

Study of Magnesium-Containing Zeolite Catalysts for the Synthesis of Lower Olefins from Dimethyl Ether

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Abstract—The catalytic properties of magnesium-containing zeolite catalysts in the synthesis of olefins from dimethyl ether (DME) were studied. The optimal concentrations of magnesium in the zeolite catalyst were found, and a procedure for its introduction was developed. The effect of the operation conditions of DME conversion into lower olefins on the catalyst activity and selectivity was studied. The stability of the catalytic properties of the synthesized catalyst after oxidative regeneration was examined.

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Recently, we have found that in the DME conversion into lower olefins ethanol is a primary precursor of ethylene and is formed mainly via isomerization of dimethyl ether [1]. The introduction of ethanol formation-promoting components into the zeolite catalyst should enhance the selectivity for lower olefins in the DME conversion. Magnesium is well known to be an element that participates in the isomerization of hydrocarbons with functional groups [2–4]. In order to develop a selective catalyst for the synthesis of lower olefins (ethylene, propylene, and butylenes) from DME, we studied the catalytic properties of zeolite catalysts containing magnesium and the influence of the operation conditions on the activity, selectivity, and stability of these catalysts.

EXPERIMENTAL

The chemical used as the feedstock was DME (99.8%) produced at the OAO “Azot” Novomoskovsk joint stock company.

In the synthesis of lower olefins from DME, catalyst samples based on ZSM-5 zeolite (the high-silica zeolite TsVM, the domestic analog of ZSM-5, with a $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio of 37 (OAO Angarsk Catalyst and Organic Synthesis Plant) containing at most 0.04 wt % sodium oxide) were studied. The hydrogen form of the zeolite (HZSM-5) with a given residual content of sodium oxide is obtained via double cation exchange of Na^+ in a 1 N ammonium nitrate solution with consequent drying and calcination for 4 h at 500°C.

The zeolite-containing catalysts were obtained by mixing the zeolite HZSM-5 with a binder, alumina suspension containing 23 wt % dry Al_2O_3 (ZAO Industrial Catalysts, Ryazan) and consequent formation of granules, (extrudates) with an Al_2O_3 content of 33–

34 wt % in the resulting catalyst. The extrudates were successively dried in air and in a drying cabinet and calcined at 500°C for 4 h. Magnesium was introduced into the zeolite via ion exchange either before mixing with the binder (Al_2O_3) or by impregnating the prepared HZSM-5/ Al_2O_3 extrudates with an aqueous solution of its salt.

Experiments were carried out in a laboratory setup with a flow microreactor. Nitrogen was used as the DME diluent. The fused-silica flow reactor was loaded with the catalyst (0.2–1.0 g, of a 0.4–0.6 mm and coarser fraction). The catalyst was activated in a He stream at 400–450°C. The required reactant feed space velocity (500–10000 h^{-1}), temperature (320–450°C), and pressure (~1 atm) were established. Liquid products were condensed in a receiver, and the gas stream through a dosing valve was sent to a chromatograph for analysis. The DMA conversion products were determined on the Kristallyuks 4000M chromatograph with a flame ionization detector, a capillary column (27.5 m \times 0.32 mm \times 10 μm), and the nonpolar CP-PoraPLOT Q phase as an adsorbent, which is reasonably efficient for the separation of the main groups of products (DME, CH_3OH , C_1 – C_6 hydrocarbons). The analysis was carried out in the temperature-programmed mode (80–150°C at a heating rate of 30°C/min) with helium as a carrier gas (30 ml/min). The chromatograms were processed with the NetChromWin program.

RESULTS AND DISCUSSION

To select a procedure for the preparation of the magnesium-containing catalyst, we examined the catalytic properties of the samples prepared by various methods of magnesium introduction (Table 1). The DME conversion is altered insignificantly by changing

Table 1. Effect of the procedure of magnesium introduction into the zeolite catalyst on the catalytic properties

Magnesium introduction procedure	Conversion, %	Selectivity, wt %							
		CH ₄	C ₂ ⁼	C ₃ ⁼	C ₄ ⁼	C ₅ ⁼	Σ C ₂ –C ₄ ⁼	Σ C ₂₊	C ₂ ⁼ /C ₃ ⁼
Ion exchange	69.2	2.7	29.4	15.2	4.6	0.1	49.2	48.0	1.9
Ion exchange without zeolite washing	67.4	2.2	30.8	19.2	6.3	0.2	56.3	41.3	1.6
Impregnation of extrudates with zeolite pretreatment with water	70.5	1.9	26.7	15.3	11.0	0.1	53.0	45.0	1.7
Impregnation of extrudates	69.3	0.7	33.1	29.3	1.2	0.8	63.6	34.9	1.1

Note: Conditions: $T = 320^{\circ}\text{C}$, $P = 0.1\text{ MPa}$, feed mixture: 20% DME + 80% N₂, $v_0 = 2000\text{ h}^{-1}$, magnesium content, 0.1 wt %.

Table 2. DME conversion under the olefin synthesis conditions

Catalyst	Conversion, %	Selectivity, wt %							
		CH ₄	C ₂ ⁼	C ₃ ⁼	C ₄ ⁼	C ₅ ⁼	Σ C ₂₊	Σ C ₂ –C ₄ ⁼	C ₂ ⁼ /C ₃ ⁼
HZSM/Al ₂ O ₃	94.3	1.1	21.6	23.3	11.5	6.8	35.8	56.4	0.9
La-Zr/HZSM/Al ₂ O ₃	70.0	2.5	26.0	44.4	6.4	3.6	17.1	76.8	0.6
Mg/HZSM/Al ₂ O ₃	85.6	weak	33.6	21.6	12.0	2.4	30.4	67.2	1.6

Note: $T = 340^{\circ}\text{C}$, $P = 0.1\text{ MPa}$, feedstock: DME + N₂, $v_0 = 2000\text{ h}^{-1}$.

the procedure. However, the ratio between lower olefins components and their total yield substantially depends on the procedure of magnesium introduction into the zeolite catalyst. The ethylene/propylene ratio varies twofold from 1.9 to 1.1. In actual practice, it is possible to vary the output of ethylene, propylene, and butylenes depending on the demand. The best results with respect to the total yield of lower olefins were obtained in the case of magnesium deposition by impregnating the finished HZSM/Al₂O₃ extrudates. The propylene yield was substantially higher on this sample, and the methane yield was the lowest.

Based on the obtained results, the further investigation was performed with the samples prepared by the impregnation of the finished catalyst extrudates, when magnesium modifies not only the zeolite component, but also the alumina binder.

The study of the effect of the magnesium concentration in the zeolite catalyst on its catalytic properties in DME conversion at various temperatures (Table 2) has shown that the DME conversion decreases and the selectivity for C₂–C₄ olefins passes through a maximum with an increase in the magnesium concentration in the catalyst. The best results were obtained on a catalyst containing 1.0 wt % magnesium. The overall selectivity for C₂–C₄ olefins is ~80.8 wt %, of which almost 80 wt % is made by ethylene and propylene. A high yield of butylenes (up to 14.6 wt %) is observed for the magnesium-containing catalysts at 360°C, which may be of practical interest. The ethylene/propylene ratio decreases insignificantly with an increase in the amount of magnesium introduced. The total yield of

alkanes decreases pronouncedly with an increase in the magnesium concentration up to 1.0 wt %, and remains almost unchanged upon further increase in the magnesium content in the catalyst (Table 2). The observed enhancement of the selectivity for butylenes and total alkanes and a simultaneous decline in the selectivity for ethylene and propylene with an increase in the temperature from 320 to 360°C indicate that the activation energy of the ethylene and propylene formation is lower than that of the formation of alkanes and olefin polymerization.

Interestingly, the methane formation is low on the magnesium-containing zeolite catalysts, thus increasing substantially the selectivity of the process as a whole.

The comparison of the magnesium-containing zeolite catalysts with the lanthanum–zirconium-promoted [5] and the decationized catalysts (Table 3) investigated in detail earlier shows that the introduction of magnesium in the zeolite catalyst enhances (relative to the decationized sample of the zeolite catalyst) the selectivity for lower olefins by more than 10 wt % with a decrease in the DME conversion from 94.3 to 85.6 wt %. Simultaneously, the ethylene/propylene ratio increases drastically from 0.9 to 1.6; i.e., the introduction of magnesium results in a preferential increase in the ethylene selectivity and the corresponding decrease in the selectivity for butylenes and amylenes. The relative amount of alkanes in the reaction products decreases. Interestingly, the selectivity for ethylene and butenes is lower for the lanthanum- and zirconium-containing zeolite catalyst than that

Table 3. Effect of the superficial velocity of the feed gas mixture on the DME conversion and the distribution of reaction products

m/V , g/ml of catalyst	Superficial velocity, m/s	t , h	Conversion, %	selectivity, wt %							
				CH ₄	C ₂ ⁼	C ₃ ⁼	C ₄ ⁼	C ₅ ⁼	ΣC ₂ –C ₄ ⁼	ΣC ₂₊	C ₂ ⁼ /C ₃ ⁼
1.0/2.0	2.5×10^{-2}	1	100	0.7	15.5	30.6	14.5	4.6	60.6	34.1	0.51
		5	100	0.7	15.2	32.4	15.8	4.8	63.4	31.1	0.47
0.5/1.0	1.2×10^{-2}	1	100	0.6	14.5	29.0	16.0	7.1	59.5	32.8	0.50
		5	100	0.7	14.7	31.7	18.2	4.9	64.5	29.9	0.46
0.3/0.6	7.4×10^{-3}	1	100	0.6	15.1	30.7	15.3	4.5	61.2	33.7	0.49
		5	100	0.7	15.1	32.3	17.1	4.7	64.5	30.0	0.47

Note: $T = 450^\circ\text{C}$, $P = 0.1$ MPa, feedstock: 10% DME + N₂, $v_0 = 2000 \text{ h}^{-1} = \text{const}$, $w_{\text{DME}} = 0.75 \text{ h}^{-1} = \text{const}$.

Table 4. Effect of the catalyst particle size on the DME conversion and the product distribution

Catalyst fraction, ml	m/V , g/ml of catalyst	t , h	Conversion, %	Selectivity, wt %							
				CH ₄	C ₂ ⁼	C ₃ ⁼	C ₄ ⁼	C ₅ ⁼	ΣC ₂ –C ₄ ⁼	ΣC ₂₊	C ₂ ⁼ /C ₃ ⁼
0.2–0.4	0.5/1.0	1	100	0.7	14.8	35.5	17.4	5.1	67.7	26.5	0.42
		5	100	1.0	14.8	35.4	17.9	5.8	68.1	25.1	0.42
0.4–0.6	0.5/1.0	1	100	0.6	14.5	29.0	16.0	7.1	59.5	32.8	0.50
		5	100	0.7	14.7	31.7	18.2	4.9	64.5	29.9	0.46
0.6–1.0	0.5/1.05	1	100	0.6	15.7	31.9	14.9	4.7	62.6	32.1	0.49
		5	100	0.7	15.4	33.9	16.7	5.1	66.0	28.2	0.45
1.0–1.6	0.5/1.06	1	100	0.7	13.9	31.6	16.8	4.7	62.3	32.3	0.44
		5	100	0.6	15.1	34.3	16.8	5.5	66.1	27.8	0.44

Note: $T = 450^\circ\text{C}$, $P = 0.1$ MPa, feedstock: 10% DME + N₂, $v_0 = 2000 \text{ h}^{-1} = \text{const}$, $w_{\text{DME}} = 0.8 \text{ h}^{-1} = \text{const}$.

for the magnesium-containing sample by 7.6 and 5.6 wt %, respectively, whereas the propylene selectivity is substantially higher (by 22.8 wt %). Therefore, the selectivity for C₂–C₄ olefins increases by 76.8 wt %, but the ethylene/propylene ratio decreases down to 0.6. Under conditions accepted for the comparison, the yield of alkanes is lower on the lanthanum–zirconium-containing zeolite catalyst than that on the magnesium-containing catalyst, but the yield of methane is significantly higher; i.e., the appearance of strong acid sites characteristic of the lanthanum- and zirconium-containing catalysts results in the enhancement of methane formation.

The comparison of the lanthanum–zirconium-containing and magnesium-containing zeolite catalysts shows that each of them is applicable in practice, depending on the plant demand for one or another olefin.

In view of the potential use of the magnesium-containing zeolite catalyst, we studied the effect of certain processing parameters on the DME conversion and the selectivity for olefins.

First, in order to estimate the possible effect of the external diffusion limitation in the DME conversion

into olefins, the experiments at various superficial velocities of the feedstock in the reactor at a constant feed space velocity per catalyst unit volume were carried out (Table 3). In order to estimate the possible effect of the internal diffusion limitation, the catalytic properties were studied for catalyst sample with various particle sizes (Table 4).

The experiments were carried out at 450°C, the highest temperature possible for this reaction, because the external and internal diffusion retardation increases with an increase in the temperature. One can see from the data presented, the external and internal diffusion retardation is insignificant even at the highest temperature, therefore, it can be concluded with certainty that the reaction proceeds in the kinetic region at the test temperatures.

In further experiments, the variable parameters of the process were changed in the temperature range of 320 to 450°C and the feed space velocity range from 500 to 10000 h^{–1}.

The data on the DME conversion and the product selectivity for the extreme values of the temperatures at different feed space velocities are given in Fig. 1 and Table 5. The DME conversion rate at 450°C is so high

Table 5. Effect of the space velocity of the feed gas mixture on the DME conversion and the product distribution ($T = 320^{\circ}\text{C}$, $P = 0.1\text{ MPa}$).

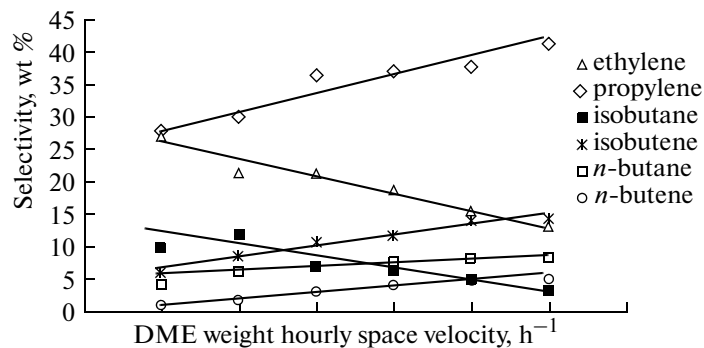
Space velocity, h^{-1}	Conversion, %	Selectivity, wt %							
		CH_4	$\text{C}_2^=$	$\text{C}_3^=$	$\text{C}_4^=$	$\text{C}_5^=$	$\Sigma\text{C}_2-\text{C}_4^=$	ΣC_{2+}	$\text{C}_2^=/\text{C}_3^=$
2000	94.0	0.6	48.7	27.0	2.2	0.1	77.9	21.4	1.8
3000	57.9	weak	38.2	40.5	1.7	0.6	80.5	18.9	0.9
4000	48.2	weak	37.5	41.0	2.2	1.1	80.7	18.2	0.9
5000	32.0	weak	35.5	41.9	1.7	1.6	79.1	19.2	0.9
6000	26.1	weak	35.5	41.6	1.4	1.7	78.5	19.7	0.9
7000	28.0	weak	35.2	42.0	1.7	1.8	78.9	19.3	0.8

that the degree of conversion is 100 wt % over the entire space-velocity range examined. However, an increase in the feed weight hourly space velocity (WHSV) results in a substantial change of the product composition at the constant 100% DME conversion due to the change in the conditions of occurrence of secondary reactions (Fig. 1). A decrease in the space time (growth of WHSV) is most likely unfavorable for the secondary reactions. A regular increase in the propylene yield accompanied by an almost equivalent decrease in the ethylene yield is observed. The propylene/ethylene ratio is 3.1 at the highest WHSV equivalent to the liquid space velocity of 6 h^{-1} and varies toward the value obtained in the Lurgi methanol-to-propylene process [6–11].

It should be pointed out that there is correlation between the yield of isobutane and ethylene on one hand and the yields of isobutene and *n*-butene with propylene on the other hand. Similarly, the yield of amylene decreases and that of alkanes increases with an increase in the space time; i.e., there is interrelation between the olefin formation stages and the hydrogen transfer stages yielding alkanes. This indicates that the mechanism of the olefin formation at high tempera-

ture is very complex. In fact, the product composition observed at high temperature is determined by the mechanism of the secondary transformation reactions of olefins and alkanes that have been formed at a high rate in the primary reactions, with the propylene selectivity being inversely proportional to the isobutane selectivity (Fig. 2). A similar dependence is observed in the catalytic cracking of hydrocarbons on zeolite-containing catalysts [12].

Unlike the case of the reaction temperature of 450°C , the DME conversion decreases with a decrease in the space time, and the selectivity for alkanes is independent of the space time at low temperatures (Table 5). The selectivity for butylenes and amylenes is very low and does not exceed 3–4 wt % in total. The selectivity for ethylene and propylene is high (75.7–78.5 wt %) and almost does not depend on the DME conversion. This indicates strong differences in the mechanism of the formation of olefins in the primary and secondary reactions. At a high DME conversion corresponding to the feed space velocity (2000 h^{-1}), the contribution of the secondary reactions is manifested and a rise in the ethylene yield and a fall in the propylene yield are observed (Table 5).

**Fig. 1.** Effect of the DME weight hourly space velocity on the distribution of the reaction products (DME conversion = 100 wt %, $T = 450^{\circ}\text{C}$, $P = 0.1\text{ MPa}$).

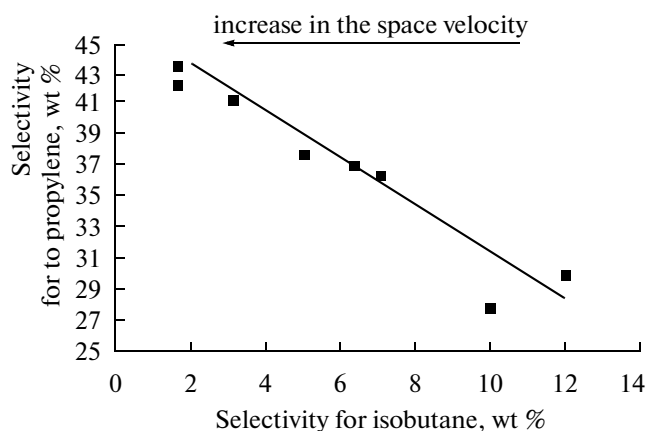


Fig. 2. Interrelation between the formation of propylene and isobutane in the DMA conversion into olefins (DMA conversion = 100 wt %, $T = 450^{\circ}\text{C}$, $P = 0.1\text{ MPa}$).

The assumption that the contribution of secondary reactions to the reaction mechanism, rather than the decrease in the amount of DME adsorbed under the reaction conditions, manifests itself at a high DME conversion is confirmed by the fact that the selectivity for olefins at the same conversion does not depend on the DME concentration in the stream. In this case, a rise in the olefin yield is observed even at a high DME conversion.

The magnesium-containing zeolite catalyst is relatively stable in operation after multiply repeated oxidative regeneration cycles. The data show that the oxidative regeneration of the catalyst almost does not alter its catalytic properties; even a slight increment in the DME conversion is observed.

Thus, the introduction of magnesium into the zeolite-containing catalyst substantially enhances the selectivity for $\text{C}_2\text{--C}_4$ olefins (80.8 wt %), of which ethylene and propylene make almost 80 wt %. A variation in the space velocity of the feedstock and the reaction

temperature makes it possible to pass from the primary to the secondary reactions and to control the ratio between ethylene, propylene, and butenes over a wide range. The synthesized catalyst retains a high activity and selectivity after oxidative regeneration.

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