CATALYTIC SYNTHESIS OF LOWER UNSATURATED HYDROCARBONS FROM DIMETHYL ETHER

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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 vapour, on the structure, texture, acidic characteristics and catalytic activity of the catalyst with a new composition created in the catalytic conversion of dimethyl ether to ethylene and propylene was considered. In order to increase the stability of the Mg-Zn-Zr-B:HSZ catalyst, it was proved that unmodified Mg-Zn-Zr-B:HSZ showed high activity when it was modified with P and Fe and used in the synthesis of lower alkenes from methanol and dimethyl ether. In the work, the catalytic conversion of dimethyl ether to lower alkenes was carried out in the Mg-Zn-Zr-B:HSZ -containing catalyst under the following optimal conditions: (T = 340 °C, R = 0.1 MPa, V_{ar} = 1000-2000 h^{-1}. Raw materials: DME (15%)÷N2(85%) in the modification of zirconium- and magnesium-containing zeolite catalysts with B, it was proved that the selectivity for C_2-C_4 unsaturated hydrocarbons and the decrease in the amount of paraffins were observed in almost all cases.

The purpose of the work is to study the catalytic conversion of dimethyl ether to lower unsaturated hydrocarbons in a catalyst containing Mg-Zn-Zr-B:HSZ.

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

Introduction

At present, a Cu:ZnO:Al_2O_3 catalyst is used to obtain methanol from carbon dioxide and hydrogen. The reaction is carried out in the temperature range of 270-300 °C and pressure in the range of 5-10 MPa [1].

Unsaturated hydrocarbons are produced from methanol in two ways by following reactions:

$$5\,CH_3OH \rightarrow C_2H_4 + C_3H_6 + 5H_2O; \quad 2\,CH_3OH \rightarrow (CH_3)_2O +$$
$$+ H_2O4(CH_3)_2O \rightarrow C_2H_4 + 2C_3H_6 + 4H_2O$$

The first method is based on obtaining ethylene and propylene by direct conversion of methyl alcohol in silicoaluminophosphate catalysts at temperatures of 450-550oC. 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] .
The development of the "unsaturated hydrocarbon" complex is accelerated by the increase in demand for consumer products [4-5]. Today, the global production of lower unsaturated hydrocarbons has exceeded 280 million tons per year [6]. The demand for ethylene and propylene is especially high, and the production of unsaturated hydrocarbons is more than 90% of the total volume [7-9]. Today, the most common catalysts in the synthesis of ethylene and propylene from dimethyl ether are high-silica zeolites.

Experimental part

HSZ type zeolite with SiO_2:Al_2O_3=26 mol ratio was used in the work. Zirconium and zinc were added to the catalysts by means of ion exchange. Boron was introduced by ingestion.
Tests of Mg-Zn-Zr-B:HSZ catalyst samples with a mass of 0.5 g and a volume of 1 cm^3 in the catalytic conversion of dimethyl ether to ethylene and propylene were conducted in a catalytic flow device at a pressure of 0.1 MPa and a temperature range of 320-380 °C. The volume velocity of the initial gas mixture was changed in the range of 1000-2000 h^{-1}, the concentration of dimethyl ether in the initial mixture was 15% by volume.
The reaction products were chromatographically analyzed on a "Crystal 5000" chromatograph with a capillary column and a flame-ionization detector. Hydrogen and carbon oxides were determined on a Crystal-5000 chromatograph equipped with a thermal conductivity detector and a PropakQ phase retention column. Separation conditions: carrier gas - helium; capillary column filled with foam Q, size 27.5m*0.32mm, adsorption layer thickness - 10 μm.

Results and Discussion

First, the effect of boron on the catalytic properties of zirconium- and magnesium-containing zeolite catalysts, which were previously developed for the conversion of dimethyl ether to lower unsaturated hydrocarbons, was investigated. When modifying these catalysts with boron, in almost all cases, an increase in the selectivity for C_2-C_4 unsaturated hydrocarbons and a decrease in the amount of paraffins were 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 the Mg-HSZ.

Table 1. Conversion of dimethyl ether to unsaturated hydrocarbons on zeolite catalysts

Catalyst	Selectivity, %			
	Unsaturated carbohydrates			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 °C, 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 paraffins is 19.7%.

According to the data obtained by the method of temperature-programmed desorption of ammonia, modification of Zr-HSZ and Zn-HSZ samples with magnesium and boron led to a significant decrease in the total amount of acid centers, and it was proved that the zinc-retaining catalyst has a small amount of superacidic centers, unlike the zirconium-retaining catalyst (Table 2).

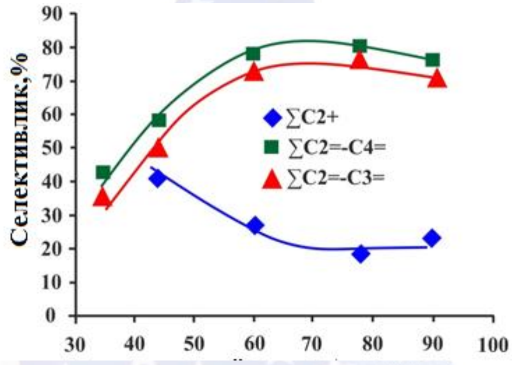
Table 2. Distribution of the amount of acidic centers according to the data obtained by the method of temperature-programmed desorption of ammonia

Catalyst	Total amount of acidic centers, µmol:g	The amount of centers (E<130 kJ:mol li), µmol:g	The amount of centers (130<E<180 kJ:mol li), µml:g
HSZ	720	295	425
Zr-HSZ	700	275	455
Mg-HSZ	680	340	335
Mg-Zr-HSZ	690	340	350
Mg-Zr-Zn-HSZ	750	360	370
Mg-Zr-Zn-B-HSZ	785	325	460

The addition of boron(B) to Mg-Zr-Zn-HSZ also caused an increase in total acidity.

Thus, the Mg-Zr-Zn-B-HSZ catalyst is an effective catalyst for the synthesis of 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 proven by the occurrence of superacidity.

The Mg-Zn-Zr-B:HSZ catalyst shows the highest activity in the conversion of dimethyl ether in the amount of water vapor in the raw material above 65 wt.%, under these conditions, the conversion of dimethyl ether is higher than 70% and the selectivity for C_2-C_4 unsaturated hydrocarbons is higher than 80 wt.% will be high (Fig. 1).



T=340 ℃*, R = 0.1 MPa,* V_{aral} **=1200h^{-1}. Raw material: 15%***dimethyl ether +85%*N_2

Figure 1. Dependence of the selectivity of the reaction products in the Mg-Zr-Zn-B-HSZ catalyst on the amount of water vapor in the initial dimethyl ether:mixture

Conclusion

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 unsaturated hydrocarbons, 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 lower unsaturated hydrocarbons, but the catalyst operation time 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.

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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