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Change Of Dimethyl Ether To Lower Alkenes In Boron And Phosphorus-Containing Catalysts

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ABSTRACT

In this study, the possibility of the formation of lower olefins from dimethyl ether and methanol on catalysts containing Mg-Zn-Zr-B-HSZ and Mg-Zn-Zr-P-HSZ was studied, and the process was evaluated quantum chemically. According to the results obtained by IR-Fur spectroscopy, during the catalytic conversion of DME (dimethyl ether) on the surface of catalysts containing Mg-Zn-Zr-B-HSZ and Mg-Zn-Zr-P-HSZ ketenes at temperatures below 180 °C and oxonium intermediates at 320 °C (intermediate). compounds) are confirmed by experimental spectra and theoretical quantum-chemical calculations. It was shown that the formation of olefins below DME occurs by the carbene mechanism at low temperatures and by the oxonylide mechanism at high temperatures.

KEYWORDS

Spectroscopy method, catalysts, experimental spectra, high siliceous zeolites, low-carbon, natural gas.

ABBREVIATION

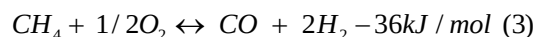
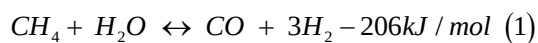
DME-dimethyl ether; MTO - methanol to olefins; DTO - dimethyl ether to olefins; ZSM-5 - Zeolite Socony Mobil 5; HMDA – Hexamethylenediamine; Dimethyl ether-DME; HSZ – high siliceous zeolites;

INTRODUCTION

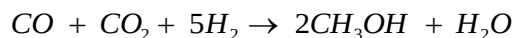
At present, the world's annual demand for ethylene is 187 million tons, and this demand is growing by 4.5% per year [1-6]. Currently, about 5% of natural gas is used in the production of valuable products, the rest is used as fuel [7-9]. Ethylene is an important product of petrochemistry and gas chemistry and is used in the production of polyethylene, polyvinyl chloride, polystyrene, alkylbenzenes,

ethylene oxide, etc. [10-14]. Currently, there are 3 different ways of producing ethylene from natural blood. The first method is to obtain ethylene by synthesizing dimethyl ether or methanol, the second is by dimerization of methane, and the third is through methyl chloride. The chain of conversion of natural gas to ethylene with methanol consists of 3 stages:

- Synthesis - gas extraction:

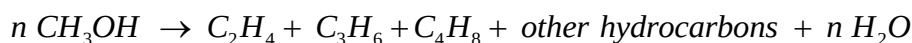


- Extraction of methanol:



T = 220 - 280°C; P = 5-10 MPa, catalyst Cu/Zn.

- Conversion of methanol in the presence of a catalyst:



The conversion rate of methane in synthesis gas extraction processes (1-3) is high, in reaction (3) oxygen is fully involved in the reaction. Methane homologues are completely transformed into CO and H₂. The reaction mechanism of the MTO process (methanol to olefins-MTO) is fully studied in [15 - 18]. Catalysts of the MTO and DTO processes, their thermodynamics, kinetics and mechanism are described in [19-21]. Many catalysts have been tested in the MTO reaction [22 - 24]. 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 C₆₊ are obtained. At present, in the reactions for converting methanol to olefins, ethylene and propylene are produced in a high yield on a modified aluminosilicate phosphate

catalyst SAPO-34 co-produced by UOP and Norsk Hydro.

Work aims to study the possibility of the formation of lower olefins from dimethyl ether and methanol in catalysts containing Mg-Zn-Zr-B-HSZ and Mg-Zn-Zr-P-HSZ, as well as a quantum-chemical evaluation of the process.

EXPERIMENTAL PART

DME with a purity of 99.99% (manufactured by AkzoNobel Industrial Chemicals Specialty Chemicals, Netherlands) was used as a starting reagent.

In the reaction for obtaining lower olefins from DME, samples of HSZ zeolite catalysts with a SiO₂/Al₂O₃ molar ratio of 26 and a

content of no more than 0.07 wt. Active metals (Mg, Zn, Zr) were introduced by impregnating finished zeolite extruders at room temperature with an aqueous solution of a metal salt (Al_2O_3), then dried and calcined at 500 °C for 4–6 hours. The content of Zn and Zr in the finished catalyst is 0.1%, Mg - 1%. The zeolites used for the preparation of the catalyst are a local analogue of the foreign zeolite of the chabazite type - the molar ratio of high-modulus zeolite (HSZ) $\text{SiO}_2/\text{Al}_2\text{O}_3 = 26$ was synthesized in the scientific laboratory of Samarkand State University. The reaction was carried out in a flow-through quartz reactor, to which 0.3–1.0 g (0.6–2.0 ml) of a catalyst 0.2–1.6 mm in size was added. The required consumption of reagents ($500\text{--}10000\text{ h}^{-1}$), temperature (240–450 °C), and pressure (~ 1

atm.) Were established. The condensed liquid products were collected in a receiver, and the gas stream was fed to chromatographic analysis using a crusher (loop volume 1 ml). The reaction products were analyzed by gas chromatography. Quantum-chemical calculations were performed using the density functional method B3LYP in the Gaussian-03 software package using the 6-31 + G (d, p) base set, as well as the PRIRODA software in the PBE functional structure. To calculate the structures of the zeolite, a model with the MFI structure type with HSZ zeolite in the composition of the zeolite lattice was chosen (Fig. 1).

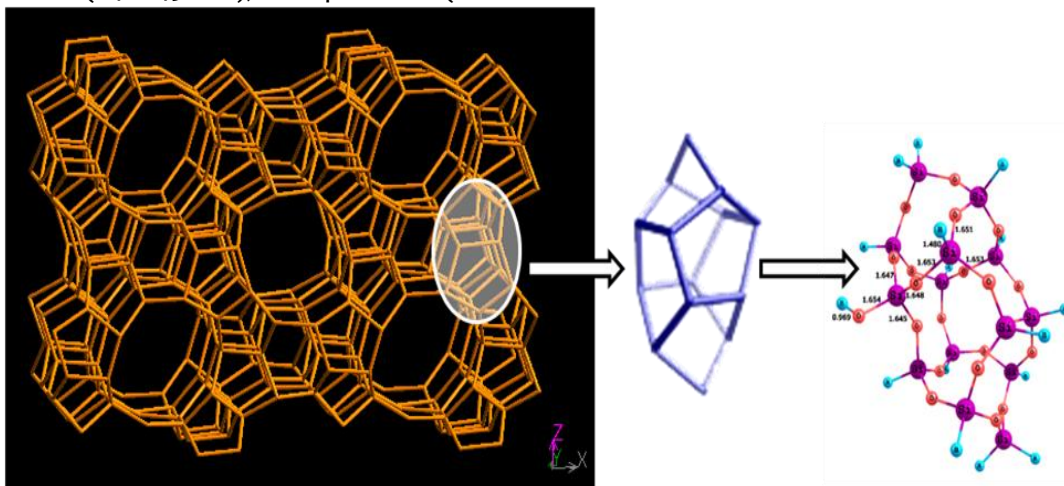


Figure 1. Selection of a zeolite structure model for calculations.

RESULTS AND DISCUSSION

The conversion of methanol to lower olefins was studied using Mg-Zn-Zr-B-HSZ and Mg-Zn-Zr-P-HSZ as catalysts. The overall yield of olefins C₂-C₄ (Fig. 2a) has a maximum value of 78%, and its activity decreases to 10% after 3 hours of catalyst operation. Methane yield no more than 5%, C₅+ hydrocarbons no more than 3%. As seen in Figure 2b, the ethylene yield in SAPO-34 increased slowly over the previous

two hours, while the propylene yield decreased (Figure 2c).

After 3 hours of catalyst operation, its activity and selectivity drop sharply. The output of ethane and propane is about 10-12% of the total. The yield of butanes decreases with time (Fig. 2, g), while the yield of butanes practically does not change and exceeds 2%.

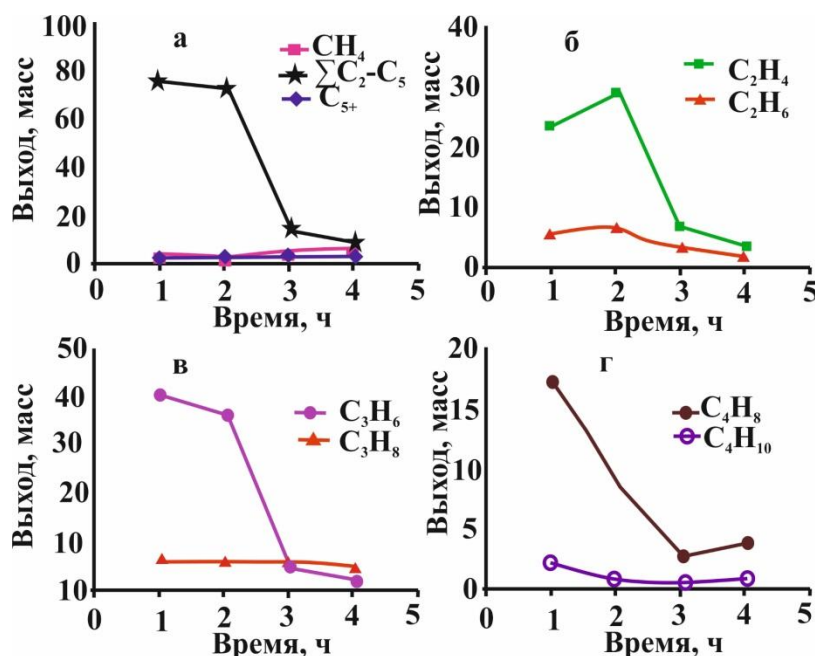


Figure 2. Dependence of the yield of reaction products on the catalyst operation time. ($V_{N_2} = 2000 \text{ h}^{-1}$, $V_{\text{Methanol}} = 1 \text{ h}$, $T = 375 \text{ }^\circ\text{C}$, $P = 0.1 \text{ MPa}$)

When the temperature rises to $450 \text{ }^\circ\text{C}$, there is an increase in methane production and a significant decrease in the yield of ethylene and propylene. However, when the CH_3OH space velocity increases from $450 \text{ }^\circ\text{C}$ to 7 h^{-1} , a sharp increase in the ethylene yield is observed at the initial moment (Fig. 2), but after 30 minutes its yield begins to decrease. On the other hand, the propylene yield decreases under these conditions. To increase the stability of the SAPO-34 catalyst, it was modified with the metals Zn and Fe.

However, the modification with metals leads to a decrease in the yield of lower olefins. Thus, unmodified SAPO-34 is highly active (we observe high yields of lower olefins), but it is unstable. The decrease in the activity of the catalyst over time is due to the coking of the

acid sites of the catalyst, which are responsible for the formation of olefins, and the clogging of the fine pores and channels of the zeolite.

HSZ based catalysts modified with boron or phosphorus compounds were tested for the conversion of DME dimethyl ether to olefins at 270 and $320 \text{ }^\circ\text{C}$. As can be seen from Table 1, the composition of the conversion and conversion products depends not only on the properties of the modifier metal but also on the temperature of the experiment (Table 1).

Since the target products of the investigated reactions are lower olefins, the determination of a sufficiently large amount of ethanol in the reaction products on the Mg-Zn-Zr-B-HSZ zeolite catalyst at $T = 270 \text{ }^\circ\text{C}$ is of interest for

understanding the mechanism of olefin formation. The absence of alcohols in the reaction products Mg-Zn-Zr-P-HSZ under the same temperature conditions and with an increase in temperature in both catalysts to 320 °C Alcohols are intermediate products formed in sequentially or sequentially parallel reactions. indicates that this is possible.

Table 1. Conversion of DME to olefins in the catalysts Mg-Zn-Zr-P-HSZ and Mg-Zn-Zr-B-HSZ.

Catalyst	DME conversion, %	The composition of the reaction products, wt. %						$C_2^{\equiv}/C_3^{\equiv}$
		CH ₄	C ₂ ⁼	C ₃ ⁼	$\Sigma C_2^{\equiv}-C_4^{\equiv}$	ΣC_{2+}	EtOH	
<i>T=270°C; P=0,1 MPa; initial mixture:10 vol.% DME + 90 vol.% N₂</i>								
Mg-Zn-Zr-P-HSZ	32.8	4.7	17.9	35.0	56.7	31.2	6.1	0.51
Mg-Zn-Zr-B- HSZ	40.7	0.1	37.0	32.6	69.7	30.2	–	1.14
<i>T=320°C (P=0,1 MPa; initial mixture : 10 vol.% DME + 90 vol. % N₂</i>								
Mg-Zn-Zr-P- HSZ	87.4	0.4	28.2	35.4	75.2	24.4	–	0.80
Mg-Zn-Zr-B- HSZ	87.5	0.1	38.5	34.7	76.7	23.2	–	1.11

IR spectroscopy data showed a correlation with the results of catalytic experiments, as well as with differences in the relative composition of various reaction products in the system, as well as in the case of modified catalysts with different metals. Most of the characteristic ethanol bands (3600, 1045, 1090, 895 cm⁻¹) are found only in the spectra of the Mg-Zn-Zr-P-HSZ surface at 140–200 °C. In the spectrum of Mg-Zn-Zr-P-HSZ at a temperature of 120-180 °C all bands characteristic of ketene (3055, 2080, 965 cm⁻¹), and the spectra of Mg-Zn-Zr-B-HSZ from 150 °C is observed at low temperatures. IRDO spectra of the surface of zeolite catalysts containing boron and phosphorus, preliminarily calcined at 400 °C, were recorded in a DME stream at 320 °C; no traces of flax or ethanol were found. Moreover, under these temperature conditions, after 15 minutes of contact of DME with the surface, the adsorbed DME on the surface of the zeolite is not fixed and all lines that are characteristic

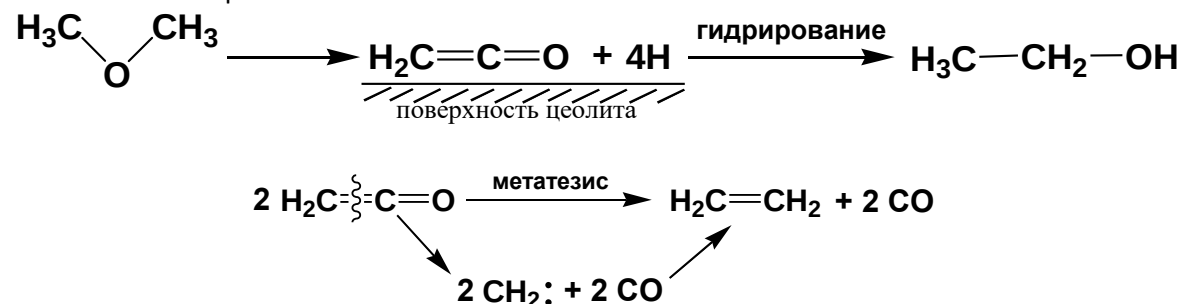
only of olefins and alkanes appear. This paper presents the properties of the mechanism of conversion of DME in phosphorus-modified zeolite catalysts, as well as experimental and theoretical methods of vibration spectroscopy, as well as quantum-chemical modelling at different temperatures (120–320 °C).

The mechanism of olefin formation from DME on the surface of zeolites at 120-200 °C.

Discussing the formation of ketol and its participation in the catalytic reaction, ketene is a very unstable molecule that readily decomposes to form carbyne and carbon monoxide (Scheme 1). In this case, strong Lewis acid sites (LAC) can be present in zeolite catalysts modified with phosphorus, the spectral properties of which are discussed in [1]. The hydrogenation ability of P-containing catalysts is well known; therefore, the

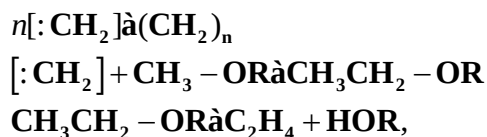
hydrogenation of ketene to ethanol can occur on the surface of the Mg-Zn-Zr-P-HSZ:

Scheme 1. Decomposition of ketol.



Further transformation of objects can go along the following paths:

- carbene polymerization



where $R=H$ or alkyl.

To confirm the potential for the formation of flax and other products from DME, we calculated the energy balance of these substances:

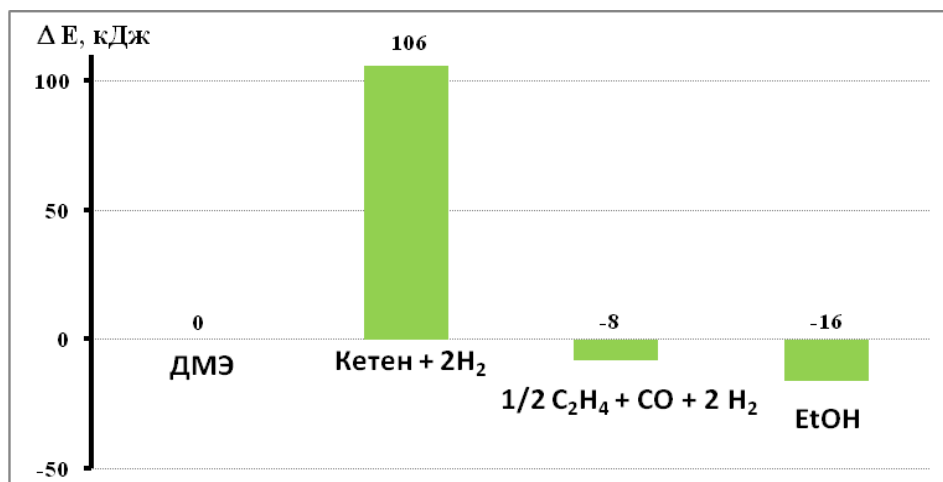


Figure: 3. Energy diagram of the conversion of DME through the formation of ketene.

As can be seen from the diagram, the energies of the 106 kJ / mol intermediate compounds

are low enough for such reactions to occur at sufficiently low temperatures. Thus, according

to in situ IR spectroscopy data, at temperatures below 200 °C, the carbenium mechanism to form the primary C - C bond can be realized [20-24].

The mechanism of formation of olefin from DME on the surface of zeolites at 320 °C. Analysis of the spectra at temperatures above

300 °C showed that the composition of the products differed significantly from those recorded at temperatures below 200 °C (Figure 4).

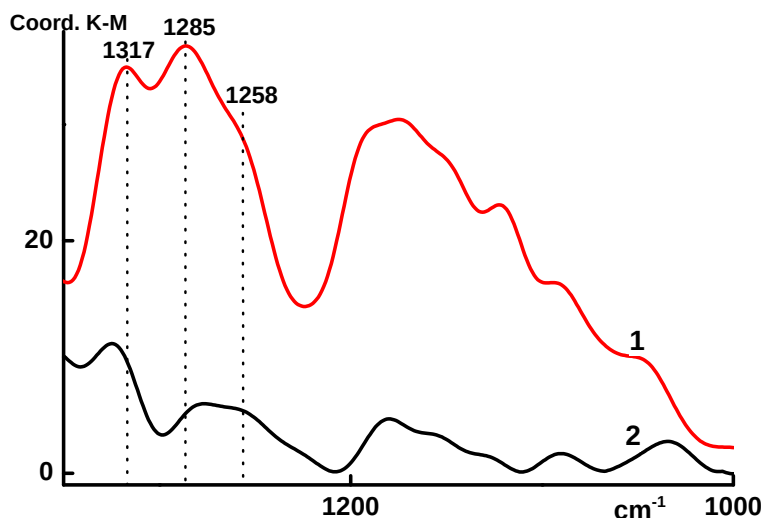


Figure: 4. Comparison of the differential spectra of IR LEDs of the surface of the catalyst Mg-Zn-Zr-B-HSZ in a current of DME at a temperature of 320 °C after 5 (1) and 100 (2) minutes of interaction.

In the spectrum of the Mg-Zn-Zr-B-HSZ surface, significant differences are observed in the region of 1100–1300 cm⁻¹ (Fig. 4), depending on the temperature at which the spectrum is recorded. At temperatures above 200 °C, very dense bands are observed in the 1200-1300 cm⁻¹ range. The high intensity of these bands indicates that they belong to C - O compounds, but their attachment to the adsorbed DME on the surface is inappropriate since the C - O bonds inside the DME are characterized by lines below 1180 cm⁻¹.

Therefore, it can be assumed that these bands are related to intermediate products of ozone, which arise as a result of the conversion of

DME. Calculations of models of intermediates (CH₃)₃O⁺ and (CH₃)₂O⁺ + CH₂⁻ associated with active centres of zeolite (Fig. 4) showed extended vibration frequencies of C - O bonds. Compounds move to the region of 1250–1280 cm⁻¹.

That is, the theoretical frequencies of ozone intermediates, adapted to the surface of the zeolite, are in good agreement with the experimental data of high-temperature IR in situ studies. It can be assumed that at high temperatures in the IRDO spectra it is possible to determine the intermediate products of the reaction of DME with olefins and to confirm the mechanism of oxidation of this reaction.

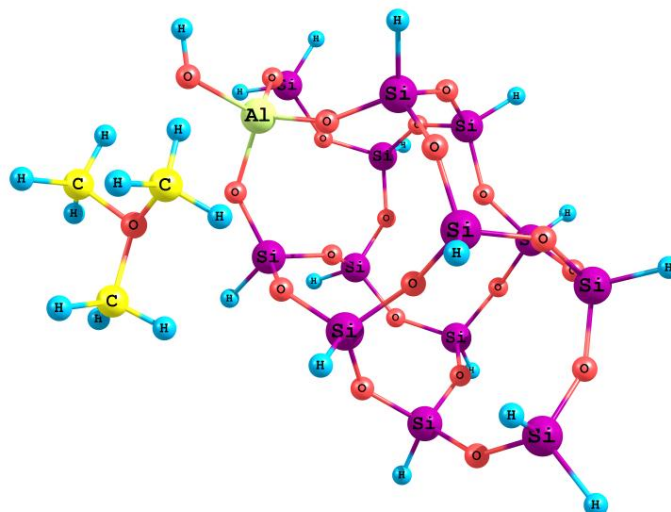


Figure 5. Model of coordination of trimethylammonium cation in a structural cell of zeolite.

CONCLUSION

On the surface of catalysts based on HSZ zeolite modified with boron and phosphorus, high-temperature FT-IR spectroscopy DR revealed intermediate compounds during the conversion of DME on them: ketones at temperatures below 180 °C and oxane intermediates at 320 °C. Theoretical quantum-chemical calculations of such models of intermediates are in good agreement with experimental spectra. The formation of olefins from DME can occur by two mechanisms that are not completely related to each other, depending on the temperature: at low temperatures by the carbenium mechanism and high temperatures by the oxidative sludge mechanism.

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