transformations of stable gas condensate hydrocarbons into high-octane gasoline components over ZSM-5 zeolite catalyst. *Journal of Natural Gas Science and Engineering* 2020. 84, article 103605, 1–8. <https://doi.org/10.1016/j.jngse.2020.103605>.

14. Velichkina L., Barbashin Y., Vosmerikov A. Effect of Acid Treatment on the Properties of Zeolite Catalyst for Straight-Run Gasoline Upgrading. *Catalysis Research* 2021. 1(4), 1–16. <https://doi.org/10.21926/cr.2104004>.
15. Shukla D.B., Pandya V.P. Estimation of Crystalline Phase in ZSM-5 Zeolites by Infrared Spectroscopy. *Journal of Chemical Technology and Biotechnology* 1989. 44(2), 147–54. <http://doi.org/10.1002/jctb.280440206>.
16. Treacy M.M., Higgins J.B. Collection of simulated XRD powder patterns for zeolites fifth (5th) revised edition. Amsterdam, The Netherlands: Elsevier Science, 2007. 485.
17. Hidalgo C.V., Itoh H., Hattori T., Niwa M., Murakami Y. Measurement of the acidity of various zeolites by temperature-programmed desorption of ammonia. *Journal of Catalysis* 1984. 85(2), 362–369. [https://doi.org/10.1016/0021-9517\(84\)90225-2](https://doi.org/10.1016/0021-9517(84)90225-2).
18. Dettmer-Wilde K., Engewald W. Practical gas chromatography. 1st ed. Berlin: Springer, 2014. 902.
19. European Parliament, Council of the European Union. Regulation (EC) No 715/2007 of the European Parliament and of the Council of 20 June 2007 on type approval of motor vehicles with respect to emissions from light passenger and commercial vehicles (Euro 5 and Euro 6) and on access to vehicle repair and maintenance information [Internet]. Luxembourg: Official Journal of the European Union; 2007. Available from: <http://data.europa.eu/eli/reg/2007/715/oj>.
20. Bogdan V.I., Koklin A.E., Kazanskii V.B. Gas-phase and supercritical n-pentane isomerization on H-mordenite. *Kinetics and Catalysis* 2007. 48, 785–788. <https://doi.org/10.1134/S0023158407060031>.