

CATALYTIC CONVERSION OF DIMETHYL ETHER TO ETHYLENE AND PROPYLENE

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Abstract. *In this work, the results on the creation of highly efficient catalytic systems with new content modified with various elements are summarized. At the same time, the effect of the nature of the modifying element, as well as the high-temperature treatment with water vapor, on the texture, acidic characteristics and catalytic properties of the zeolite catalyst in the conversion of dimethyl ether to ethylene and propylene was considered. In order to increase the stability of the Mg-Zn-Zr-B/YuKTs catalyst, it was proved that unmodified Mg-Zn-Zr-B/YuKTs exhibited high activity when it was modified with P and Fe and used in the synthesis of ethylene and propylene from methanol and dimethyl ether. In the work, the catalytic conversion of dimethyl ether to ethylene and propylene was carried out on the Mg-Zr-Zn-B-YuKTs catalyst under the following optimal conditions: ($T = 340\text{ }^{\circ}\text{C}$, $R = 0.1\text{ MPa}$, $V_{ar} = 1000\text{-}2000\text{ h}^{-1}$. Raw materials: DME (15%) ÷ N_2 (85%). In the case of modification of zeolite catalysts containing zirconium and magnesium with B, it was proved that in almost all cases, an increase in the selectivity for $C_2\text{-}C_4$ ethylene and propylene and a decrease in the amount of paraffins were observed. According to the obtained results, with an increase in zirconium concentration from 0.4 to 3.2 wt.%, there is an increase in the selectivity for $C_2\text{-}C_4$ ethylene and propylene from 42.1 to 74.5 wt.%. Paraffins are formed from 0.4 wt.% to 57 wt.% of zirconium. Thus, Mg-Zn-Zr-B/YuKTs is an effective catalyst of methanol to ethylene and propylene, the addition of water to the raw material as a diluent significantly increases the activity of the catalyst and the yield of target products increases and the time of stable operation of the catalyst increases.*

Also, as a result of studying the textural and physicochemical characteristics of the catalyst by IR-spectroscopy, differential thermal analysis and thermogravimetry methods, it was proved that the treatment of zeolite with zirconium and boron compounds does not lead to the destruction of the zeolite structure.

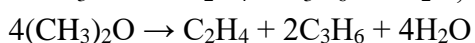
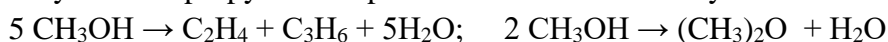
Keywords: *dimethyl ether, methanol, ethylene, propylene, conversion, catalyst, synthesis, kinetic law.*

INTRODUCTION

Purpose of work is to study the catalytic conversion of dimethyl ether to ethylene and propylene in the Mg-Zr-Zn-B-YuKTs catalyst.

Currently, methanol synthesis is carried out on Cu/ZnO/Al₂O₃ catalyst at temperatures of 270-300°C under pressure of 5-10 MPa[1].

Ethylene and propylene are produced from methanol by two reactions:



The first method is based on obtaining ethylene and propylene by direct conversion of methyl alcohol in silicoaluminophosphate catalysts at temperatures of 450-550°C. The second

method is based on obtaining ethylene and propylene in 99.6-99.8% purity and 70-90% yield in ZSM-5 type zeolites at temperatures of 430-550°C by dehydrating methanol, and propylene is produced more in this process [2-3].

Currently, processes for obtaining ethylene and propylene and polyethylene and polypropylene from methanol and dimethyl ether compete with the processes of naphtha pyrolysis and ethane cracking currently used in industry.

The development of this method is accelerated by the increase in demand for consumer products [4-5]. Today, the world production of ethylene and propylene is 280 mln. exceeded tons[6]. The demand for ethylene and propylene is especially high, they account for more than 96% of the total volume of production of unsaturated hydrocarbons [7-9], the volume of production capacity has doubled since the beginning of the century.

The most common catalysts in the synthesis of ethylene and propylene from dimethyl ether are high-silica zeolites of the ZSM type.

The influence on the properties of zeolite catalysts consists of modification with metal compounds[5-9], which leads to changes in their texture and acidic properties[10-12]. The influence of the nature of the modifying element on the properties of zeolite catalysts [13-17] has been widely studied, but until now, no unified theory has been developed to understand the role of the nature of the modifying element in the change of their catalytic properties [18-21]. A change in acidic properties can be achieved by pre-treatment of catalysts at high temperature or by changing the amount of water in the initial feedstock.

EXPERIMENTAL PART

In the work, high silicon zeolite with $\text{SiO}_2/\text{Al}_2\text{O}_3=26$ mol ratio was used [22-25]. Zirconium and zinc were added to the catalysts by means of ion exchange. Boron was introduced by absorbing granules obtained by extrusion from a mixture of zeolite with a binder.

Tests of catalyst samples in the conversion of dimethyl ether to ethylene and propylene were conducted in a microcatalytic flow device at a pressure of 0.1 MPa and a temperature range of 270-450°C. The flow rate of the initial gas mixture was changed in the range of 500-1500 h^{-1} , the concentration of dimethyl ether in the initial mixture was 10% by volume. Catalyst weight (0.5 g, 1 cm^3), 2 cm^3 quartz nozzles were loaded into the reactor. Catalytic conversion of methanol to ethylene and propylene was studied on Mg-Zn-Zr-B/YuKTs catalyst.

IR-spectroscopy, differential thermal analysis, and thermogravimetric methods were used to study structural and textural characteristics of zirconium- and magnesium-retaining samples; also, the adsorption capacity of zeolite for benzene was measured by calculating the threshold values of adsorption using the Dubinin equation. The acidic properties of the catalysts were studied by the method of temperature-programmable desorption of ammonia.

Catalyst tests were conducted in a device with a flow-type reactor at a temperature of 320-380 °C and atmospheric pressure. The volume of the catalyst was varied between 3 and 10 cm^3 .

To determine the topography of the sample surface, the powder was placed in a JEOL JSM6390A scanning electron microscope. A sample of the studied powder is placed on a carbon tape for analysis. Non-solid particles were removed from the tape surface. The elemental composition of the obtained products was determined using X-ray spectral microanalysis (RSMA) with a JEOL JED-2200 EDS attachment on a JEOL JSM6390A scanning electron microscope.

The phase composition of the synthesis products was determined using X-ray phase analysis (XPA). X-ray spectra were recorded on an ARL X'trA automated diffractometer (Thermo

Scientific) using CuK_α radiation at a 2-degree angle scanning from 10 degrees to 80 degrees at a rate of 2 degrees. Olingan spektrlar maxsus WinXRD dasturiy to'plami yordamida qayta ishlandi. Kristalitning kattaligi diffraktogrammada interferentsiya chizig'ining kengayishi hisobiga aniqlangan.

The study of the porous structure of the sample was carried out using the temperature adsorption method of nitrogen on the ASAP-2010 device of Micromeritics. First, the sample was vacuumed to 0.4 Pa at a temperature of 350 °C. N_2 adsorption was carried out at 77K.

Acidic properties were studied by the method of thermoprogrammed desorption of ammonia in a universal sorption gas analyzer USGA-101.

The qualitative and quantitative composition of the reaction products was analyzed by the chromatographic method in the "Crystal 5000" chromatograph with a capillary column and a flame-ionization detector. The amount of hydrogen and carbon oxides was determined on a "Crystal-5000" chromatograph equipped with a thermal conductivity detector and a PropakQ phase retention column.

DISCUSSION OF RESULTS

Initially, the effect of boron on the catalytic properties of zirconium- and magnesium-supported zeolite catalysts was investigated for the conversion of dimethyl ether to ethylene and propylene. When modifying these catalysts with boron, in almost all cases, an increase in the selectivity for $\text{C}_2\text{-C}_4$ ethylene and propylene and a decrease in the amount of paraffins were observed (Table 1). Modification of Zr-YuKTs with magnesium leads to a significant increase in ethylene selectivity from 18.6 to 29.2 wt.%. The proportion of propylene and butenes in the Zr-Mg-YuKTs catalyst is slightly higher than that of Mg-YuKTs.

Table 1

Conversion of dimethyl ether to ethylene and propylene on zeolite catalysts

Catalyst	Selectivity, mas %			
	Ethylene and propylene			Paraffins C_{1+}
	C_2	C_3	$\sum \text{C}_2\text{-C}_3$	
IOKI	12,9	18,7	31.6	39,5
Zr-IOKI	18,6	32,3	50.9	28,4
Mg-IOKI	19,8	33,1	52.9	27,6
Mg-Zr-IOKI	29,2	34,4	63.6	25,9
Mg-Zr-Zn-IOKI	31,7	34,2	65.9	25,7
Mg-Zr-Zn-B-IOKI	32,5	35,2	67.7	19,7

Conditions: $T = 340\text{ }^\circ\text{C}$, $R = 0.1\text{ MPa}$, $\text{Var} = 500\text{-}1500\text{ h}^{-1}$. Conversion of dimethyl ether = 65-75%. Raw materials: DME (15%) ÷ N_2 (85%).

As can be seen from Table 1, in the presence of a Mg-YuKTs catalyst, the selectivity to ethylene is 19.8%, the selectivity to propylene is 33.1%, and the selectivity to paraffins is 27.6%. In the presence of Mg-Zr-Zn-B-YuKTs catalyst, selectivity to ethylene is 32.5%, selectivity to propylene is 35.2%, and selectivity to paraffins is 19.7%.

The modification of Zr-YuKTs and Zn-YuKTs samples with magnesium and boron led to a significant decrease in the total amount of acidic centers, and the zinc-retaining catalyst has a small amount of superacidic centers, unlike the zirconium-retaining catalyst (Table 2).

Table 2

Distribution of the amount of acidic centers according to the desorption activation energies of ammonia

Catalyst	Total amount of acidic centers, $\mu\text{mol/g}$	The amount of centers ($E < 130$ kJ/mol), $\mu\text{mol/g}$	The amount of centers ($130 < E < 180$ kJ/mol), $\mu\text{mol/g}$	The amount of centers ($E > 180$ kJ/mol li) $\mu\text{mol/g}$
IOKI I	700	275(36%)	485(64%)	-
IOKI I	880	340(38%)	540(61,3%)	5(0,7%)
Zr-IOKI I	700	275(35%)	455(65%)	-
Mg-IOKI I	680	340(50%)	335(49,3%)	5(0,7%)
Mg-Zr-IOKI I	630	340(54%)	290(46%)	-
Mg-Zr-Zn-IOKI I	450	260(58%)	180(40%)	10(2%)
Mg-Zr-Zn-B-IOKI I	445	220(49%)	165(37%)	60(13%)

The addition of boron(B) to Mg-Zr-Zn-YuKTs also caused a decrease in total acidity, a decrease in the percentage of medium-strength acidic centers, and a significant increase in the amount of superacidic centers.

Thus, the Mg-Zr-Zn-B-YuKTs catalyst is an effective catalyst for the synthesis of molecular ethylene and propylene from dimethyl ether, but the amount of isoparaffins in the liquid product is slightly lower than that of the Mg-Zr-YuKTs sample, which is due to the presence of superacidity.

By changing the contact time, a significant increase in the selectivity for gasoline hydrocarbon components was achieved up to 86 wt.%, but the percentage of isoparaffins decreased by 10%, and the amount of aromatic hydrocarbons increased almost twice, while maintaining the high catalytic activity of the Mg-Zr-Zn-B-YuKTs system. It was 46.1% by mass (Table 3).

Table 3

Effect of contact time on activity and selectivity of Mg-Zr-Zn-B-YuKTs system

1/W, ch	Conversion (%)	Selectivity, mas. %		Hydrocarbon composition of the resulting products, % macc				
		Gas	Selectivity to hydrocarbons, %	Isoparaffins	Normal paraffins	Cycloparaffins	An aromatic hydrocarbon	Olefins
0,094	99,8	34,9	75,1	57,0	7,9	6,6	28,6	6,5
0,189	99,5	23,7	76,3	51,4	4,3	3,4	33,9	7,0
0,37	99,5	13,8	86,2	46,5	2,4	5,0	46,1	8,1

Oxidative regeneration of Mg-Zr-Zn-B-YuKTs catalyst at high temperature did not affect the activity of the catalyst. There was a slight increase in the selectivity of gasoline hydrocarbon components and a change in the distribution of hydrocarbon products: after regeneration, the amount of isoparaffins decreased from 57 to 43 wt.%, and the amount of aromatic hydrocarbons in liquid products increased sharply and was about 50 wt.% compared to the new sample.

In order to increase the stability of the Mg-Zn-Zr-B/YuKTs catalyst used in the synthesis of ethylene and propylene from methanol and dimethyl ether, various modifiers such as P and Fe were added and experiments were conducted. As a result of the conducted experiments, it was proved that modification with P and Fe leads to a decrease in the yield of ethylene and propylene. Thus, unmodified Mg-Zn-Zr-B/YuKTs show high activity, the decrease in catalyst activity over time, i.e. decrease in ethylene and propylene yield, is due to coking of acid centers of the catalyst and clogging of thin pores and channels of zeolite.

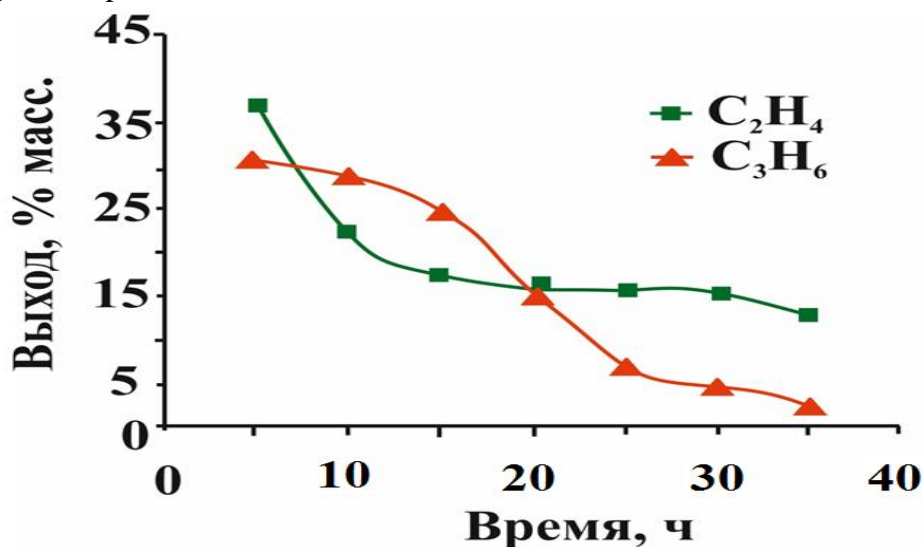


Figure 1. Dependence of ethylene and propylene yields on catalyst operating time ($=1000$ hours $^{-1}$, $T=340$ °C, $P=0.1$ MPa)

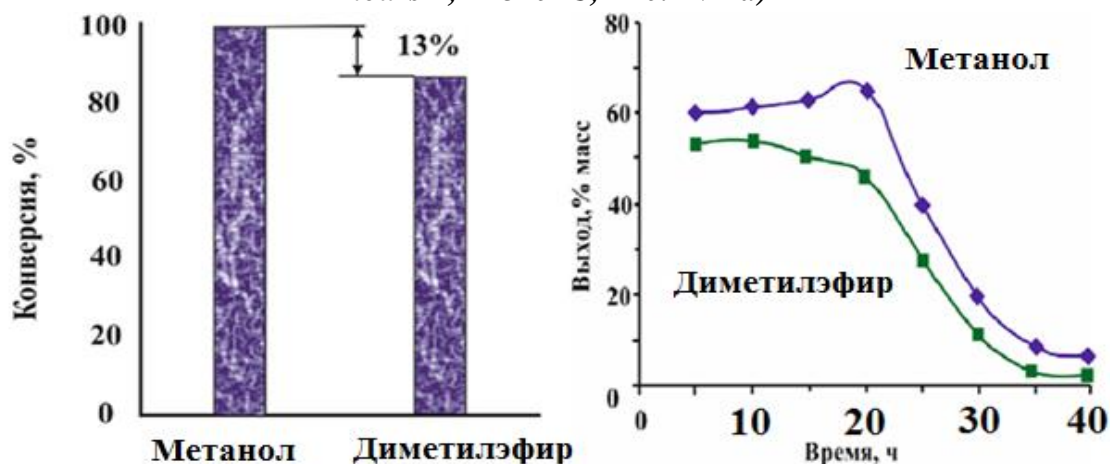


Figure 2. Conversion of dimethyl ether and methanol in Mg-Zn-Zr-B/YuKTs ($=1000$ h $^{-1}$, $T=340$ °C, $P=0.1$ MPa)

For some processes carried out on zeolite catalysts, the addition of water increases the catalyst residence time. In this regard, the effect of Mg-Zn-Zr-B/YuKTs catalytic water was investigated.

As can be seen in Table 4, the addition of water to the raw material slightly increases the yield of ethylene and propylene, but the working time of the catalyst increases by ≈ 2 times. In this case, the yield of ethylene is much higher than when pure methanol is used.

Table 4

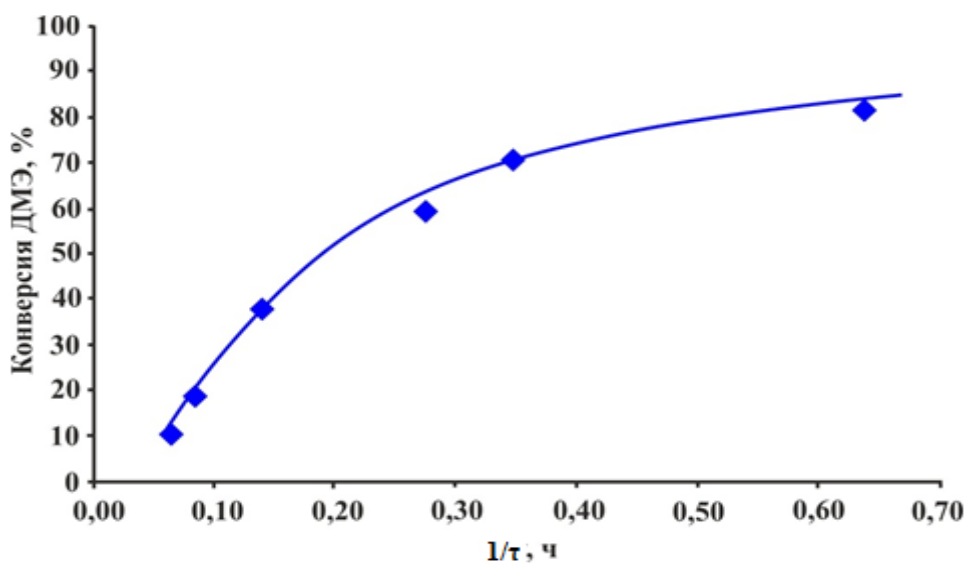
Dependence of the yield of ethylene and propylene on the working time of the catalyst based on Mg-Zn-Zr-B/YuKTs in the presence and absence of water in the raw material ($V_{N_2}=1000$ hour⁻¹, $V_{Methanol}=15$ coam⁻¹, $T=340^\circ C$, $P=0,1$ MPa)

Catalyst working time	Methanol			Methanol+water		
	Ethylene	Propylene	Butene	Ethylene	Propylene	Butene
5	19,8	40,4	18,6	25,4	35,5	13,8
10	22,2	38,6	16,8	25,9	35,8	12,9
15	26,6	37,5	11,4	28,2	34,7	12,6
20	30,4	35,2	9,4	31,5	34,7	11,5
25	15,4	25,3	7,4	29,4	30,5	10,9
30	6,7	5,7	2,8	27,4	27,2	10,3
35	3,5	5,4	2,9	24,4	25,7	9,8
40	1,6	3,9	3,5	20,6	22,8	9,9

Because water molecules blocking strong acid centers prevent ethylene from turning into hydrocarbons of high molecular mass.

Thus, Mg-Zn-Zr-B/YuKTs is an effective catalyst of methanol to ethylene and propylene, the addition of water to the raw material as a diluent significantly increases the activity of the catalyst and increases the yield of the target products and increases the stable working time of the catalyst.

Figure 3 shows the dependence of the conversion of dimethyl ether on the contact time ($1/\tau$), from which it can be seen that the activity of the catalytic system increases with the increase of $1/\tau$. At the same time, the selectivity for ethylene and C₂₊ paraffins partially increased with the increase of dimethyl ether conversion, the selectivity for C₂-C₅ ethylene and propylene did not change. Because at this time, the oligomerization reaction rate of ethylene is lower than the hydrogenation reaction rate.



$T=340^\circ C$, $P = 0,1$ MPa, $V_{\text{аpал}}=1000$ ч⁻¹. Raw materials: 15% dimethyl ether +85%N₂

Figure 3. Dependence of the dimethyl ether conversion on the conditional contact time ($1/\tau$) in the Mg-Zr-Zn-B-YuKTs catalyst

CONCLUSION

Thus, unmodified Mg-Zn-Zr-B/YuKTs show high activity, the decrease in catalyst activity over time, that is, the decrease in the production of ethylene and propylene, is explained by the coking of the acid centers of the catalyst and the clogging of the thin pores and channels of the zeolite. The addition of water to the raw material slightly increases the yield of ethylene and propylene, but the working time of the catalyst increases by ≈ 2 times. In this case, the yield of ethylene is much higher than when pure methanol is used. This is because water molecules blocking strong acid centers prevent ethylene from turning into high molecular weight hydrocarbons.

Based on the research, it can be seen that the zinc-modified YuKTs catalyst is the most effective among the studied samples for obtaining ethylene and propylene from dimethyl ether. The introduction of zinc into the zeolite not only increases the total yield of $C_2=C_4$ ethylene and propylene, but also leads to a decrease in methane formation.

In summary, the Mg-Zr-Zn-B-YuKTs sample is an effective catalyst for the synthesis of gasoline hydrocarbon components from dimethyl ether, but the amount of isoparaffins in the liquid product is slightly lower than that of the Mg-Zr-YuKTs sample, which is due to the presence of superacidity.

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