Catalytic Synthesis Of Lower Olefins From Methanol And Dimethyl Ether

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ABSTRACT

Currently, the main source of feedstock for the production of lower olefins is oil. The implementation of the sequential change "$CH_4 \rightarrow CH_3OH \rightarrow$ lower olefins" allows us to consider natural gas as an alternative raw material for the production of expensive raw materials for petrochemicals-ethylene and propylene. The most promising catalysts for converting methanol to olefins are crystalline microporous silicoaluminophosphates (SAPO-34 and SAPO-18) With a chabazite structure and high siliceous zeolites (HSZ) synthesized from kaolin. Despite the existence of industrial processes for converting methanol using HSZ to olefins, the improvement of these catalysts is an urgent task in order to increase the selectivity and stability of the operation of ethylene and propylene. Therefore, we conducted the process of producing ethylene and propylene from methanol by incorporating metals of various nature from natural kaolin to HSZ. The purpose of this work is to study the effect of the nature and amount of the introduced metal on the physicochemical and catalytic properties of the HSZ.

KEYWORDS

Alternative fuel, catalysts, economical use of natural gas, high siliceous zeolites, low-carbon, natural gas.

ABBREVIATION

HSZ – high siliceous zeolites; MTO - methanol to olefins; DTO - dimethyl ether to olefins; ZSM-5 - Zeolite Socony Mobil 5; HMDA – Hexamethylenediamine; Dimethyl ether-DME;

INTRODUCTION

Rational use of oil and gas will allow the chemical industry to develop at a higher level. Special attention is paid to the use of high-efficiency, low-waste, economical, environmentally friendly technologies for the efficient use of oil and natural gas, as well as environmental protection. At a time when oil reserves are declining, natural gas is of great interest as an alternative fuel in petrochemical production. The current conventional method of converting natural gas into liquid fuel is multistage, at high temperature and high pressure. There are 3 most important ways to recover ethylene from natural gas [1-5]. The first method is the production of ethylene by the synthesis of dimethyl ether or methanol, the second - by dimerization of methane, the third - through methyl chloride.

Extraction of olefins from natural gas with methyl chloride.

Production of methyl chloride by methane oxychlorination [6-9]:

$$nCH_4 + nHCl + \frac{n}{2}O_2 \xrightarrow{CuCl:KCl:LaCl_3=1:1:0,3} nCH_3Cl + nH_2O$$

The methane oxychlorination reaction proceeds at atmospheric pressure at 550-4200 °C. $CH_4:HCl:O_2$=12:2:1; volumetric velocity 8100 l/l cat. hour; $\tau = 1,8$ sec. $\tau = 1,8$ cm³.

Conversion of methyl chloride to olefins.

$$nCH_3Cl \rightarrow C_2H_4 + C_3H_6 + C_4H_8 + nHCl$$

• Catalyst-SAPO-34

• Methyl chloride conversion -80%

• Selectivity to ethylene and propylene 80-85%

• Temperature -420-450 °C

Preparation of ethylene by the synthesis of dimethyl ether or methanol involves the following processes [10-15]:

$$2CH_4 + H_2O + O_2 \rightarrow CO + CO_2 + 5H_2$$
$$CO + CO_2 + 5H_2 \rightarrow 2CH_3OH + H_2O$$
$$nCH_3OH \rightarrow C_2H_4 + C_3H_6 + C_4H_8 + C_nH_{2n} + nH_2O$$
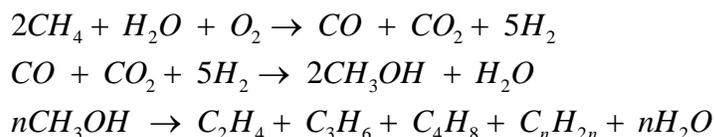
V.N. Rozanov and Yu. A. Treger in their comments [12-16] considered various technologies for the production of ethylene and propylene from natural gas.

Of all known methods, it is easiest to obtain ethylene by oxycondensation of methane, which is prevented by low ethylene yields.

The natural gas to ethylene methanol conversion chain consists of 3 steps:

- Synthesis - gas extraction:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 - 206кж/mol \ (1)$$
$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2 - 247кж/mol \ (2)$$
$$CH_4 + 1/2O_2 \leftrightarrow CO + 2H_2 - 36кж/mol \ (3)$$
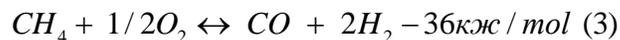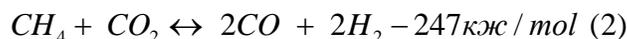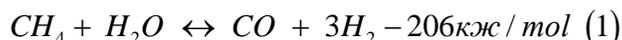
- Extraction of methanol:

$$CO + CO_2 + 5H_2 \rightarrow 2CH_3OH + H_2O$$
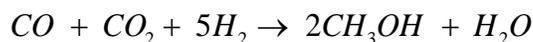
T = 220 - 280°C; P = 5-10 MPa, catalyst Cu/Zn.

- Conversion of methanol in the presence of a catalyst:

$$n \ CH_3OH \rightarrow C_2H_4 + C_3H_6 + C_4H_8 + other \ hydrocarbons + n \ H_2O$$

The conversion rate of methane in synthesis gas extraction processes (17-23) is high, in reaction (3) oxygen is fully involved in the reaction. Methane homologues are completely transformed into CO and H_2. The reaction mechanism of the MTO process (methanol to olefins-MTO) is fully studied in [24-27]. Catalysts of MTO and DTO processes (dimethyl ether to olefins), their thermodynamics, kinetics and mechanism are described in [28]. Many catalysts have been tested in the MTO reaction [29-32]. Most often, zeolites of the ZSM-5 type and molecular sieves of the SAPO type are tested in MTO reactions. In zeolites HZSM-5 paraffin, aromatics, cycloparaffins and olefins C_{6+} are obtained. More than 30 years have passed since the methane oxycondensation reaction was discovered, but this reaction has not yet been introduced into the industry due to the lack of a stable catalyst with high activity and efficiency [23 - 36].

Indicators of the methane oxidation process.

$$2CH_4 + 1/2O_2 \rightarrow C_2H_6 + 2H_2O$$
$$2CH_4 + O_2 \rightarrow C_2H_4 + 2H_2O$$
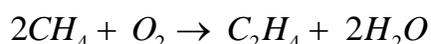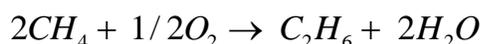
- Hydrocarbon yield C2 up to 25%

- Hydrocarbon selectivity S2 - up to 80%.

• Selectivity to ethylene - up to 55%.

EXPERIMENT

The synthesis of catalysts was carried out from a reaction mixture of the composition xMeO * Al_2O_3 * $2B_2O_3$ * $2SiO_2$ * $4(C_2H_5)_4NOH$ * $96H_2O$, where x = 0,005 ÷ 0,1. Me = Mg, Zn, Zr. The HSZ sample was synthesized by the hydrothermal method. As the initial components, a solution of the salt $Al(NO_3)_3$·$9H_2O$ and a solution of liquid glass Na_2SiO_3 (29% SiO_2; 9% Na_2O; 62% H_2O) were obtained. Hexamethylenediamine (GMDA) was obtained as a matrix. The reaction mixture was prepared by vigorously stirring aqueous solutions of the components at pH ≅ 10.8 and adding a solution of HNO_3 (0,1 N). Silicon oxide used for the synthesis of HSZ was introduced in an amount of 1-1.5% by weight. Analysis of transformation products was carried out using gas chromatography. Chromatograph "Chromatek - Kristall 5000.1" flame ionization detector and thermal conductivity detector based on the calculation program "Chromatek gasoline".

The analysis of gaseous hydrocarbons was carried out in a stainless steel column (length 3 m, inner diameter 3 mm) filled with 5% NaOH in Al_2O_3 (fraction 0.25-0.50 mm); liquid

hydrocarbons - DB-1 quartz glass capillary column (100 mx 0.25 mm x 0.25 μm) applied to a stationary liquid phase (SE-30 silicone oil). The catalytic activity of the samples obtained by converting methanol to lower olefins was studied in a catalytic unit at 400–550 °C and W = 2–6 g/(g * h).

It was found that the presence of metals in the reaction mixture leads to a decrease in the crystallization rate in the HSZ > Mg-B- HSZ > Mg-Zn- HSZ > Mg-Zr- HSZ > Mg-Zn-Zr- HSZ > Mg-Zn-Zr-B- HSZ. For the Mg-HSZ sample, the crystal size is 6-8 μm, which is greater than the crystal size of the HSZ reference sample. A common problem for all synthesized samples with a high structure is the low conversion of the reaction mixture, which leads to the insufficient formation of the desired crystalline phase. The weight fraction of the obtained samples was 0.3-0.4 in the reaction mixture m (MeO) + m (Al$_2$O$_3$) + m (B$_2$O$_3$) + m (SiO$_2$), which indicates the inefficient use of primary reagents. An increase in the cost-effectiveness of the crystalline phase was achieved by reducing the pH of the reaction mixture. This method led to the formation of a crystalline phase HSZ-1 instead of HSZ, the profitability of the HSZ-1 phase is 0.95-0.97 s of the entry-level.

A study of the acid properties of Me-HSZ using TPD ammonia showed that the introduction of metals led to an increase in the concentration of acid fields in the samples by increasing the proportion of strong acid centres and quickly removing samples in the catalytic reaction. All samples with HSZ-1 structure showed high activity and stability in catalytic conversion, which can be associated with a low proportion of strong acid sites in these materials. The best Zn-HSZ-1 sample was stable for 12 hours. The observed differences between Me-HSZ and Me-HSZ-1 may be related to differences in the acidic properties of samples.

RESULTS AND DISCUSSION

During the treatment of zeolite with magnesium, zinc, zirconium and boron compounds, acid properties changed and superacidal formation was shown (Table 1).

Table 1. Studies of acid properties of zeolites modified with magnesium, zinc, zirconium and boron.

Example	The total amount of acid centres, mgmol/g	The number of acidic centres (with desorption activation energy, kJ / mol), mgmol/g			
		E < 95	95 ≤ E < 130	E ≥ 130	E > 180
HSZ	570	45	260	265	10
Mg-B-**HSZ**	610	15	275	350	30
Mg-Zn-**HSZ**	680	60	400	620	100
Mg-Zr-**HSZ**	740	50	420	630	115
Mg-Zn-Zr-**HSZ**	890	65	465	658	125
Mg-Zn-Zr-B-**HSZ**	1240	72	720	735	138

E < 95 kJ/mol - slightly acidic centers, 95 ≤ E < 1 30 kJ/mol - moderate, E ≥ 130 kJ/mol - strong, E > 180 kJ/mol - superacids.

The appearance of superacidal centres allowed to reduce the reaction temperature from 330 to 270 °C while maintaining the catalytic properties of Mg-Zn-Zr-B-HSZ, as confirmed by the data of Table 2.

Table 2. Effect of temperature on the catalytic properties of HSZ and Mg-Zn-Zr-B-HSZ.

Катализатор	T, °C	DME conversion,%	Selectivity, mas.%		
			Olefins		
			C_2	C_3	$\sum C_2 - C_4$
HSZ	270	40,2	16,5	21,9	39,9
Mg-B- **HSZ**		65.6	17.2	22.3	41.2
Mg-Zn- **HSZ**		66.1	18.4	24.6	41.0
Mg-Zr- **HSZ**		67.3	18.6	20.9	41.5
Mg-Zn-Zr- **HSZ**		69.8	19.4	22.6	45.2
Mg-Zn-Zr-B- **HSZ**		79,8	29,8	30,7	77,4
HSZ	320	65,5	13,6	19,2	38,3
Mg-B- **HSZ**		67.9	15.8	20.7	42.3
Mg-Zn- **HSZ**		72.9	19.2	23.4	46.8
Mg-Zr- **HSZ**		75.8	20.7	24.3	49.6
Mg-Zn-Zr- **HSZ**		79.2	23.6	28.8	56.9
Mg-Zn-Zr-B- **HSZ**		88.7	29,4	38,5	72,6

Conditions: (R = 0.1 MPa, W_{ar} = 4000 h^{-1}. Raw materials: DME (10%) N_2 (90%). As can be seen from these data, the conversion of DME in the Mg-Zn-Zr-B-HSZ catalyst was 79.8% at 270 W_{ar} at W_{ar} = 4000 h^{-1}. At the same feed space rate, the DME conversion for the HSZ catalyst is only 65.5% at 320 °C. When the temperature in sample Mg-Zn-Zr-B-HSZ was lowered, the conversion of DME was slightly reduced, and the selectivity to olefins C_2-C_5 practically did not change. In the original unmodified sample, a sharp decrease in DME conversion to 40.2% with a decrease in temperature was observed, the olefin selectivity being decreased to 29.9 wt. %.

Table 3. Catalytic properties of Mg-Zn-Zr-P-HSZ and Mg-Zn-Zr-B-HSZ samples at T = 270 and 320 ℃ during the conversion of DME to lower olefins.

Catalyst	T, ℃	Selectivity, mas.%			
		Olefins			Paraffins C_1+
		C_2	C_3	$\sum C_2 - C_4$	
Mg-Zn-Zr-P-**HSZ**	270	25,5	32,6	58,1	33,9
Mg-Zn-Zr-B-**HSZ**		29,8	30,7	77,4	22,6
Mg-Zn-Zr-P-**HSZ**	320	26,4	28,8	55,2	37,5
Mg-Zn-Zr-B-**HSZ**		29,4	38,5	72,6	27,4

Comparison of the experimental data obtained on the samples Mg-Zn-Zr-P-HSZ and Mg-Zn-Zr-B-HSZ at 270 ℃ and 40% of conversion of DME, showed that these systems show almost identical selectivity on the lowest olefins. As can be seen from the table, as the process temperature increased from 270 ℃ to 320 ℃, the olefin selectivity decreased C_2-C_5, the number of paraffin hydrocarbons increased and reached a maximum value of 27 ms. However, in less than 5 hours, the Mg-Zn-Zr-B-HSZ catalyst system showed high stability of operation and activity compared to Mg-Zn-Zr-P-HSZ under the same test conditions. The Mg-Zn-Zr-B-HSZ catalyst system was sufficiently stable after several cycles of oxidative regeneration. As shown in Figure 1, the selectivity of the catalyst system Mg-Zn-Zr-B-HSZ to olefins C_2-C_5 was maintained at 70 ms. % even after the second catalyst regeneration.

(T = 320 ℃, P = 0.1 MPas, W_{ar} = 2000 h^{-1}. Raw materials: DME (10%) N_2 (90%).
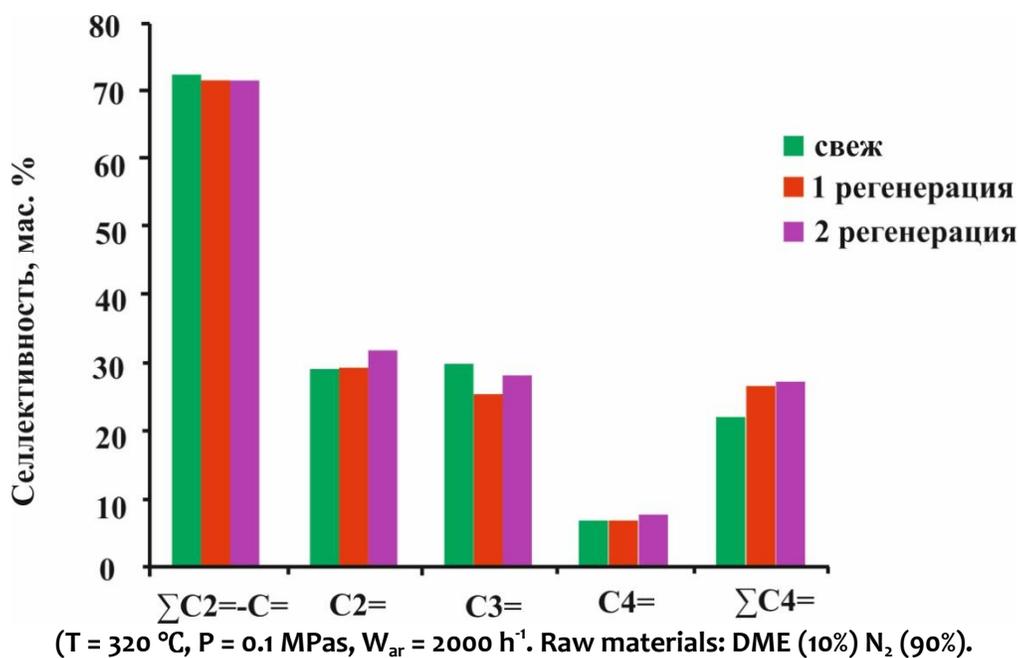
Figure 1. The dependence of DME conversion and selectivity for the target products on the regeneration rate of the oxidizing catalyst Mg-Zn-Zr-B-HSZ.

CONCLUSION

It should be noted that in samples containing zirconium, magnesium, zinc, boron and phosphorus, about 30% of paraffin are formed, consisting mainly of isoparaffins, which are valuable high octane hydrocarbons of gasoline. Therefore, zeolite catalysts containing zirconium, magnesium, zinc, boron and phosphorus and their sulphated forms have been studied in the conversion of hydrocarbon components of gasoline to DME, where steam reforming as a diluent for producing gasoline containing small amounts of aromatic hydrocarbons has the following content: 20.8 volume % CO, 72.3 volume % N_2, 4.2 volume % N_2, 2.7 volume % CO_2 synthesis gas was used.

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