Catalysts for Dimethyl Ether Conversion to Lower Olefins: Effect of Acidity, Postsynthesis Treatment, and Steam and Methanol Content in Feedstock

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Received November 5, 2018; revised November 28, 2018; accepted December 10, 2018

Abstract—The most important and interesting results obtained at the Topchiev Institute of Petrochemical Synthesis of the Russian Academy of Sciences in 2008–2015 concerning dimethyl ether conversion to lower olefins in the presence of HZSM-5 zeolite catalysts have been systematized and summarized. The effects of the nature of the modifying element and catalyst steaming on the structural, acidic, and catalytic properties of the zeolite catalyst have been discussed. Some features of the influence of steam present in the feed gas mixture as a function of the nature of the modifying element have been elucidated. Data on the effect of impurities in the feed mixture (methanol and steam) have been described.

Keywords: dimethyl ether, methanol, steam, zeolite catalysts, lower olefins, stability, high-temperature treatment of catalysts

DOI: 10.1134/S0965544119040091

Synthesis of lower olefins is a large-scale process; the production output of these materials is constantly increasing [1]. The thermal pyrolysis and catalytic cracking of hydrocarbon feedstocks remain the main methods used to produce ethylene and propylene. The rates of growth in the consumption of these valuable chemicals are far ahead of the scale of their production; therefore, it is necessary to search for another cheaper and more available—hydrocarbon feedstock. Natural gas can be this feedstock; the production and large-scale use of natural gas is forecast for a long time period. The best-known and most thoroughly studied method to produce chemicals from natural gas is their synthesis through the intermediate step of natural gas reforming to synthesis gas (CO/H_2) .

At present, a process of great interest is the production of C_2-C_3 olefins from synthesis gas through the intermediate synthesis of dimethyl ether (DME), which provides the formation of lower olefins with a high yield and a higher selectivity [2, 3]. Dimethyl ether may be thought of as one of the possible key agents in the conversion of nonpetroleum feedstocks to valuable chemicals, such as olefins [4]. The most common base for catalysts for the synthesis of lower olefins from DME is a high-silica zeolite of the ZSM-5 type. The targeted impact on the properties of zeolite catalysts consists in their modification with metal compounds [5-9], which can lead to a change in their textural and acidic characteristics [10-12]. There are a large number of reports on studying the effect of the nature of the modifying element on the properties of zeolite catalysts [13-17]; however, a concept for understanding the role of the nature of the modifying element in the change in the catalytic properties of these systems has not yet been developed. Therefore, it is important to develop a general approach to the selection of hydrocarbon conversion catalysts that would make it possible to differentiate the effect of modification of zeolites on their acidic, molecularsieving, and catalytic properties depending on the nature of the modifying element. A change in acidic properties can also be achieved by a high-temperature pretreatment of the catalysts or by changing the water content in the feedstock. In this context, it is highly relevant to obtain data on the effect of acidic properties on the catalytic properties of zeolite catalysts for DME conversion to olefins. In this case, it is significant to determine the effect of the nature of the modifying element not only on the activity, but also on the stability of the catalytic properties. These data are particularly important for reactions running in a steam atmosphere, which is used in a number of industrial processes [18–21], because steam can have a significant effect not only on the distribution of DME conversion products, but also on the structural characteristics of the zeolite catalyst.

[†] Deceased.

Sample	Crystallinity**, %	$S_{\rm BET}, m^2/g$	$V_{\rm pore}, {\rm cm}^3/{\rm g}$	$V_{\rm micropore}, {\rm cm}^3/{\rm g}$	$V_{\rm mesopore BJH}, {\rm cm}^3/{\rm g}$	Reference
NH ₄ ZSM-5*	100	314	0.201	0.154	0.047	_
HZSM-5/Al ₂ O ₃	91	311	0.200	0.152	0.048	[30]
La-HZSM-5/Al ₂ O ₃	93	313	0.214	0.145	0.069	[30]
Zr–HZSM-5/Al ₂ O ₃	90	324	0.222	0.146	0.076	[30]
La–Zr–HZSM-5/Al ₂ O ₃	90	305	0.224	0.138	0.086	[30]
Mg–HZSM-5/Al ₂ O ₃	92	286	0.214	0.133	0.081	[31]

Table 1. Characteristics of the zeolite catalysts

* A commercial ZSM-5 zeolite sample in the ammonium form.

** Degree of crystallinity was calculated as described in [32].

In this study, results of the development of fundamentally new highly efficient catalyst systems based on a ZSM-5 zeolite modified with various elements are summarized and the effect of the nature of the modifying element and a high-temperature steam treatment on the structural, acidic, and catalytic properties of the zeolite catalyst for DME conversion to olefins is discussed.

EXPERIMENTAL

The studied catalytically active systems for lower olefin synthesis from DME were based on a ZSM-5 zeolite in the ammonium form (NH_4^+) with a SiO₂/Al₂O₃ molar ratio of 37 and a sodium oxide content of at most 0.04 wt % (manufactured by the Angarsk catalyst and organic synthesis plant, Russia). The zeolite was transferred into the hydrogen form (H^+) by calcining it at 500°C for 4 h. The catalysts were synthesized by mixing an HZSM-5 zeolite with an alumina slurry used as a binder (contains 23 wt % of dry Al₂O₃, manufactured by Promyshlennye Katalizatory, Ryazan, Russia) and subsequently shaping the extrudates (Al₂O₃ content in the finished catalyst is 33-34 wt %). The catalysts were modified with magnesium, lanthanum, and zirconium compounds. These active elements were identified as the most promising for synthesizing industrial catalysts [22-29]. For each of the elements, the most optimum method for introducing it into the catalyst was determined. Thus, lanthanum was introduced directly into the zeolite by a method based on the ion exchange of the hydrogen form of the zeolite with an aqueous solution of a metal salt; zirconium was introduced by the incipient wetness impregnation of the zeolite before mixing it with the binder. Magnesium was introduced by impregnating the finished zeolite extrudates mixed with the binder with an aqueous solution of a metal salt. Characteristics of the original zeolite and the modified catalysts based on it are listed in Table 1.

Tests of the catalysts were conducted on a system with a flow reactor at a temperature of $320-380^{\circ}$ C and

atmospheric pressure. The catalyst load in the reactor was $3-10 \text{ cm}^3$.

The feedstock was DME (weight fraction of DME of 99.99%); the DME diluent was nitrogen and/or steam and methanol. The concentration of DME and methanol in the feed gas mixture was 10-75 and 10-30 vol %, respectively. The space velocity of the feed gas mixture was varied in a range of 2000-15000 h⁻¹. The procedure for testing and analyzing the reaction products is described in [33].

A high-temperature pretreatment of the zeolite was conducted as described in [34, 35] at a temperature of 750°C in an air atmosphere for 4 h. The catalysts were treated steaming at 500 and 750°C in a flow reactor as described in [32].

The structural characteristics of the original zeolite and the modified samples before and after their treatment were studied by infrared (IR) spectroscopy, Xray diffraction (XRD) analysis, benzene adsorption, and solid-state nuclear magnetic resonance (NMR); the acidic properties of the catalysts were studied by temperature-programmed desorption of ammonia (NH₃-TPD).

Diffuse Reflectance Infrared Fourier Transform (DRIFT) Spectroscopy

The DRIFT spectra were recorded in situ at high temperatures in an inert atmosphere (Ar), as well as in a stream of DME mixture with nitrogen or steam. The spectra were recorded in the temperature range of $25-450^{\circ}$ C using a PIKE Technologies DiffusIR high-temperature cell coupled with a Bruker VERTEX-70 FTIR spectrometer. The spectrum was recorded in a continuous mode for 5 min (200 scans/spectrum) at a resolution of 2 cm⁻¹ in the range of 600–4000 cm⁻¹. The mathematical processing of the IR spectra was conducted using the OPUS-7 software package.

X-ray Diffraction Analysis

The XRD data were obtained on a Stoe STADT P powder diffractometer using CuK_{α} radiation at a wave-

Sample	Total acidity, µmol/g	Number of sites with $E_{\rm d}$ < 130 kJ/mol (I)	Number of sites with $E_{\rm d} > 130$ kJ/mol (II)	I/II*
HZSM-5	778	227 (30%)	551 (70%)	0.4
HZSM-5/Al ₂ O ₃ *	757	275 (36%)	482 (64%)	0.6
La-HZSM-5/Al ₂ O ₃	634	258 (41%)	376 (59%)	0.7
Zr–HZSM-5/Al ₂ O ₃	880	383 (44%)	497 (56%)	0.8
Mg-HZSM-5/Al ₂ O ₃	534	256 (48%)	278 (52%)	0.9
La-Zr-HZSM-5/Al ₂ O ₃	586	261 (45%)	325 (55%)	0.8
	High-temperatur	re treatment of zeolite (T)	1	
La–Zr–HZSM-5(T)/Al ₂ O ₃	461	265 (58%)	196 (42%)	1.4
Mg-HZSM-5(T)/Al ₂ O ₃	367	242 (66%)	125 (34%)	1.9
	Steam	ning of catalyst	I I	
Mg-HZSM-5/Al ₂ O ₃ (500°C)	491	191 (39%)	300 (61%)	0.6
Mg-HZSM-5/Al ₂ O ₃ (750°C)	197	156 (79%)	41 (21%)	3.8
La-Zr-HZSM-5/Al ₂ O ₃ (500°C)	319	172 (54%)	147 (46%)	1.2
La–Zr–HZSM-5/Al ₂ O ₃ (750°C)	170	137 (81%)	33 (19%)	4.2

 Table 2. Acidic properties of studied zeolite catalysts

* I/II is the ratio of the fraction of medium-strength acid sites to the fraction of strong acid sites.

length of $\lambda = 1.5418$ Å, a voltage of 40 kV, and a current of 30 mA.

Solid-State NMR

The solid-state NMR spectra were recorded on an 11.7 T Varian Unity Inova 500 instrument. The Larmor frequencies were 130 and 99 MHz for ²⁷Al and ²⁹Si, respectively. The ²⁷Al spectra were recorded using a 3.2-mm probe at a spinning rate of 15 kHz, a $\pi/2$ pulse length of 1 µs, an acquisition time of 0.015 s, and an interval between the scans of 0.5 s. The ²⁹Si magic angle spinning (MAS) NMR spectra were recorded using a 7.5-mm probe at a spinning rate of 4.5 kHz, a $\pi/6$ pulse length of 2 µs, an acquisition time of 0.01 s, and an interval between the scans of 30 s. The standards for determining the positions of the ²⁹Si and ²⁷Al spectral lines were tetramethylsilane and aluminum chloride, respectively.

Benzene Adsorption

These measurements were made in a dynamic mode at 200°C by gas–solid chromatography as described in [36]. The calculation of isotherms was performed by the Glueckauf method [37].

Ammonia Temperature-Programmed Desorption

Ammonia TPD data for the synthesized samples were obtained as described in [32] and processed by fitting the shapes of the experimental and calculated curves as described in [38].

Textural Characteristics

The textural characteristics of the samples (specific surface area, total pore volume, and pore size distribution) were studied by low-temperature adsorption—desorption of molecular nitrogen on a Micromeritics ASAP-2010 instrument. Prior to analysis, all the samples were evacuated at a temperature of 350°C to 4×10^{-1} Pa. Nitrogen adsorption was run at a temperature of 77 K.

RESULTS AND DISCUSSION

The crucial factor of the effectiveness of zeolite catalysts in various versions of oxygenate conversion to hydrocarbons is the acidic properties of the catalysts, which can be varied by modifying the zeolites by postsynthesis high-temperature treatment of the original HZSM-5 zeolite or hydrothermal treatment (steaming) of the zeolite catalyst. The latter treatment leads not only to a change in the acidic properties of the catalysts, but also to the formation of additional acid sites, thereby affecting the catalytic and physicochemical properties of the zeolite catalyst. The strength distribution of acid sites as a function of the nature of the introduced element and the method of postsynthesis treatment of zeolite catalysts is shown in Table 2.

The modification of the samples with a magnesium compound and the double modification with lanthanum and zirconium lead to a significant decrease in the total acidity; at the same time, the fraction of medium-strength acid sites (I/II) slightly increases.



Fig. 1. X-ray diffraction pattern of zeolite catalysts: (1) HZSM-5/Al₂O₃, (2) Mg-HZSM-5/Al₂O₃, (3) La-Zr-HZSM-5/Al₂O₃, and (4) La-Zr-HZSM-5/Al₂O₃ steamed at 500°C.

A high-temperature treatment of the original zeolite leads to a significant decrease in the total acidity and an increase in the fraction of medium-strength acid sites. Steaming at 500°C also leads to a decrease in the total acidity; however, the fraction of strong acid sites increases in the case of Mg–HZSM-5/Al₂O₃ and decreases in the case of La–Zr–HZSM-5/Al₂O₃. Steaming at 750°C leads to an abrupt decrease in the total acidity and the fraction of strong acid sites.

Steaming of zeolite catalysts can lead to partial degradation of their structure. To verify the effect of steaming on the structural properties of zeolites, the $La-Zr-HZSM-5/Al_2O_3$ and Mg-HZSM-5/Al_2O_3 catalysts samples were subjected to XRD analysis before and after treatment to compare with original HZSM-5/Al_2O_3.

According to XRD data shown in Fig. 1 for some of the modified zeolites, all the studied samples, regardless of the nature of the modifying agent, the modification method, and the treatment temperature, correspond to the crystallographic type of the ZSM-5 zeolite. The calculated unit cell parameters are as follows: a = 20.09, b = 19.96, and c = 13.40 Å (according to published data, a = 20.02, b = 19.89, c = 13.38 Å [39]). Thus, steaming did not lead to the complete degradation of the zeolite crystal lattice. The unit cell parameters of the zeolite also remained almost unchanged.

Figure 2 shows the ²⁹Si NMR spectra of the La– Zr–HZSM-5 and Mg–HZSM-5 samples before and after steaming. Comparison of the positions of the signals with published data for the unmodified zeolite [40] allow us to attribute the reflection at -108.5 ppm in the ²⁹Si NMR spectrum to the Si(OSi)₄ moiety and the signal at -104.2 ppm, to the Si(OH)(OSi)₃ hydroxylated groups. After steaming at 500°C, the shoulder at -104.5 ppm disappears for La–Zr– HZSM-5 and decreases for Mg–HZSM-5. This effect can be attributed to the dealumination of the zeolite by steaming the catalysts. For the samples modified with lanthanum and zirconium compounds and with magnesium, the ²⁹Si reflection shifted from -108.5 to -110 ppm, indicating a change in the local environment of silicon atoms in the crystal structure of the zeolite.

More significant changes were observed in the ²⁷Al NMR spectrum (Fig. 3). The ²⁷Al reflection at 58.5 ppm corresponding to tetragonally coordinated aluminum atoms in the zeolite structure was shifted to 56 ppm by treatment with modifier compounds and to 53.6 ppm after steaming the Mg–HZSM-5 catalyst. In addition, the spectrum exhibited a broad signal, which coincided with the resonance of the standard in the region of 0 ppm. Thus, it can be concluded that some of the aluminum atoms were withdrawn from the zeolite structure and transformed into Al³⁺ ions during modification and steaming.

An interesting feature exhibited by the ²⁷Al NMR spectra is a significant decrease in the signal intensity at 56 ppm for the La–Zr–HZSM-5 catalyst after steaming, especially at 750°C. Taking into account the fact that the acquisition of signals is the same in all cases, the observed effect can be attributed to a decrease in zeolite crystallinity, including that due to dealumination. Comparison of the intensity of ²⁷Al NMR signals for these catalysts suggests that the presence of magnesium oxide in the sample contributes to some stabilization of the structure during steaming.

Figure 4 shows the results of IR spectroscopy study of the La–Zr–HZSM- $5/Al_2O_3$ crystal structure before and after steaming. The spectrum of the original HZSM- $5/Al_2O_3$ exhibits absorption bands at 720– 780 cm⁻¹, which characterize the Al–O bond with the tetrahedral aluminum environment. In the case of the



Fig. 2. ²⁹Si MAS solid-state NMR spectra for (a) La-Zr-HZSM-5 and (b) Mg-HZSM-5 catalysts: (1) HZSM-5, (2) La-Zr-HZSM-5, (3) La-Zr-HZSM-5 steamed at 500°C, (4) La-Zr-HZSM-5 steamed at 750°C, (5) Mg-HZSM-5, (6) Mg-HZSM-5 steamed at 500°C, and (7) Mg-HZSM-5 steamed at 750°C.



Fig. 3. ²⁷Al MAS solid-state NMR spectra for (a) La-Zr-HZSM-5 and (b) Mg-HZSM-5 catalysts: (1) HZSM-5, (2) La-Zr-HZSM-5, (3) La-Zr-HZSM-5 steamed at 500°C, (4) La-Zr-HZSM-5 steamed at 750°C, (5) Mg-HZSM-5, (6) Mg-HZSM-5 steamed at 500°C, and (7) Mg-HZSM-5 steamed at 750°C.

HZSM-5/Al₂O₃ zeolite catalyst modified with La and Zr (spectrum 2), the band is shifted from 795.5 to 786.9 cm⁻¹; the shift indicates the appearance of heteroatoms in the zeolite composition. Steaming the La–Zr–HZSM-5/Al₂O₃ catalyst at 500°C leads to a shift of this absorption band toward short wavelengths to 790.3 cm⁻¹ (spectrum 3), and steaming the catalyst at 750°C leads to an even more significant shift of this band, namely, to 804.7 cm⁻¹ (spectrum 4). This shift of the absorption band indicates a decrease in the number of aluminum atoms in the tetrahedral configuration and an increase in the coordination number of the remaining aluminum. At the same time, no con-

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siderable changes were found in the intensity and position of the absorption bands due to bending vibrations in the region of the structural vibrations of the zeolite framework at 450 and 550 cm⁻¹. Thus, steam treatment of the catalysts leads to dealumination; in addition, the remaining aluminum partially loses the tetrahedral environment [32].

The adsorption properties of the La–Zr–HZSM- $5/Al_2O_3$ and Mg–HZSM- $5/Al_2O_3$ catalysts before and after steaming were studied. For the La–Zr–HZSM- $5/Al_2O_3$ catalyst, the amount of adsorbed benzene decreases with an increase in steaming temperature; for the Mg–HZSM- $5/Al_2O_3$ sample, this parameter



Fig. 4. Infrared spectra of catalyst samples: (1) HZSM-5/Al₂O₃, (2) La–Zr–HZSM-5/Al₂O₃, and La–Zr–HZSM-5/Al₂O₃ steamed at (3) 500 and (4) 750°C.

increases (Table 3). It is unlikely that this effect is caused by different patterns of degradation of the zeolite crystal lattice, because lanthanum-containing forms are more stable. In this case, a crucial role is apparently played by cation migration, which vigorously occurs during the hydrothermal treatment of the catalysts. Apparently, lanthanum and zirconium are mostly concentrated in the zeolite and thereby decrease the pore volume, while magnesium is concentrated in the binder—alumina—and thereby empties the zeolite pores. At the same time, it is necessary to take into account the different characters of benzene adsorption on these catalyst samples, which probably lead to an overestimated limiting adsorption value for Mg–HZSM-5/Al₂O₃. Steaming at 750°C leads to partial degradation of the zeolite crystal structure, as evidenced by a significant decrease in ammonia adsorption according to NH₃-TPD data (Table 2).

Characteristic energies of adsorption E for benzene were calculated from the experimental data by the Dubinin equation [41]. It is evident from Table 3 that the characteristic energies of adsorption for benzene differ depending on the nature of the modifier and the calcination temperature. A nearly antibatic change in the characteristic energy of adsorption and the limit-

	<i>a</i> _e		Q, kJ/mol ±1.0			
Sample	μmol/g	E , kJ/mol ± 0.5	$a = 10$ μ mol/g	$a = 100$ μ mol/g	a = 200 μ mol/g	
HZSM-5/Al ₂ O ₃	1219	19.6	112	67	52	
La–Zr–HZSM-5/Al ₂ O ₃	1121	16.9	94	56	43	
La–Zr–HZSM-5/Al ₂ O ₃ steamed at 500° C	987	16.1	87	51	39	
La–Zr–HZSM-5/Al ₂ O ₃ , steamed at 750°C	590	20.6	103	54	38	
Mg-HZSM-5/Al ₂ O ₃	813	19.9	104	59	44	
Mg-HZSM-5/Al ₂ O ₃ , steamed at 500° C	997	17.3	94	55	48	
Mg-HZSM-5/Al ₂ O _{3,} steamed at $750^{\circ}C^{*}$	1050	16.0	88	51	39	

Table 3. Calculated values of limiting adsorption, characteristic energies, and differential molar heats of adsorption

* Benzene adsorption on this sample lies in the Henry region; therefore, the estimate of the limiting a_0 value according to the Dubinin equation is overestimated.

ing adsorption of benzene is observed. For the La– Zr–HZSM- $5/Al_2O_3$ catalyst samples, the characteristic energy of adsorption increases with a decrease in the limiting adsorption of benzene; this finding can be attributed to lanthanum and zirconium cations concentrated in the zeolite. In contrast, for the Mg– HZSM- $5/Al_2O_3$ catalyst sample, steaming decreases the characteristic energy of benzene adsorption and increases the limiting adsorption; this effect is associated with the concentrating of magnesium in the binder.

At all the given *a* values, the maximum heat of adsorption was obtained for the original HZSM- $5/Al_2O_3$ zeolite. With an increase in the *a* value, the *Q* values of adsorbed benzene regularly decrease for all the samples.

Kitaev et al. [42] observed that in the case of nonspecific adsorption of *n*-paraffins in pentasil channels, the characteristic energy of adsorption does not exceed ~22 kJ/mol. In this study, we found that the *E* value for benzene is 16-21 kJ/mol. Thus, the adsorption of benzene molecules is most probably nonspecific and the observed changes in the characteristic energy of adsorption are apparently due to diffusion factors.

The synthesized catalysts modified with different elements and subjected to different postsynthesis treatments were studied in DME conversion to lower olefins at two reaction temperatures (320 and 380°C), which correspond to the temperatures at the inlet and outlet of the reaction zone of an industrial adiabatic reactor (Table 4).

The introduction of an active element into a zeolite catalyst leads to a change not only in the acidic characteristics, but also in the catalytic properties of the sample. In all the cases, except for magnesium, modification leads to a decrease in catalytic activity at $T = 320^{\circ}$ C. The selectivity for ethylene and propylene changes symbatically with a change in the ratio of medium-strength acid sites (I) to strong acid sites (II). It is medium-strength acid sites that are involved in the catalytic formation of ethylene and propylene, while DME conversion occurs on all acid sites [32].

An increase in the reaction temperature from 320 to 380°C leads to an increase in activity and a decrease in the olefin yield, which is associated with an increase in the rate of secondary reactions.

The high-temperature treatment of the original zeolite leads to an increase in the olefin selectivity and provides a high DME conversion that is stable over time and significantly exceeds the DME conversion observed for the original catalyst [32].

Steaming the catalysts at 500°C leads to a significant increase in activity at both 320 and 380°C, while the selectivity slightly decreases; this effect is mostly due to the change in acidity (Table 4). Steaming the catalyst at 750°C leads to an abrupt decrease in the DME conversion (from 99.8 to 2.9 wt %), an increase in the olefin selectivity, and a decrease in the alkane selectivity, which is most probably due to partial degradation of the zeolite crystal structure [32].

Lower olefins are typically synthesized in an inert gas atmosphere at a DME concentration of at most 30 vol %. If the process is run in a steam atmosphere, which is used in a number of industrial processes [18– 21], the steam/feedstock ratio can have a significant effect on distribution of DME conversion products [43]. A change in this ratio can lead to both an increase and a decrease in the yield of lower C_2-C_4 olefins. In addition, in the synthesis of lower olefins from CO and H_2 through the intermediate production of DME, the production of DME from CO and H_2 is accompanied by the formation of water, which can be involved in the synthesis of lower olefins.

The effect of the DME/steam ratio on the distribution of the reaction products in the absence of nitrogen was studied at a constant DME load. The substitution of steam for nitrogen has a considerable effect on the catalytic properties of the zeolite catalysts; this effect also significantly depends on the nature of the modifying elements (Fig. 5). Thus, after the addition of steam to the feedstock, at a DME concentration of 20 vol %, in the presence of the La-Zr-HZSM- $5/Al_2O_3$ catalyst, the total selectivity for C_2-C_4 olefins remains almost unchanged and weakly depends on the steam content in the feedstock (25-90 vol %). Methanol was not detected in the reaction products: the alkane content decreased with an increase in the steam concentration in the feedstock. In the presence of the magnesium-modified zeolite catalyst in a steam atmosphere, the selectivity for lower olefins abruptly decreases. However, with an increase in the steam content, the olefin selectivity increases, while the alkane selectivity remains almost unchanged; in this case, the methanol content in the reaction products is high. Although the content of methanol decreases with an increase in the steam content, the fraction of this product remains dominant.

The in situ DRFIT spectroscopy study showed that in the case of passing DME through Mg–HZSM- $5/Al_2O_3$, the spectrum exhibits a band at 1084 cm⁻¹ due to the C–O bonds in the methoxy groups [44]; however, in the case of passing DME with H₂O, the spectrum of Mg–HZSM- $5/Al_2O_3$ recorded under the same conditions does not exhibit the above band; at the same time, the intensity of the band at 1047 cm⁻¹, which is the strongest band in the spectrum of methanol, abruptly increases. The formation of methoxy groups on the zeolite surface can occur during the interaction of DME with the base sites on the zeolite surface (absorption band at 3720 cm⁻¹) to release methanol, as shown in [45].

In many cases of synthesis of lower olefins from DME, the formation of methanol is observed; metha-

Catalyst	<i>T</i> , °C	DME conversion, %	Hydrocarbon selectivity, wt %				Σ		
			$C_2^=$	$C_3^=$	$\Sigma C_4^=$	C_1^+ paraffins	$C_2 - C_5$ olefins		
HZSM-5/Al ₂ O ₃	320	67.4	9.2	14.9	19.5	55.3	44.7		
	380	94.3	21.6	23.3	11.5	36.9	63.2		
Mg-HZSM-5/Al ₂ O ₃	320	72.6	30.2	31.5	12.8	22.2	77.8		
	380	97.3	13.7	31.6	17.4	31.6	68.4		
La-HZSM-5/Al ₂ O ₃	320	46.9	18.6	38.0	14.1	25.5	74.5		
	380	96.6	13.0	25.9	13.9	43.0	57.0		
Zr-HZSM-5/Al ₂ O ₃	320	47.3	22.3	36.0	13.1	25.4	74.6		
	380	87.2	14.3	25.8	11.5	44.6	55.4		
La–Zr–HZSM-5/Al ₂ O ₃	320	50.1	21.9	36.1	13.0	25.2	74.8		
	380	91.5	13.0	27.1	13.0	42.6	57.4		
High-temperature treatment of zeolite (T)									
La-Zr-HZSM-5(T)/Al ₂ O ₃	320	65.0	25.1	30.0	8.4	26.7	73.3		
	380	95.4	20.9	29.2	8.9	34.4	65.6		
<u>'</u>		St	eaming at 50	00°C		1	<u>-</u>		
Mg-HZSM-5/Al ₂ O ₃	320	93.4	26.8	24.1	14.6	30.1	69.9		
	380	93.2	10.4	36.0	17.2	30.5	69.5		
La-HZSM-5/Al ₂ O ₃	320	99.7	20.0	16.0	14.8	44.5	55.5		
	380	98.4	11.9	29.2	15.7	38.0	62.0		
Zr–HZSM-5/Al ₂ O ₃	320	99.2	19.0	16.1	13.5	47.0	53.0		
	380	95.0	13.1	29.8	14.3	38.5	61.5		
La–Zr–HZSM-5/Al ₂ O ₃	320	95.9	24.8	20.9	14.7	35.0	65.0		
	380	90.8	12.1	33.6	14.8	34.3	65.7		
Steaming at 750°C									
La–Zr–HZSM-5/Al ₂ O ₃	380	2.9	8.7	36.1	13.4	19.6	80.4		

Table 4. Dimethyl ether conversion to lower olefins in the presence of zeolite catalysts (P = 0.1 MPa; feedstock: 10 vol % DME + 90 vol % N₂; $W_{\text{DME}} = 0.9$ h⁻¹, $T = 320^{\circ}$ C, $W_{\text{DME}} = 3.7$ h⁻¹, $T = 380^{\circ}$ C, the data for 4 h on stream

nol in turn can affect the composition of the DME conversion products.

Data on the effect of methanol on the catalytic properties of La-Zr-HZSM-5/Al₂O₃ are shown in Table 5. It is evident from the table that the addition of methanol to DME hardly affects the total olefin selectivity; with an increase in the methanol concentration from 10 to 30 vol %, the ethylene content increases from 25.8 to 30.9 wt %, while the amount of propylene slightly decreases; in this case, the products contain many alkanes in which the proportion of methane is about 15 wt %. With an increase in the DME concentration in the feedstock to 30 vol % in the presence of methanol, the selectivity for olefins, in particular, for ethylene, decreases, while the alkane content increases. A decrease in the space velocity of the feed mixture to 4000 h^{-1} leads to a decrease in the alkane content and an increase in the olefin selectivity.

Thus, in the case of the reaction run in a nitrogen atmosphere, at a DME concentration of 20 vol %, the

presence of methanol in the reaction zone does not significantly affect the catalytic properties of La–Zr– $HZSM-5/Al_2O_3$; however, at a DME concentration of up to 30 vol %, the presence of methanol leads to a decrease in the selectivity for ethylene and propylene.

Upon the substitution of steam for nitrogen (Table 6), in the presence of methanol, the total olefin selectivity remained almost unchanged; the use of an equilibrium mixture of oxygenates with steam as the feedstock leads to an increase in the proportion of ethylene in the products.

CONCLUSIONS

The nature of the active element has a significant effect on the catalytic and acidic properties of the modified zeolite catalyst for DME conversion to lower olefins. The selectivity for lower olefins changes symbatically with an increase in the ratio of mediumstrength acid sites to strong acid sites with a decrease in the total acidity. Thus, medium-strength acid sites are



Fig. 5. Effect of feedstock dilution with steam on the catalytic properties of $La-Zr-HZSM-5/Al_2O_3$ and $Mg-HZSM-5/Al_2O_3$.

		Н	$\Sigma C = C$ alofina				
Feed mixture, vol %	Parameters	$C_2^=$	$C_3^=$	$\Sigma C_4^=$	C_1^+ paraffins	$2C_2-C_5$ orefins	
$DME(20) + N_2(80)$	$V_{\rm mix} = 6000 \ {\rm h}^{-1}$	26.4	34.8	9.4	21.6	78.4	
	$W_{\rm DME} = 4.1 \ {\rm h}^{-1}$						
$DME(20) + MeOH(10) + N_2(70)$	$V_{\rm mix} = 6000 \ {\rm h}^{-1}$	25.8	33.8	8.2	25.1	74.9	
	$W_{\rm DME} = 4.1 \ {\rm h}^{-1}$						
	$W_{\rm MeOH} = 1.6 \ {\rm h}^{-1}$						
$DME(20) + MeOH(20) + N_2(60)$	$V_{\rm mix} = 6000 \ {\rm h}^{-1}$	28.1	33.2	7.9	23.8	76.2	
	$W_{\rm DME} = 4.1 \ {\rm h}^{-1}$						
	$W_{\rm MeOH} = 3.2 \ {\rm h}^{-1}$						
$DME(20) + MeOH(30) + N_2(50)$	$V_{\rm mix} = 6000 \ {\rm h}^{-1}$	30.9	32.5	7.1	24.2	75.8	
	$W_{\rm DME} = 4.1 \ {\rm h}^{-1}$						
	$W_{\rm MeOH} = 4.8 \ {\rm h}^{-1}$						
$DME(30) + MeOH(30) + N_2(40)$	$V_{\rm mix} = 6000 \ {\rm h}^{-1}$	25.4	31.1	7.2	30.5	69.5	
	$W_{\rm DME} = 6.8 \ {\rm h}^{-1}$						
	$W_{\rm MeOH} = 4.8 \ {\rm h}^{-1}$						
$DME(30) + MeOH(30) + N_2(40)$	$V_{\rm mix} = 4000 \ {\rm h}^{-1}$	27.5	33.3	7.6	25.7	74.3	
	$W_{\rm DME} = 4.6 \ {\rm h}^{-1}$						
	$W_{\rm MeOH} = 3.2 \rm h^{-1}$						
$MeOH(20) + N_2(80)$	$V_{\rm mix} = 6000 \ {\rm h}^{-1}$	25.8	23.1	7.5	38.7	71.8	
	$W_{\rm MeOH} = 3.2 \rm h^{-1}$						

Table 5. Effect of methanol addition to the feed mixture on the catalytic properties of La–Zr–HZSM-5/Al₂O₃ (P = 0.1 MPa, $T = 340^{\circ}$ C, the data for 4 h on stream)

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	Parameters]	$\Sigma C_2 - C_5$			
Feed mixture		$C_2^=$	$C_3^=$	$\Sigma C_4^=$	C_1^+ paraffins	olefins
$DME(30) + MeOH(30) + N_2(40)$	$W_{\rm DME} = 4.6 \ {\rm h}^{-1}$	27.5	33.3	7.6	25.7	74.3
	$W_{\rm MeOH} = 3.2 \ {\rm h}^{-1}$					
$DME(30) + MeOH(30) + H_2O(40)$	$W_{\rm DME} = 4.0 \ {\rm h}^{-1}$	31.9	33.4	6.1	25.3	74.7
	$W_{\rm MeOH} = 3.2 \ {\rm h}^{-1}$					
	$W_{\rm H_2O} = 2.0 \ \rm h^{-1}$					

Table 6. Oxygenate conversion to lower olefins in the presence of the La–Zr–HZSM-5/Al₂O₃ catalyst (P = 0.1 MPa, $T = 340^{\circ}$ C, $V_{mix} = 4000$ h⁻¹, the data for 4 h on stream)

involved in the catalytic formation of ethylene and propylene, while the DME conversion occurs on all acid sites.

A postsynthesis high-temperature treatment of the HZSM-5 zeolite and steaming the catalyst at 500°C lead to a significant increase in the catalyst stability.

The presence of steam in the feedstock has different effects on the catalytic properties of the zeolite catalysts. Thus, for La–Zr–HZSM-5/Al₂O₃, the presence of steam leads to an increase in stability and selectivity, while for Mg–HZSM-5/Al₂O₃, it provides an abrupt decrease in the selectivity for lower olefins and the presence of a large amount of methanol in the products.

The use of an equilibrium mixture of oxygenates with steam (DME + MeOH + H_2O) as the feedstock leads to an increase in the amount of ethylene in the reaction products.

ACKNOWLEDGMENTS

This work was performed at the Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences and supported by the Russian Science Foundation. project no. 17-73-30046.

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Translated by M. Timoshinina