The Effect of Steam on the Conversion of Dimethyl Ether to Lower Olefins and Methanol over Zeolite Catalysts

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Abstract—The effect of steam on the catalytic properties of La–Zr–HZSM- $5/Al_2O_3$ and Mg–HZSM- $5/Al_2O_3$ in the synthesis of olefins from dimethyl ether (DME) has been studied. It has been found that the presence of steam has a significant effect on the ethylene-to-propylene ratio regardless of the nature of the modifier; the formation of methanol was observed only on Mg–HZSM- $5/Al_2O_3$. In situ high-temperature diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy has revealed that the formation of methanol on Mg–HZSM- $5/Al_2O_3$ occurs owing to the formation of methoxy groups on the surface of the zeolite during the interaction between DME and basic sites. The resulting methoxy groups can be easily converted to methanol in the presence of steam.

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Dimethyl ether (DME) can be regarded as one of the possible key agents in the conversion of nonpetroleum feedstock to motor fuels and valuable chemical products, such as olefins [1]. A method for producing lower olefins from DME has been developed at the Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences. It is recommended that zeolite catalysts based on ZSM-5 modified with magnesium, lanthanum, and zirconium should be used to catalyze this process. Lower olefins are generally synthesized in an inert gas environment at a DME concentration of less than 30 vol %.

If the process is conducted in a steam environment, which is appropriate under industrial conditions, the steam-to-feedstock ratio can have a significant effect on the distribution of the DME conversion products [2]. A change in this ratio can lead to both an increase and decrease in the content of low-molecular-weight C_2-C_4 olefins. In addition, in the synthesis of lower olefins from CO and H₂ through DME, the production of DME from CO and H₂ is accompanied by the formation of water, which can be involved in the synthesis of lower olefins.

Therefore, this study is focused on the examination of the effect of the steam-to-feedstock ratio on the yield and selectivity for lower olefins over zeolite catalysts that contain magnesium and the ones containing lanthanum and zirconium.

EXPERIMENTAL

DME with a purity of 99.8% (manufactured by OAO NAK Azot, Novomoskovsk, Russia) was used as a feedstock. The catalytically active systems for synthesizing lower olefins from DME were prepared from

a ZSM-5 zeolite in the ammonium form (NH_4^+) with a SiO₂/Al₂O₃ molar ratio of 40 and a Na₂O concentration of at most 0.07 wt % (manufactured by OAO AZKiOs, Russia) modified with lanthanum and zirconium and with magnesium. The catalysts were synthesized by mixing an HZSM-5 zeolite with an alumina slurry (contains 23 wt % of dry Al₂O₃, manufactured by ZAO Promyshlennye katalizatory, Ryazan, Russia) as a binder and the subsequent shaping of extrudates; the concentration of the Al₂O₃ binder in the finished catalyst was 33-34 wt %. Lanthanum and zirconium were introduced by the incipient wetness impregnation of the zeolite before mixing with the binder; magnesium was introduced by impregnating the prepared extrudates of the zeolite and the binder with an aqueous solution of the metal salt at room temperature with the subsequent drying and calcination at 500°C for 4– 6 h.

Diffuse reflectance infrared Fourier transform (DRIFT) spectra were recorded using a PIKE Technologies DiffusIR high-temperature cell, which gives the possibility to in situ record DRIFT spectra of the surface of solid catalyst samples at room temperature and above (up to 500°C). The cell is equipped with a device for feeding gases and steams which interact

Feed mixture, vol %	$DME(20) + N_2(80)$	$\frac{\text{DME}(20) +}{\text{H}_2\text{O}(25) + \text{N}_2(55)}$	$\frac{\text{DME}(20) +}{\text{H}_2\text{O}(50) + \text{N}_2(30)}$	$\frac{\text{DME}(20) +}{\text{H}_2\text{O}(75) + \text{N}_2(5)}$						
DME conversion, %	53.3	56.8	55.0	54.3						
Selectivity for hydrocarbons, wt %										
$C_2^=$	27.0	29.7	32.6	35.7						
$C_3^=$	34.9	29.7	27.9	30.1						
$\Sigma C_{4=}^+$	16.4	12.6	10.0	8.7						
$\Sigma C_2 - C_4^=$	69.3	67.9	67.4	71.5						
ΣC_{2^+}	19.2	26.0	27.0	23.5						
$C_{2}^{-}/C_{3}^{=}$	0.8	1.0	1.2	1.2						

Table 1. Effect of the steam content in the feed mixture on the selectivity for lower olefins in DME conversion over the La–Zr–HZSM-5/Al₂O₃ catalyst ($T = 350^{\circ}$ C, $W_{DME} = \text{const} = 4.1 \text{ h}^{-1}$. The feed mixture: DME + H₂O + N₂, the data for 4 h)

with the surface of the powder placed in a special ceramic crucible with the sample. The cell equipped with an electronic temperature controller was placed in the cell compartment of a VERTEX-70 Fouriertransform spectrometer. A weighted portion of the zeolite (20 mg) in a ceramic crucible was heated at 350–400°C until the complete dehydration of the surface. After that, the zeolite was cooled in a flow of high purity argon to 350°C and exposed to DME (10 vol %) mixed with nitrogen and steam fed at a flow rate of 0.3 L/h; the load on the catalyst in these experiments was 2.75 h⁻¹. Water vapor was added to the DME + N_2 mixture by bubbling the mixture through water at room temperature. DRIFT spectra were recorded during the feeding of DME at 350°C in a continuous mode every 5 min (200 scans) for 3 h (a recording range of $4000-600 \text{ cm}^{-1}$, a resolution of 2 cm^{-1}). The spectra of the catalysts were recorded and mathematically processed (baseline and normalization) under the same conditions; therefore, the relative intensity of the bands under discussion can serve as a criterion for the concentration of functional groups attributed to these bands. The mathematical processing was carried out using the OPUS-7 software package.

The catalysts were tested in a flow-type reactor described in [3]. DME was used as a feedstock; nitrogen and/or steam was used as a DME diluent. The DME concentration in the feed gas mixture was 5 to 65 vol %. The space velocity of the feed gas mixture was varied in a range of $2000-30000 \text{ h}^{-1}$. The reaction products were analyzed by GLC using a 27.5 m × 0.32 mm × 10 µm capillary column equipped with flame-ionization and thermal-conductivity detectors, a nonpolar CP-PoraPLOT Q phase as an adsorbent, and helium as a carrier gas. The resulting chromatograms were processed using the NetChromWin software. To provide a desired feed space velocity, the gas flow rate and the fluid flow rate were controlled with

RRG-10 gas flow regulators and a fluid pump, respectively.

RESULTS AND DISCUSSION

Initially, the effect of steam content in the feed mixture on the catalytic properties La–Zr–NZSM-5/ Al_2O_3 was studied. In this case, the starting point was the feed mixture composed of 20 vol % DME and 80 vol % N₂ 80. In the subsequent experiments, the DME concentration remained constant, while nitrogen was partially replaced by steam. The results are shown in Table 1.

It is evident from the table that an increase in the steam content in the feed mixture has little effect on the total selectivity for C_2-C_4 olefins; however, the selectivity for ethylene increases, while the selectivity for propylene slightly decreases. A significant decrease in the $\Sigma C_{4+}^{=}$. concentration is also observed. It should be noted that methanol was not detected in the reaction products.

The effect of the DME-to-steam ratio on the distribution of reaction products in the absence of nitrogen was studied at a constant DME load. It is evident from Table 2 that the selectivity for ethylene and propylene increases as this ratio decreases; in addition, the formation of ethylene occurs faster than the formation of propylene with increasing water content. The total selectivity for lower olefins also increases with a decrease in the selectivity for paraffins. In this case, the formation of methanol is not observed either.

Similar studies were conducted for Mg–HZSM- $5/Al_2O_3$. The results are shown in Fig. 1.

It is evident from the figure that the reaction products contain a large amount of methanol upon the addition of water to DME. Although the concentration of methanol decreases with increasing steam con-

Table 2. Effect of the DME-to-steam ratio on the selectivity for lower olefins in DME conversion over the La–Zr–HZSM-5/Al₂O₃ catalyst ($T = 350^{\circ}$ C, $W_{DME} = \text{const} = 4.1 \text{ h}^{-1}$, $U_{\text{lin}} = \text{const} = 0.04 \text{ m/s}$). The feed mixture: DME + H₂O, the data for 4 h)

	DME conversion, %	Selectivity, wt %					
Conditions		$C_2^=$	$C_3^=$	$\Sigma C_2^-/C_3^=$	$C_{2}^{=}/C_{3}^{=}$	$\Sigma C_2^-/C_4^=$	ΣC_{2^+}
DME : $H_2O = 50 : 50 \text{ vol }\%;$ $V_{DME : H_2O} = 2428.6 \text{ h}^{-1} (25.5 \text{ L/h});$ $W_{H_2O} = 1.6 \text{ h}^{-1}$	58.0	24.2	24.3	48.5	1.0	53.8	44.5
DME : $H_2O = 40 : 60 \text{ vol }\%;$ $V_{DME : H_2O} = 3500 \text{ h}^{-1} (24.5 \text{ L/h});$ $W_{H_2O} = 3.1 \text{ h}^{-1}$	55.0	19.2	31.2	50.4	0.6	58.0	40.7
DME : $H_2O = 20$: 80 vol %; $V_{DME : H_2O} = 5785.7 h^{-1} (27 L/h);$ $W_{H_2O} = 6.2 h^{-1}$	78.7	40.9	36.3	77.2	1.1	81.7	17.7
DME : $H_2O = 15 : 85 \text{ vol }\%;$ $V_{DME : H_2O} = 7692.3 \text{ h}^{-1} (25 \text{ L/h});$ $W_{H_2O} = 8.7 \text{ h}^{-1}$	66.0	41.4	35.3	76.7	1.2	81.2	18.3
DME : $H_2O = 5 : 95 \text{ vol } \%$; $V_{DME : H_2O} = 27931.0 \text{ h}^{-1} (27 \text{ L/h})$; $W_{H_2O} = 35.8 \text{ h}^{-1}$	70.6	46.0	26.4	72.4	1.7	76.3	23.4

tent, the amount of it remains dominant. An increase in the steam content and a decrease in the DME concentration in the feed mixture lead to a sharp increase in the selectivity for ethylene, while propylene increases insignificantly. It should be noted that the presence of water on the Mg–HZSM-5/Al₂O₃ catalyst has hardly any effect on the content of ΣC_{2^+} .paraffins.

Thus, we can state that the presence of steam has a significant effect on the ethylene-to-propylene ratio; in addition, depending on its concentration in the feed mixture, a more considerable increase in this ratio is observed on Mg–HZSM-5/Al₂O₃. In this case, methanol was formed only on Mg–HZSM-5/Al₂O₃; this is apparently attributed to the presence of more basic sites on which DME interacts with H₂O to form methanol.

The interaction between DME and the surface of Mg–HZSM-5/Al₂O₃ at a temperature of 350° C was studied by in situ DRIFT spectroscopy in the absence and presence of steam.

The spectrum of Mg–HZSM-5/Al₂O₃ heated at 350° C in an argon stream exhibits three bands from the isolated –OH bonds (3661 and 3720 cm⁻¹) and one band from the weakly associated –OH groups contained in the Brönsted acid site (BAS) at 3595 cm^{-1} (Fig. 2). The feeding of DME leads to almost a complete disappearance of the band at 3595 cm^{-1} (BAS) and a sharp decrease in the intensity

of the bands from the isolated –OH groups at 3661 and 3720 cm⁻¹; in this case, the broad band peaking at 3562 cm⁻¹ is the most intense; it can be attributed to methanol adsorbed on the surface. The spectra of the zeolite surface purged with a mixture of DME and water, along with the band at 3661 cm⁻¹, exhibit a new weak band from the isolated –OH groups at 3644 cm⁻¹. The intensity of the bands from these groups insignificantly decreases over time; however, the intensity of the bands in the spectra of the surface of Mg–HZSM-5/Al₂O₃–DME–H₂O is slightly higher than that of the bands in the spectra of Mg–HZSM-5/Al₂O₃–DME.

Thus, the flowing of DME through the zeolite leads to a complete disappearance of the band at 3595 cm^{-1} corresponding to the BAS, a sharp decrease in the intensity of the bands from the isolated -OH groups on the zeolite surface, and the occurrence of a band attributed to the surface of methanol at 3562 cm^{-1} . The presence of steam in the gas mixture leads to a higher intensity of the bands from the isolated -OH bonds and the appearance of a weak band at 3644 cm^{-1} , which is preserved throughout the experiment.

The disappearance of the band from the BAS and the decrease in the intensities of the bands at 3661 and 3720 cm^{-1} are accompanied by the appearance of a number of bands in a region of $3020-2800 \text{ cm}^{-1}$,



Fig. 1. Effect of steam in the feed gas mixture on the cataby properties of Mg–HZSM-5/Al₂O₃ in DME conversion (T = 350° C, W = 3.4-10.3 h⁻¹, DME conversion = const = 50%, P = 0.1 MPa, the flow rate of H₂O from the pump is 0.2 mL/min). The feed mixture (vol $\frac{1}{8}$): DME + H₂O. (1) MeOH, (2) $\Sigma C_2 - C_4$, (3) $\Sigma C_2^+ +$, (4) $C_3 =$, (5) C₂=, and (6) C₄=.

which are attributed to the stretching vibrations of the C-H bonds (Fig. 2). The absence of bands at 2998, 2925, and 2817 cm⁻¹, which are characteristic of the methyl groups in DME [4], suggests that even a 5-min contact between DME and the zeolite surface at a temperature of 350°C leads to an instantaneous conversion of DME. The two bands observed in the spectrum of the zeolite surface after a 5-min contact between DME and the surface at 2848 and 2956 cm⁻¹

Coord. K-M

can be attributed to the methoxy groups (CH_3 –O–Al) formed on the surface [5, 6]. The bands from the C–O bonds in the methoxy groups in a region of 1084 cm⁻¹ [7] can be observed in the spectra of the surface of Mg-HZSM-5/Al₂O₃-DME, and its intensity decreases with increasing time of interaction with DME. This band in the spectrum of Mg-HZSM-5/Al₂O₃-DME (30-min contact) has a medium intensity (Fig. 3): however, in the spectrum of Mg-HZSM-5/Al₂O₃-DME-H₂O recorded under the same conditions, this band is absent, while the intensity of the band at 1047 cm⁻¹, which is the strongest band in the spectrum of methanol, sharply increases. The formation of methoxy groups on the zeolite surface can occur during the interaction between DME and the basic sites on the zeolite surface, which correspond to the band at 3720 cm⁻¹, according to Scheme 1:

The methoxy groups formed on the surface in the presence of steam can be easily converted to methanol to form a new isolated -OH group (Scheme 2), a band from which is detected in the spectrum at 3644 cm⁻¹ (Fig. 2).

$$\begin{array}{c} \text{OCH}_3 & \text{OH}\\ \text{Al}\\ \text{Al} \end{array} + \text{HOH} \longrightarrow \text{CH}_3\text{OH} + \begin{array}{c} \text{H}\\ \text{Al}\\ \text{HOH} \end{array}.$$
Scheme 2





Fig. 2. Comparison of the spectra of the surface of Mg–HZSM-5/Al₂O₃ at 350°C in a stream of (1) Ar; (2) DME, 5 min; (3) DME, 30 min; (4) DME, 120 min; (5) DME + H₂O, 5 min; (6) DME + H₂O, 30 min; and (7) DME + H₂O, 120 min.



Fig. 3. Comparison of the spectra of the surface of (1) Mg $-HZSM-5/Al_2O_3-DME-H_2O$ and (2) Mg $-HZSM-5/Al_2O_3-DME$ after a 30-min contact in the region of absorption of MeOH.

Owing to this, the amount of methanol on the surface of Mg–HZSM-5/Al₂O₃–DME–H₂O is significantly higher than that detected on the surface of Mg–HZSM-5/Al₂O₃–DME under the same conditions (Fig. 3). The intensity and position of the bands of the stretching vibrations of CH in a region of 3200– 2800 cm^{-1} (Fig. 2) continuously change as the time of flowing of DME through the zeolite increases; however, the intensity of the bands on Mg–HZSM-5/Al₂O₃–DME is always higher than in the experiment on Mg–HZSM-5/Al₂O₃–DME–H₂O.

It should also be noted that no absorption bands corresponding to the formation of methanol are observed during the feeding of DME over $La-Zr-HZSM-5/Al_2O_3$.

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