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Effect of Solid-Phase Modification of High-Modulus Zeolite TsVM with Cerium Oxide in Conversion of Bioethanol to Hydrocarbons

The catalysts used for the conversion of bioethanol into hydrocarbons were obtained by solid-phase modification of high-modulus zeolite HTsVM (SiO_2:Al_2O_3 = 40) of the ZSM-5 type with cerium carbonate followed by heat treatment at 550 °C for 4 hours. The reactions were carried out in a flow reactor with a fixed catalyst bed in the temperature range of 300–450 °C at atmospheric pressure in order to study the effect of cerium oxide concentration in the HTsVM on its selectivity for isomerization and aromatization products. The modification of zeolite HTsVM with cerium oxide was shown to result in a change in its structural and acidic characteristics, as well as its selectivity for cracking, isomerization and aromatization reactions. The isomerisation selectivity of a catalytic system based on zeolite ZSM-5 can be increased by modifying it with rare earth or transition metals, which gives the catalyst a bifunctional character. This increase in isomerisation selectivity and decrease in aromatization selectivity are due to a significant reduction in the density of strong acid sites, the formation of additional Lewis cation sites and a decrease in total pore volume, as well as an increase in mesopore volume. The optimal 3 % CeO_2/HTsVM catalyst demonstrates high stability (30 hours) and high selectivity for isomerization products (44.90–46.06 %) within the temperature range of 300–350 °C. The gasoline fraction obtained using the 3 % CeO_2/HTsVM catalyst at 300 °C is enriched in isoparaffinic hydrocarbons (48.73 wt.%) and complies with the Euro 5 standard with regard to aromatic hydrocarbon content (21.17 wt.%) and benzene content (<1.0 wt.%).

Keywords: zeolite TsVM, cerium oxide, modification, selectivity, isomerization, aromatization, catalyst, surface, porosity, acid centers, bioethanol

Introduction

In recent years, special attention has been paid to new highly efficient methods for obtaining valuable olefin, aromatic and isoparaffin hydrocarbons from alternative renewable raw materials in the presence of catalytic systems based on high-silica zeolites [1, 2].

One of the methods for obtaining gasoline hydrocarbons and other valuable organic substances is the production of bioethanol from biomass [3].

The possibility of obtaining high-octane components of motor fuels from bioethanol in the presence of various types of zeolite catalysts has been shown in [4–7]. However, achieving high selectivity for isoparaffin hydrocarbons with sufficient selectivity for aromatic hydrocarbons requires the development of new catalytic systems with polyfunctional properties. ZSM-5 zeolite is the most promising candidate among the various types of molecular sieves for the production of high-octane components from bioethanol due to its inherent advantages, such as a high specific surface area, greater resistance to coke formation and the presence of various types of acid sites and systems of interconnected sinusoidal and straight channels [8]. The isomerization selectivity of the catalytic system based on ZSM-5 zeolite can be increased by modifying it with rare earth or transition metals (Pt, Pd, Ni) to impart a bifunctional character to the catalyst [9–12]. Rare earth metals are used as promoting additives to increase the isomerization activity and stability of catalysts in the processes of processing hydrocarbon feedstock from alcohols [3, 13–15]. Zeolite catalysts modified with cerium dioxide nanopowders make it possible to increase the isomerization activity of the catalyst in the process of converting hydrocarbon feedstock into high-octane components [16]. In the process of converting hydrocarbon feedstock and bioethanol, modification of HZSM-5 zeolite with Ga, Fe, Cr, Zn, Pd, Pt [15, 17] increases the yield of aromatic hydrocarbons, while the addition of Zr [18], Co [7] and La, Ce [19, 20] increases the yield of isoparaffin hydrocarbons. Modification of HZSM-5 zeolite with transition and rare earth metals can lead to the formation of Brønsted and Lewis acid sites of varying strength, as well as new active sites capable of directly interacting with intermediates formed during ethanol conversion. This imparts a polyfunctional character to the catalyst, giving it a predominant isomerizing ability [21, 22].

The method of impregnation with aqueous solutions of transition and rare-earth metal compounds is widely used to modify zeolites [4, 10, 13, 14]. However, modification of zeolite catalysts by impregnation followed by oxidative treatment, as a rule, does not lead to a highly dispersed distribution of the modifier on its surface.

Meanwhile, the method of solid-phase modification based on topochemical processes occurring during the interaction of transition metal oxides or salts with zeolites has proved to be very promising [23–25].

This paper presents the results of the influence of the concentration of cerium oxide in the composition of HTsVM zeolite prepared by solid-phase modification method on the selectivity of cracking, isomerisation and aromatization products in the conversion of bioethanol.

Experimental

Commercial high-silica zeolite TsVM (an analogue of zeolite ZSM-5) produced by Nizhny Novgorod Sorbents, Russia, was used for the preparation of catalysts.

The initial zeolite, with a SiO_2/Al_2O_3 molar ratio of 40 and a Na_2O content of less than 0.05 wt.%, was calcined in air at 550 °C for four hours prior to modification. Modification of the HTsVM zeolite with cerium carbonate was conducted via a dry mixing process in a vibrating ball mill for two hours. This was followed by calcination at a temperature of 550 °C for a period of four hours. The unmodified and modified samples were subsequently pelletized through a pressing method. For the subsequent studies, particles with a diameter ranging from 0.5 to 1.0 millimetres were utilized.

X-ray diffractograms of the samples were obtained on a RIGAKU MINIFLEX diffractometer (source CuK_{α}, $\lambda = 0.15046$ nm, 40 mA, 45 kV). Measurements were taken over a scanning angles $2\theta = 3–80°$ at a rate of 2° per minute.

The surface area by BET and pore volume by BJH were determined by adsorption method with liquid nitrogen at –196 °C using ASAP-2010 instrument by Micromeritics. The samples were degassed for 4 h in vacuum ($1–10^{-3}$ Pa) at 250 °C.

The acid characteristics of the studied samples were determined by ammonia TPD method using sorption analyzer USGA-101 (“Unisit”) according to the method described in [14].

The catalytic activity of the samples under investigation was determined in a quartz reactor with a fixed layer of catalyst (2 g) at atmospheric pressure. Prior to the commencement of the experiments, the samples were activated in a stream of dry air for 2 h at 550 °C. The reaction was carried out within the temperature range of 300–450 °C, with the volumetric rate of ethanol feed equal to $1.0\ h^{-1}$.

To determine the confidence interval, the experimental results were processed statistically using Microsoft Excel [26, 27]:

$$\mathrm{CI} = \bar{x} \pm z\frac{s}{\sqrt{n}},$$

where CI is the confidence interval, $\bar{x}$ is the sample mean, z is the confidence level value, s is a sample standard deviation, n is a sample size. The confidence level was 95 %. The standard deviation (S) was calculated based on the results of three measurements ($n = 3$).

The data presented in Table 1 were obtained with experiment duration of one hour. Experiments were also performed on the modified catalysts between 1–50 hours. The deactivated catalyst was regenerated in a stream of dry air at a rate of 4 l/hour. Regeneration started at 100 °C, with the temperature rising at a rate of 5 °C/min to reach 500 °C, which was then maintained for one hour. Analysis of the gaseous reaction products was conducted using an Agilent GC 782A gas chromatograph equipped with Porapak Q columns and a “5A” brand molecular sieve. Analysis of the liquid reaction products was performed using a quartz glass capillary column (100 mm × 0.25 mm × 0.25 μm) with a ZB-1 liquid phase applied to a PerkinElmer Autosystem XL chromatograph [7].

Product selectivity was determined using the following ratio:

$$\text{Selectivity, \%} = \frac{\text{final product, wt.\%}}{\sum \text{products, wt.\%}} \times 100\ \%.$$

Results and Discussion

X-ray diffraction patterns of freshly prepared HTsVM and cerium-modified zeolite catalysts, are shown in Figure 1.

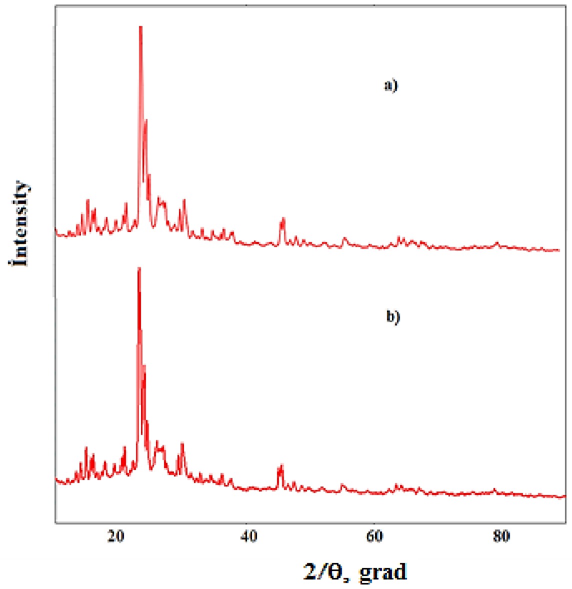

Figure 1. X-ray diffraction patterns of unmodified zeolite HTsVM (*a*) and modified catalyst 3 % CeO_2/ HTsVM (*b*)

Peaks at 2θ = 7.96°, 8.88°, 23.2° and 24° are observed for all samples, which are characteristic of zeolite with an MFI framework [28]. This indicates that the HTsVM framework is well preserved after modification. No obvious peaks are found on the modified samples within the investigated angles, which indicates a homogeneous dispersion of cerium oxide in the zeolite

Table 1 shows the results of the effect of temperature on the composition of ethanol conversion products in the presence of HTsVM.

Table 1

Effect of temperature on the activity of HTsVM catalyst in the process of ethanol conversion (SiO_2/Al_2O_3=40)

Products. wt.%	300 °C	350 °C	400 °C	450 °C
H_2	1.00 ± 0.12	1.42 ± 0.09	1.63 ± 0.10	1.72 ± 0.03
C_1–C_2	0.88 ± 0.03	1.52 ± 0.09	3.14 ± 0.44	3.77 ± 0.29
C_2H_5OH	1.90 ± 0.04	1.03 ± 0.11	0.96 ± 0.06	–
C_2H_4	6.61 ± 0.15	2.25 ± 0.13	1.15 ± 0.06	0.11 ± 0.05
C_3H_6	2.68 ± 0.09	1.32 ± 0.07	0.34 ± 0.06	–
C_3H_8	12.86 ± 1.26	16.12 ± 0.52	17.39 ± 0.41	19.51 ± 0.69
H-Alkanes C_{4+}	2.38 ± 0.03	2.02 ± 0.12	1.43 ± 0.06	0.74 ± 0.06
iso-C_4	1.61 ± 0.04	1.53 ± 0.04	1.42 ± 0.08	1.05 ± 0.08
iso-C_5-C_6	8.78 ± 0.07	7.94 ± 0.43	7.15 ± 0.46	3.44 ± 0.13
iso-C_7-C_{14}	1.72 ± 0.07	1.26 ± 0.21	0.727 ± 0.04	0.32 ± 0.02
Σ iso-C_5-C_{14}	10.60 ± 0.29	9.14 ± 0.06	7.87 ± 0.57	4.75 ± 0.17
Alkenes C_{4+}	3.94 ± 0.08	2.42 ± 0.14	1.72 ± 0.08	0.64 ± 0.04
C_6H_6	1.23 ± 0.04	1.71± 0.07	1.93 ± 0.09	2.35 ± 0.10
ArC C_7-C_8	12.46 ± 1.38	17.07 ± 5.10	17.37 ± 0.71	11.55± 0.36
ArC C_{9+}	3.32 ± 0.36	4.73 ± 0.54	5.20 ± 0.43	8.40 ± 0.32
Σ ArC C_6-C_{9+}	17.48 ± 0.56	22.16 ± 0.61	24.30 ± 0.78	26.91 ± 0.68
Naphthalenes C_{5+}	0.84 ± 0.04	0.63 ± 0.08	0.52± 0.03	0.31 ± 0.03
H_2O	38.12 ± 0.47	38.98 ± 1.04	39.05 ± 0.98	39.87 ± 0.97

Table 2

Effect of temperature on cracking selectivity

Products. wt.%	2 % CeO_2				3 % CeO_2				4 % CeO_2			
	300 °C	350 °C	400 °C	450 °C	300 °C	350 °C	400 °C	450 °C	300 °C	350 °C	400 °C	450 °C
H_2	0.82±0.03	1.04±0.06	1.14±0.06	1.42±0.03	0.92±0.03	1.13±0.07	1.22±0.041	1.64±0.07	1.12±0.039	1.23±0.05	1.32±0.05	1.54±0.04
C_1-C_2	0.61±0.02	0.82±0.02	1.46±0.17	1.92±0.03	0.71±0.01	0.91±0.01	1.22±0.041	1.82±0.04	0.63±0.001	0.70±0.01	1.04±0.05	1.62 ±0.05
C_2H_5OH	2.35±0.17	1.64±0.07	1.21±0.07	–	2.12±0.13	1.53±0.05	1.22±0.041	0.20±0.01	2.40±0.017	1.90±0.02	1.83±0.14	1.13 ±0.08
C_2H_4	2.96±0.15	1.64±0.06	0.30±0.01	–	2.83±0.08	1.14±0.05	0.42±0.001	0.10±0.01	2.93±0.006	2.23±0.07	1.13±0.08	0.42±0.01
C_3H_6	0.72±0.02	0.41±0.02	0.10±0.01	–	0.61±0.01	0.32±0.01	0.11±0.001	–	0.85±0.005	0.50±0.01	0.30±0.01	-
C_3H_8	8.253±0.16	9.74±0.13	12.98±0.72	14.80±0.52	7.94±0.23	8.84±0.44	11.86±0.141	13.97±0.01	7.47±0.026	8.34±0.15	11.10±0.50	13.59±0.62
n- Alkanes C_{4+}	2.843±0.12	2.44±0.04	2.14±0.07	1.32±0.03	2.24±0.08	2.44±0.05	2.05±0.003	1.50±0.01	3.02±0.019	2.94±0.08	2.34±0.09	2.14±0.07
iso-C_4	1.82 ±0.03	1.63±0.07	1.02±0.03	0.71±0.01	2.16±0.21	1.93±0.07	1.55±0.002	0.90±0.65	1.95±0.006	1.73±0.07	1.21±0.01	0.80±0.01
iso C_5-C_6	20.54±1.37	19.94±1.19	17.22±1.21	14.49±0.61	22.40±1.06	21.32±1.00	18.23±0.325	15.55±0.08	20.94±0.594	19.57±0.66	17.41±0.77	14.82±0.75
iso C_7-C_{14}	5.45 ±0.08	5.39±0.29	3.74±0.10	2.64±0.08	5.93±0.07	5.73±0.07	4.46±0.013	2.93±1.05	5.70±0.050	5.43±0.14	4.33±0.08	2.63±0.08
Σ iso C_5-C_{14}	26.24±1.38	25.21±1.26	20.93±1.43	17.09±0.73	28.31±1.24	27.03±1.12	22.61±0.374	18.52±0.01	26.41±0.463	25.02±1.06	21.86±1.34	17.40±0.81
Alkenes C_{4+}	0.94 ±0.04	0.60±0.01	0.51±0.01	0.41±0.01	0.61±0.01	0.51±0.01	0.40±0.001	0.30±0.02	0.61±0.015	0.50±0.01	0.41±0.01	0.20±0.01
C_6H_6	0.73±0.02	0.50±0.01	0.41±0.01	0.60±0.01	0.60±0.01	0.41±0.01	0.30±0.001	0.22±0.56	0.61±0.001	0.40±0.01	0.30±0.01	0.23±0.09
ArC C_7-C_8	10.77±0.55	12.39±0.54	15.02±0.69	17.93±0.97	9.99±0.34	11.61±0.66	13.68±0.125	16.76±0.06	9.57±0.056	11.36±0.29	13.41±0.67	16.43±0.89
ArC C_{9+}	1.93 ±0.01	2.33±0.05	2.83±0.04	3.13±0.05	1.73±0.04	1.82±0.05	2.54±0.005	2.83±0.80	1.43±0.003	1.72±0.10	2.33±0.08	2.62±0.11
Σ C_6-C_{9+}	13.28±1.25	15.19±0.50	18.17±0.70	21.61±0.96	12.37±0.76	13.81±0.80	16.52±0.255	19.77±0.04	11.56±0.101	14.01±0.64	16.01±0.70	19.20 ±0.96
Naphthalenes C_{5+}	1.64 ±0.08	1.24±0.06	0.91±0.01	0.90±0.01	1.54±0.10	1.13±0.08	0.92±0.009	0.82±1.07	2.10±0.011	1.92±0.08	1.64±0.06	1.52±0.07
H_2O	38.25±1.60	38.98±1.31	39.93±1.26	40.3±1.09	38.64±2.33	39.80±1.54	40.73±1.042	40.93±0.07	39.67±0.484	40.12±1.47	40.52±1.26	40.95±1.36

It can be seen that the reaction temperature significantly affects the distribution of products. In the presence of HTsVM, an increase in the reaction temperature from 300 °C to 450 °C was observed, which led to an increase in the yield of C_1–C_3 alkanes. There was also a decrease in the yield of C_2–C_{4+} alkenes and C_4–C_{14} isoparaffinic hydrocarbons, and an increase in the yield of C_6–C_{9+} aromatic hydrocarbons.

The highest yields of C_1–C_3 alkanes (23.28 wt.%) and C_6–C_{9+} aromatic hydrocarbons (26.91 wt.%) are observed at 450 °C. Figure 2 shows the effect of temperature on selectivity for cracking isomerization and aromatization reactions. High cracking and aromatizing activity of unmodified HTsVM is observed in the temperature range of 400–450 °C. Under these conditions, the selectivity for cracking and aromatization reactions is 33.68–38.71 % and 39.86–44.75 %, respectively.

The isomerization selectivity of the catalyst decreases significantly with increasing temperature. The lowest selectivity (7.90–14.98) for the isomerization reaction is observed in the temperature range 400–450 °C.

Modification of HTsVM zeolite with cerium oxide significantly changes its catalytic properties.

It can be seen from Figure 2 that the highest selectivity for the isomerisation reaction is achieved in the temperature range of 300–350 °C.

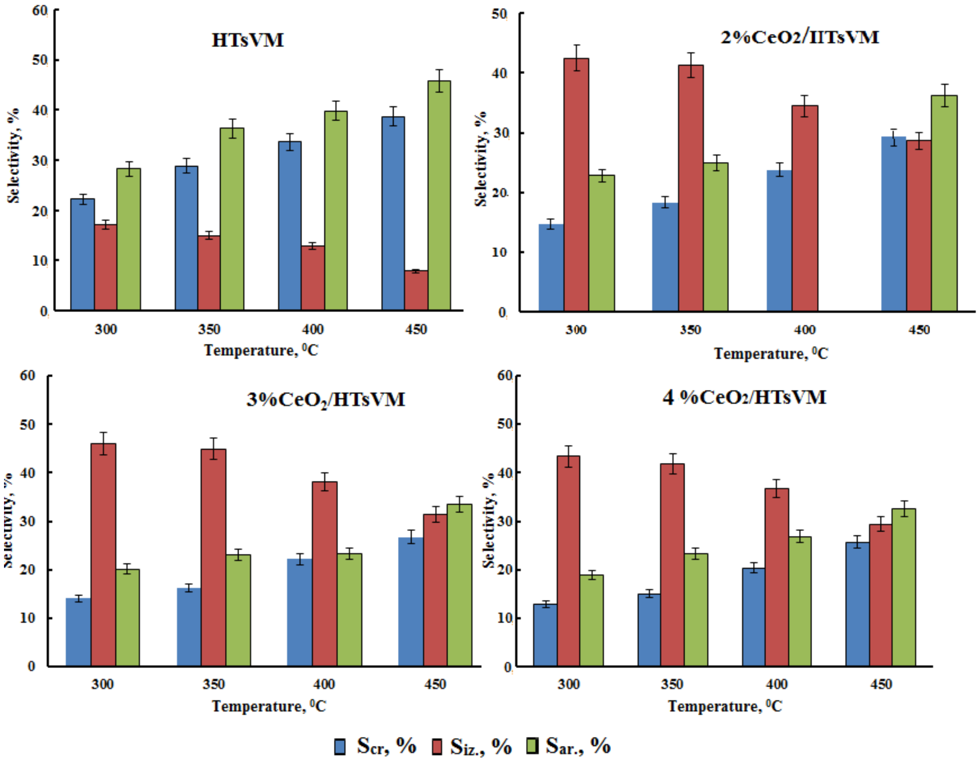

Figure 2. Temperature dependence of selectivity for cracking products ($S_{kr.}$), isomerization (S_{iz}) and aromatization (S_{ar})

The maximum yield of isoparaffinic hydrocarbons iso-C_5-C_6 + iso-C_7H_{16} (27.12–28.33 wt.%) with selectivity on isomerization reaction equal to 46.11–44.9 % is achieved on the sample modified with 3.0 wt.% cerium oxide. Further increase of reaction temperature up to 450 °C sharply reduces the yield of isoparaffin hydrocarbons (up to 18.52 wt.%) and selectivity for isomerization reaction (31.35 %). An increase in the content of cerium in the HTsVM composition decreases the cracking and aromatizing activity of the catalyst. An increase in selectivity for cracking and aromatization products is observed with increasing reaction temperature (Figure 2).

It is important to note that the modification results in a significant reduction of benzene content in the reaction products. On samples containing 3.0-4.0 wt.% cerium oxide, the benzene content in the reaction products decreases to 0.22-0.61 wt.%.

Thus, the selectivity for isomerization, aromatization and cracking products is determined by the content of cerium oxide in the catalyst and the temperature of the process.

The catalyst 3 % CeO_2/HTsVM shows high isomerization selectivity in the temperature range 300–350 °C (Figure 2), and the obtained liquid hydrocarbons have high octane number (105–110). The liquid products obtained at temperatures of 300–350 °C correspond to modern standards for Euro-4 and Euro-5 motor fuels in terms of isoparaffinic (44.9–46.1 wt.%), aromatic (20.1–22.9 wt.%), olefinic (<1.0 wt.%) and benzene (<1.0 wt.%) content.

Apparently, the change of catalytic properties of HTsVM is connected with the change of its structural and acid characteristics as a result of modification. Unmodified HTsVM zeolite has the highest total pore volume and specific surface area. However, the distribution of micro- and mesopore volume and average pore diameter depends on the concentration of cerium oxide added to HTsVM zeolite (Table 3).

Table 3

Structural characteristics of cerium-containing zeolite catalysts

Catalyst	HTsVM	2 % CeO_2/ HTsVM	3 % CeO_2/ HTsVM	4 % CeO_2/ HTsVM
S_{BET}. m^2/g	265.33±21.31	255.60±22.50	244.90±16.25	236.47±15.12
S_{micro}. m^2/g	125.03±3.65	122.67±5.52	113.97±3.58	107.73±2.42
$S_{\text{meзo}}$. m^2/g	142.40±1.46	134.47±0.96	131.27±1.15	129.80±4.10
V_{total}. cm^3/g	0.24±0.01	0.23±0.01	0.21±0.01	0.19 ±0.01
V_{meso}. cm^2/g	0.061±0.001	0.081±0.001	0.091±0.001	0.10±0.001
V_{micro}. cm^2/g	0.18±0.01	0.15±0.01	0.12 ±0.01	0.09 ±0.01
$V_{meso}/V_{total.\ \%}$	24.96	34.72	42.42	54.53

where S_{BET} is the specific surface area of the catalyst; S_{micro} and S_{mezo} are the specific surface area of micro- and mesopores; V_{total} is a total specific pore volume; V_{micro} and V_{mezo} are a volume of micro- and mesopores; 4V/Å is an average pore diameter.

Modification of HTsVM with cerium oxide decreases its specific surface area, total pore volume, micropore volume and average pore diameter. The modification of zeolite with cerium oxide also increases the mesopore volume and the V_{meso}/V_{total} ratio. The most noticeable decrease in pore diameter (from 36.21 to 31.41–32.49) is observed in samples containing 3.0-4.0 wt.% cerium oxide. The occurring changes in structural characteristics are obviously associated with the localization of modifier particles in the pores or in the pore mouths, as well as on the surface of zeolite crystals.

Table 4 shows the acid characteristics of unmodified and cerium-containing zeolite catalysts.

Table 4

Acid characteristics of initial and cerium-containing zeolite catalysts

Catalyst	Concentration of weak acid centres, μmol/g (100–300 °C)	Concentration of strong acid centres, μmol/g (300–600 °C)	Total concentration of acid centres, μmol/g
HTsVM	394.67±5.10	235.33±4.22	630.00
2 % CeO_2/ HTsVM	325.57±2.53	183.67±8.19	509.23
3 % CeO_2/ HTsVM	275.50±6.65	162.42±3.94	437.92
4 % CeO_2/ HTsVM	258.33±6.19	139.00±4.05	397.33

All samples have two peaks of acid centres: low-temperature ones with ammonia desorption region from 100 to 300 °C (mainly Lewis acid centres), and high-temperature ones in the region of 300–600 °C (mainly strong Brønsted acid centres). The unmodified HTsVM has the highest concentration of strong acid centres (235.33 μmol/g). The introduction of 2.0–4.0 wt.% of cerium oxide into zeolite HTsVM significantly reduces the concentration of strong acid centres. At the content of cerium oxide in HTsVM up to 4.0 wt.% the concentration of strong acid centres decreases 1.8 times.

The catalytic activity of cerium-containing zeolite catalysts with respect to yield and selectivity for isoparaffin hydrocarbons agrees well with the results of their structural and acid properties.

The changes in the structural and acid characteristics of zeolite catalysts resulting from modification can be explained by the preparation of catalysts with cerium oxide and subsequent calcination at 550 °C in an air environment for 5 hours. The cerium oxide nanoparticles are localized in the zeolite channels and on the zeolite's outer surface, where they form additional Lewis acid sites, including cerium ions and cationic sites ($Ce(OH)_2^+$ and $Ce(OH)_2^+$), as well as acid-base pairs (Ce^+–O). These pairs are formed when the cerium oxide interacts with Brønsted acid sites. The metal-containing sites formed in this process can activate ethanol molecules and intermediates. At the moderate acidic sites of Brønsted, these undergo skeletal rearrangement, predominantly forming isoparaffinic hydrocarbons.

One of the important operational properties of the catalyst is its regenerability and stability of operation.

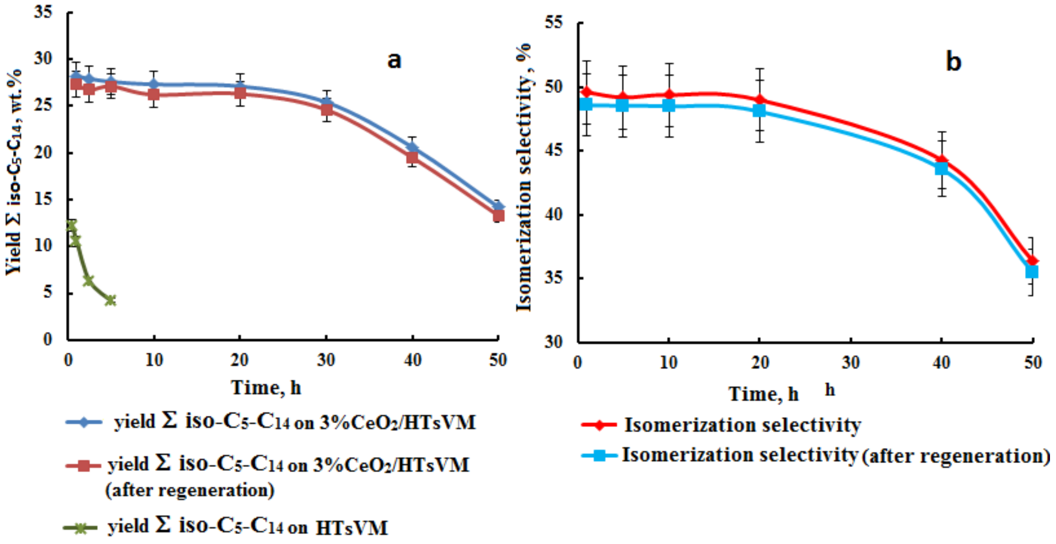

Figure 3. Dependence of yield (*a*) and selectivity for isoparaffin hydrocarbons ΣC_5-C_{14} (*b*) on the duration of operation

Figure 3 shows the dependence on the yield of the amount of isoparaffinic hydrocarbons ΣC_5-C_{14} and the selectivity to isomerization products on the running time for unmodified HTsVM and the optimal 3 % CeO_2/ HTsVM. It is evident that the catalyst deactivates rapidly after two hours of operation. This deactivation may be related to the accumulation of coking compounds on the catalyst, which reduces the access of bioethanol to the active sites located in the zeolite pores. Coke deposition on zeolites is strongly correlated with strong acidity, which explains the rapid deactivation of the initial HTsVM, which concentrates strong acidic sites (Table 3). Modification with cerium oxide increases the stability of the catalyst. From Figure 3 it is evident that the optimal catalyst 3 % CeO_2/HTsVM exhibits high stability of operation and practically retains its initial activity for 30 hours of operation. After 30 hours of operation, a noticeable decrease in the catalyst activity is observed. However, after 50 hours of operation, the catalyst fully restores its activity after regeneration. High isomerization activity and stability of the modified catalyst are obviously associated with changes in the acidic and textural characteristics of the HTsVM zeolite because of modification process. The low density of Brønsted acid sites and the higher concentration of various types of cationic Lewis sites ($Ce(OH)_2^+$ and $Ce(OH)^{2+}$), which are formed during the interaction of cerium oxide with strong Brønsted acid sites, facilitate the interaction of bioethanol with the active sites of the zeolite, reduce the hydrogen transfer reaction [21, 29], suppress coke deposits and increase the isomerization efficiency and stability of the catalyst. In addition, modification of the HTsVM zeolite with cerium oxide leads to an increase in the mesopore volume, which improves mass transfer during the reaction.

Conclusions

The solid-phase modification method was used to obtain catalysts based on zeolite HTsVM modified with cerium oxide (2.0–4.0 wt.%). As a result of modification and calcination of the zeolite, a dispersed distribution of the modifier occurs on the external surface and in the pores of the zeolite, where the modifier particles interact with both surface and localized in the pores of the zeolite strong Brønsted acid centers. As a result, there is a decrease in the density of strong acid centers, the formation of Brønsted acid centers of moderate strength, cationic Lewis acid centers, acid-base pairs Ce^+-O- and an increase in the volume of mesopores, which leads to a decrease in the redistribution of hydrogen, isomerizing efficiency and stability of the catalyst. The optimal catalyst of the 3 % CeO_2/HTsVM composition demonstrates regenerability, high stability (30 hours), selectivity for isomerization products (44.90–46.06 %) and provides a high octane number of the catalysate (105–110) in the temperature range of 300–350 °C.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. CRediT: **Eyyub Sabit oglu Mammadov** performed XRD and acidity study of the obtained catalysts and analyzed the obtained data; **Fuad Shamseddin oglu Kerimli** participated in the preparation of catalysts and catalytic experiments; **Nargiz Firudin gizi Akhmedova** took part in catalytic experiments and in writing the paper; **Sabit Eyyub oglu Mammadov** took part in setting, formulation and task of the research, in analyzing scientific and technical literature and writing the article; **Sakina Eylaz gizi Mirzaliyeva** participated in the analysis and identification of reaction products and their processing.

Conflicts of Interest

The authors declare no conflict of interest.

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