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CATALYTIC CONVERSION OF DIMETHYL ETHER TO ETHYLENE AND PROPYLENE

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Abstract

In this article, the results of 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 vapour, on the texture, acidic characteristics and catalytic properties of the zeolite catalyst in the conversion of dimethyl ether to ethylene and propylene was considered. To increase the stability of the Mg-Zn-Zr-B/HSZ catalyst, it was proved that unmodified Mg-Zn-Zr-B/HSZ 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-HSZ catalyst under the following optimal conditions: ($T = 340$ °C, $R = 0.1$ MPa, $V_{ar} = 1000\text{-}2000\ h^{-1}$. Raw material: DME (15%) ÷ N_2(85%). The purpose of the work is to study the catalytic conversion of dimethyl ether to ethylene and propylene in the Mg-Zr-Zn-B-HSZ catalyst.

Keywords: methanol, dimethyl ether, catalyst, conversion, unsaturated hydrocarbons, high-silica zeolite.

Introduction

Currently, methanol synthesis is carried out on $Cu/ZnO/Al_2O_3$ catalyst at temperatures of 270-300 °C under pressure of 5-10 MPa[1].

Ethylene and propylene are produced from methanol by two methods according to the following reactions:

$$5CH_3OH \rightarrow C_2H_4 + C_3H_6 + 5H_2O;\ 2\ CH_3OH \rightarrow (CH_3)_2O +$$
$$+ H_2O4\left(CH_3\right)_2 O \rightarrow C_2H_4 + 2C_3H_6 + 4H_2O$$

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

At present, processes for obtaining ethylene and propylene and polyethene 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], and the volume of production capacity has doubled since the beginning of the century.

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 effect of the nature of the modifying element on the properties of zeolite catalysts [13-16] has been widely studied.

Experimental part

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 cm3.

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 350 °C. N_2 adsorption was carried out at 77K.

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

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

First, the effect of boron on the catalytic properties of zirconium- and magnesium-supported zeolite catalysts, which were previously developed for the conversion of dimethyl ether to ethylene and propylene, was investigated. When modifying these catalysts with boron, in almost all cases, an increase in the selectivity for C_2-C_4 ethylene and propylene and a decrease in the amount of paraffin was observed (Table 1). Modification of Zr-HSZ 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-HSZ catalyst is slightly higher than that of Mg-HSZ.

Table 1. Conversion of dimethyl ether to ethylene and propylene on zeolite catalysts

Catalyst	Selectivity, %			
	Ethylene and propylene			Paraffins are C^{1+}
	C_2	C_3	$\sum C_2 - C_3$	
HSZ	12.9	18.7	31.6	39.5
Zr-HSZ	18.6	32.3	50.9	28.4
Mg-HSZ	19.8	33.1	52.9	27.6
Mg-Zr-HSZ	29.2	34.4	63.6	25.9
Mg-Zr-Zn-HSZ	31.7	34.2	65.9	25.7
Mg-Zr-Zn-B-HSZ	32.5	35.2	67.7	19.7

Conditions: T = 340 ℃, R = 0.1 MPa, Var = 500-1500 h-1. Conversion of dimethyl ether = 65-75%. Raw materials: DME (15%) ÷ N2 (85%).

As can be seen from Table 1, in the presence of a Mg-HSZ 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-HSZ catalyst, selectivity to ethylene is 32.5%, selectivity to propylene is 35.2%, and selectivity to paraffin is 19.7%.

Modification of the Zr-HSZ and Zn-HSZ samples with magnesium and boron resulted in a significant decrease in the total amount of acid centres, and the zinc-retaining catalyst had fewer superacidic centres than the zirconium-retaining catalyst (Table 2). The addition of boron(B) to Mg-Zr-Zn-HSZ also caused a decrease in total acidity, a decrease in the percentage of medium-strength acidic centres, and a significant increase in the amount of superacidic centres.

Table 2. Distribution of the amount of acidic centres according to the desorption activation energies of ammonia

Catalyst	The total amount of acidic centres, µmol/g	The number of centres (E<130 kJ/mol li), µmol/g	The amount of centers (130<E<180 kJ/mol li), µml/g	The amount of centers (E>180 kJ/mol li) µmol/g
HSZ	700	275(36%)	485(64%)	-
HSZ	880	340(38%)	540(61.3%)	5(0.7%)
Zr-HSZ	700	275(35%)	455(65%)	-
Mg-HSZ	680	340(50%)	335(49.3%)	5(0.7%)
Mg-Zr-HSZ	630	340(54%)	290(46%)	-
Mg-Zr-Zn-HSZ	450	260(58%)	180(40%)	10(2%)
Mg-Zr-Zn-B-HSZ	445	220(49%)	165(37%)	60(13%)

Thus, the Mg-Zr-Zn-B-HSZ 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-HSZ 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 number of aromatic hydrocarbons increased almost twice while maintaining the high catalytic activity of the Mg-Zr-Zn-B-HSZ system. It was 46.1% by mass (Table 3).

Table 3. Effect of contact time on activity and selectivity of Mg-Zr-Zn-B-HSZ system

1/W, hour^{-1}	Conversion (%)	Selectivity, %	Hydrocarbon content of the products, % mass

		Gas	Selectivity to hydrocarbons, %	Iso-paraffin	Normal-new paraffin wax	Cycloparaffin	Aromatic UV	Olef-iny
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 the Mg-Zr-Zn-B-HSZ catalyst at high temperatures had almost no effect on 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 number of isoparaffins decreased from 57 to 43 wt.%, and the number of aromatic hydrocarbons in liquid products increased sharply and was about 50 wt.% compared to the new sample.

To increase the stability of the Mg-Zn-Zr-B/HSZ 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/HSZ exhibits high activity, the decrease in catalyst activity over time, i.e., the decrease in the production of ethylene and propylene, is due to the coking of the acidic centres of the catalyst and the clogging of the thin pores and channels of the zeolite.

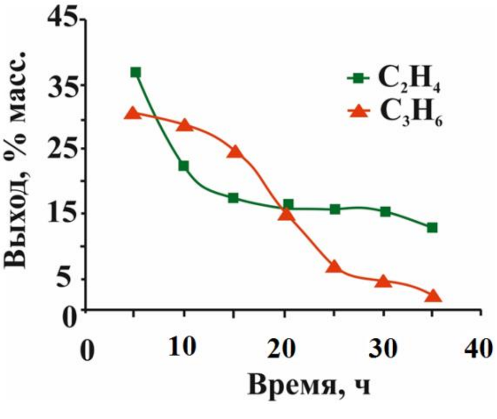


Figure 1. Dependence of ethylene and propylene yields on catalyst operating time (=1000 hours^{-1}, T=340 °C, P=0.1 MPa)$\mathbf{V_{N_2}}$

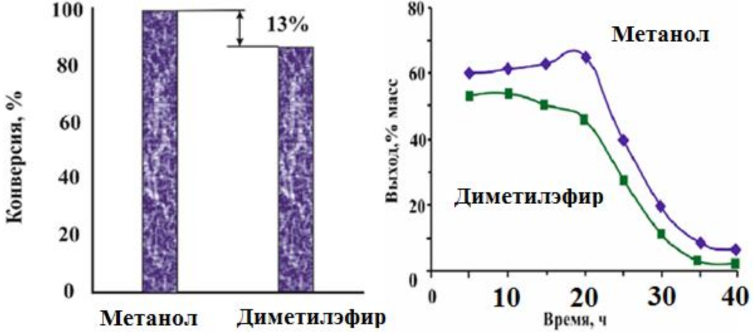
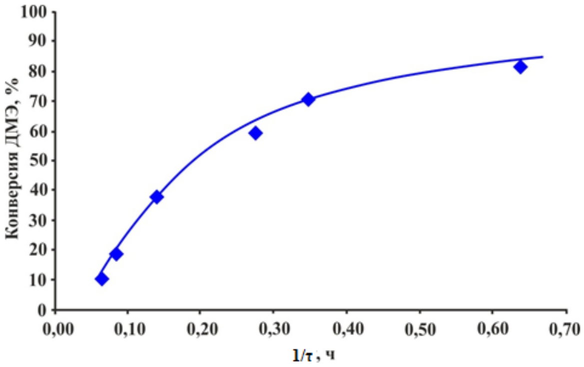


Figure 2. Conversion of dimethyl ether and methanol in Mg-Zn-Zr-B/HSZ (=1000 h^{-1}, T=340 °C, P=0.1 MPa)$\boldsymbol{V_{N_2}}$

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/HSZ catalytic water was investigated.



T=340°C, R = 0.1 MPa, =1000 h^{-1}. V_{aral} ***Raw materials: 15%***dimethyl ether +85%N_2

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

Figure 3 shows the dependence of the conversion of dimethyl ether on the contact time (1/t), from which it can be seen that the activity of the catalytic system increases with the increase of 1/t. At the same time, the selectivity for ethylene and S2+ paraffins partially increased with the increase of dimethyl ether conversion, the selectivity for S2-S5 ethylene and propylene did not change. Because at this time, the oligomerization reaction rate of ethylene is lower than the hydrogenation reaction rate.

Conclusions

Thus, unmodified Mg-Zn-Zr-B/HSZ exhibits high activity, the decrease in catalyst activity over time, that is, the decrease in the yield of ethylene and propylene formation, is explained by the coking of the acidic centres of the catalyst and the clogging of the thin pores and channels of the zeolite.

In summary, the Mg-Zr-Zn-B-HSZ 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-HSZ sample, which is due to the presence of superacidity.

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