

Synthesis of Lower Olefins from Dimethyl Ether in the Presence of Zeolite Catalysts Modified with Rhodium Compounds

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Abstract—The catalytic properties of zeolite catalysts modified with rhodium compounds in the synthesis of olefins from dimethyl ether (DME) and methanol (MeOH) have been studied. The optimum concentration of rhodium in the composition of a zeolite catalyst has been determined. It has been shown that one of the possible precursors of ethylene in the conversion of DME is ethanol, which, under reaction conditions, can be formed through both the DME isomerization and methanol homologation stages.

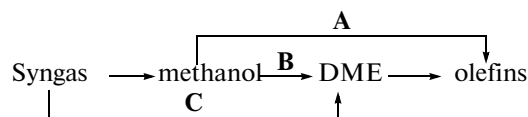
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The production of lower olefins is of a large scale and is constantly increasing [1]. The processes of thermal pyrolysis and catalytic cracking of hydrocarbon feedstock remain the basic methods to obtain ethylene and propylene. The rates of growth in the consumption of these useful chemicals are far ahead of the scale of their production, thereby entailing the search for another, cheaper, and more available hydrocarbon feedstock. This raw material is natural gas; its production and large-scale use are forecast for a long period.

The most known and explored method for obtaining chemicals from natural gas is their production via a preliminary conversion of natural gas to syngas (CO/H_2). The methane-derived syngas can be subsequently converted into olefins, which are the most important feedstock of the petrochemical industry. This conversion is carried out either in one stage (using the Fischer–Tropsch process) or via an intermediate production of methanol or dimethyl ether (DME).

Iron catalysts, which are the most active and selective in the Fischer–Tropsch synthesis of olefins, produce lower olefins ($\text{C}_2\text{--C}_4$) with a yield of at most 27% [2]. Unlike the Fischer–Tropsch process, the processes of syngas conversion to lower olefins via methanol and/or DME give the possibility to obtain ethylene and/or propylene with yields at a level of 75–90% [3–7].

Several routes to obtain $\text{C}_2\text{--C}_3$ olefins from natural gas via methanol and/or DME are under development (Scheme 1).



Scheme 1. Production of $\text{C}_2\text{--C}_3$ olefins from natural gas via methanol and/or DME.

Route A implies the production of olefins from syngas via methanol in one stage in the presence of ZSM-5. This method of direct conversion of methanol to olefins was developed by a number of companies (Mobil Oil Corporation, UOP, etc.) for over 30 years and commercialized [8].

The same period was marked by the appearance of a more efficient process that employs a highly selective H-SAPO-34 catalyst at the stage of synthesis of olefins from methanol. Being developed by UOP and Norsk Hydro [4, 8–12], this process is focused on the production of ethylene and propylene; in addition, it is intended to utilize by-products, including butenes, as a fuel for heat power plants. The yield of $\text{C}_2\text{--C}_3$ olefins is 75–90 wt %.

Route B includes the stage of DME synthesis from methanol by the dehydration of CH_3OH with the subsequent conversion of a mixture of methanol, DME, and H_2O to olefins; it is being developed by the Lurgi Co. in cooperation with some other German companies (MG Technologies AG) [6, 7, 13–16]. The process is aimed to obtaining propylene on a ZSM-5-based catalyst. The Lurgi process gives the possibility to process more than 99% methanol, of which 70% is consumed to produce propylene, 26% makes gasoline, and 4% acts as a heat transfer agent. The Lurgi process has been patented in a number of countries [7, 13, 14], and a demonstration unit is in operation [6].

Further development of the synthesis of lower olefins from natural gas can even more significantly increase the advantages of this method in comparison with the traditional technique. For example, at present, great interest is aroused by the version of production of C_2 – C_3 olefins that involves a direct synthesis of DME from syngas (**route C**), which is being developed by the JGC Corp. (Japan) [17], by the Chinese group [4], and in our studies [18, 19]. In [4, 17], natural gas is converted at the first stage to syngas (a mixture of CO/H_2) using steam or autothermal reforming. At the second stage, syngas is converted to a mixture of CH_3OH , DME, and H_2O (at a temperature of 210–300°C and a pressure of 4–150 atm) in the presence of a bifunctional catalyst that comprises the “metal” component, i.e., a methanol synthesis catalyst (CuO – ZnO/Al_2O_3 or ZnO – Cr_2O_3/Al_2O_3), and the “acid” component, i.e., an alcohol dehydration site (aluminum oxide or zeolite), thus in one stage combining the production of methanol and its dehydration to DME. The resulting $CH_3OH/DME/H_2O$ mixture, without separation into individual components, is placed into an olefin synthesis reactor, where at a temperature of 380–550°C and a pressure of 1–6 atm, in the presence of H-SAPO-34, a hydrocarbon product is obtained from which the ethylene and propylene fractions are isolated and the remaining components are used as a heat transfer agent for thermal power plants. Lower olefins are produced with a high yield (86%) and high selectivity (80–90%), with ethylene and propylene making about 80% of the hydrocarbon product.

However, with a decreasing content of methyl alcohol and an increasing amount of DME in the original feedstock, the yield of olefins decreases. This is due to the properties of the selected catalyst: the microporous SAPO-34 material, which proved to be the best catalyst for the synthesis of olefins from methanol, is not so effective in the reaction with DME and is rapidly deactivated because of heavy coking.

Unlike the cited authors [4, 17], in [18, 19] we synthesized olefins from DME that barely contained methanol, and its conversion was carried out over a catalyst based on high-silica pentasil, which is an analogue of H-ZSM-5, modified with La and Zr. This was possible owing to the development of both a single-step syngas-to-DME process [20] and an efficient catalyst for the conversion of DME to olefins. The selectivity for C_2 – C_4 olefins was up to 80% with a DME conversion of ~80%.

The key factor of high selectivity for the yield of olefins from CO and H_2 via DME is the rate and direction of formation of the single C–C bond from the C–O bond. Most researchers assume that the primary product in this process is ethanol and/or methyl ethyl ether [21–27]. In this work, in order to improve the properties of catalysts, we studied the effect of their modification with rhodium compounds, which are

good catalysts for methanol homologation, and analyzed certain features of olefin synthesis from DME.

EXPERIMENTAL

Dimethyl ether with a purity of 99.8% (manufactured by the OAO NAK Azot, Novomoskovsk, Russia) was used as a feedstock. In the reaction of formation of lower olefins from DME, we studied catalyst samples based on zeolite ZSM-5, or, more precisely, its domestic analog high-silica zeolite TsVM with a SiO_2/Al_2O_3 mole ratio of 30 (which, produced by ZAO Nizhegorodskie sorbenty, contains no more than 0.11 wt % sodium oxide). To obtain the hydrogen form of the zeolite (HZSM-5) with a preset residual sodium oxide content, we used a double cation exchange of Na^+ in a 1 N ammonium nitrate solution with subsequent drying and calcining at 500°C for 4 h.

Zeolite-containing catalysts were prepared via mixing the HZSM-5 zeolite with an alumina slurry (with 18 wt % dry Al_2O_3 produced by ZAO Nizhegorodskie sorbenty) as a binding agent and the subsequent shaping of granular extrudates (the Al_2O_3 content of the resulting catalyst was 33–34 wt %). After that, the extrudates were successively dried in air and in a drying oven and calcined at 500°C for 4 h. To introduce active metals into the zeolites, we used the ion exchange of the zeolites with an aqueous solution of a metal salt (La, Zr) followed by mixing with the binding agent (Al_2O_3) or the impregnation of the resulting zeolite–binder extrudates with an aqueous solution of a macromolecular metal (Rh) complex.

The experiments were carried out using a laboratory setup employing a flow-type microreactor. The feedstock was DME (or methanol), and the DME and methanol diluent was helium. A 0.5-g (1.0 ml) charge of the catalyst (a fraction of 0.4–0.63 mm) was placed in a quartz flow reactor. After that, the catalyst was activated in a flow of helium at 400°C. The desired reactant feed space velocity (500–5000 h^{-1}), temperature (240–340°C), and pressure (~1 atm) were set. Liquid products were condensed in a receiver; the gas flow, using a dosing cock, was supplied to a chromatograph for analysis. The reaction gas stream of DME conversion is a mixture of C_1 – C_6 hydrocarbons; the main method of their analysis is gas–liquid chromatography (GLC).

The gas mixtures were analyzed on a Kristallyuks 4000M chromatograph with a flame ionization detector. The dimensions of the capillary column were 27.5 m × 0.32 mm × 10 μm ; the nonpolar CP-poraPLOT Q phase was used as an adsorbent; this phase proved to be fairly efficient in separation of the basic groups of the products (DME, CH_3OH , C_1 – C_6 hydrocarbons). The temperature was programmed from 80 to 150°C at a heating rate of 30°C/min; helium was used as a carrier gas (a flow rate of 30 ml/min). The resulting chromatograms were processed using the NetChromWin software.

Table 1. Effect of rhodium concentration in an Rh/HZSM/Al₂O₃ zeolite catalyst on its catalytic properties in the conversion of DME to olefins

Rh concentration in the catalyst, wt %	Conversion, %	Product composition, wt %						
		CH ₄	C ₂ ⁼	C ₃ ⁼	C ₄ ⁼	C ₅ ⁼	ΣC ₂₊	ΣC ₂ ⁼ – C ₄ ⁼
0.05	99.6	0.8	19.9	18.3	7.9	3.5	50.4	46.1
0.1	99.9	0.2	24.3	19.4	6.3	2.7	47.1	50.0
0.2	99.5	0.9	21.4	20.3	7.1	3.0	48.2	48.8

Note: $T = 340^{\circ}\text{C}$, $P = 0.1$ MPa; feed mixture: 10% DME + He; $v_0 = 2000$ h⁻¹.

Table 2. Effect of the nature of a rhodium compound on the catalytic properties of a zeolite catalyst

Rh introduction mode	$T, ^{\circ}\text{C}$	Conversion, %	Product composition, wt %						
			CH ₄	C ₂ ⁼	C ₃ ⁼	C ₄ ⁼	C ₅ ⁼	ΣC ₂₊	ΣC ₂ ⁼ – C ₄ ⁼
from RhCl ₃	320	79.1	1.3	29.2	27.2	14.6	3.8	23.9	71.0
	340	99.7	1.2	18.6	11.4	10.1	5.4	53.3	40.1
from AcAc	320	97.2	1.6	24.5	14.3	15.2	6.1	38.3	54.0
	340	99.6	1.6	10.9	7.4	8.7	3.4	68.0	27.0
from PEI	320	87.4	0.4	28.2	35.4	11.6	0.9	23.5	75.2
	340	99.9	0.2	24.3	19.4	6.3	2.7	47.1	50.0

Note: $P = 0.1$ MPa; feed mixture: 10% DME + He; $v_0 = 2000$ h⁻¹; an Rh (0.1%)–HZSM/Al₂O₃ catalyst; AcAc is acetylacetonate; PEI is polyethyleneimine.

RESULTS AND DISCUSSION

The initial H-ZSM-5 zeolite was modified with a rhodium complex and tested in the conversion of DME to olefins. First, we studied the effect of rhodium concentration in the zeolite catalyst on its catalytic properties (Table 1). The data in Table 1 show that under these conditions, the reaction occurs with almost total conversion of DME; an increase in the concentration of rhodium from 0.05 to 0.1 wt % leads to an increase in the selectivity for ethylene and propylene by 4.4 and 1.1 wt %, respectively; the further increase in the rhodium loading is accompanied by a decrease in the ethylene selectivity and an insignificant increase in the propylene selectivity. The best results were obtained for rhodium loading of 0.1 wt %.

The effect of the nature of a rhodium compound on the catalytic properties of a zeolite catalyst was studied

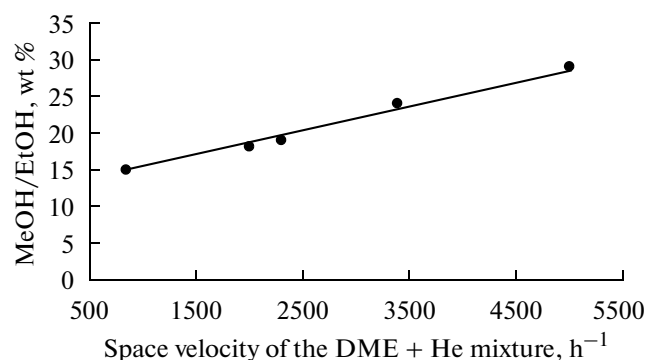
(Table 2). The highest selectivity for C₂–C₄ olefins (50.0–75.2 wt %) was obtained on the sample modified with the rhodium macromolecular (polyethyleneimine) complex.

To study the direction of formation of a primary C–C bond from a C–O bond in the conversion of DME to olefins, the rhodium-containing catalyst was tested under the “methanol homologation conditions” at 240°C and atmospheric pressure (Table 3). The DME conversion is fairly low in this case; significant amounts of methanol and up to 8.2 wt % ethanol were found in the product, as well as a large number of alkanes. A rise in the reaction temperature to 270°C leads to an appreciable increase in the selectivity for ethylene and propylene and to a decrease in the amount of ethanol and methanol, with the decline in

Table 3. Conversion of DME on an Rh (0.1)/HZSM/Al₂O₃ catalyst

$T, ^{\circ}\text{C}$	Conversion, %	Product composition, wt %							
		CH ₄	C ₂ ⁼	C ₃ ⁼	C ₄ ⁼	C ₅ ⁼	ΣC ₂₊	MeOH	EtOH
240	8.6	1.0	5.8	16.9	0.1	—	24.1	43.9	8.2
270	20.4	1.5	22.0	29.2	0.1	2.3	7.1	35.2	2.8

Note: $P = 0.1$ MPa; feed mixture: 10% DME + He; $v_0 = 2000$ h⁻¹.



Dependence of the MeOH/EtOH ratio on the space velocity of the feed gas mixture on Rh/HZSM/Al₂O₃ ($T = 270^\circ\text{C}$; original mixture: 10% DME + He).

the yield of ethanol being more considerable. The methanol/ethanol ratio varies from 5.4 to 12.6.

The study of the effect of space velocity on the methanol/ethanol ratio showed that an increase in the space velocity is accompanied by an increase in the MeOH/EtOH weight ratio, thereby suggesting that methanol is an intermediate product in the formation of ethanol (figure).

To verify this assumption, we carried the homologation of methanol on an Rh/HZSM/Al₂O₃ catalyst. Table 4 shows that methanol homologation occurs at an extremely low rate under these conditions. The amount of ethanol in the product of methanol conversion at a low temperature is significantly lower than that of the product of DME conversion under the same conditions (Table 3).

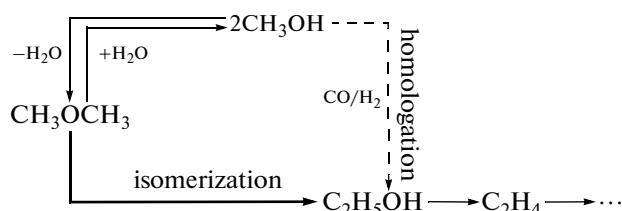
Based on these data, we can conclude that ethanol is most probably formed mainly through the isomerization of DME; that is, the reaction of methanol homologation to ethanol is much more difficult than the isomerization of DME to ethanol.

The conversion of DME and MeOH was studied under the "homologation conditions" on a La-Zr-HZSM/Al₂O₃ catalyst modified with the rhodium macrocomplex. Table 5 shows that the selectivity for ethanol on La-Zr-Rh-HZSM/Al₂O₃ in the conversion

of DME is much lower than that on Rh-HZSM/Al₂O₃ (Table 3); the conversion of methanol in an atmosphere of CO and H₂ on the La-Zr-Rh-HZSM/Al₂O₃ catalyst, unlike the Rh-HZSM/Al₂O₃ catalyst, occurs with the formation of trace amounts of ethanol. The occurrence of the DME conversion reaction in a flow of syngas instead of helium leads to an insignificant increase in the conversion of DME and an increase in the total selectivity for C₂–C₄ olefins with a higher increase for propylene.

The appreciably lower yield of ethanol on La-Zr-Rh-HZSM/Al₂O₃ can be explained by a higher activity of the catalyst in the synthesis of olefins. The increase in the selectivity for olefins in the DME conversion in an atmosphere of CO and H₂ suggests that, along with the isomerization of DME, a competitive reaction of DME dehydration to methanol takes place, and ethanol can also be formed via its homologation reaction.

Based on the above results, we can assume that the formation of lower olefins follows Scheme 2, which implies ethanol is produced mostly via the isomerization of DME.



Scheme 2. Formation of ethylene from DME or methanol.

An increase in the temperature to 340°C sharply enhances the selectivity for the formation of olefins from DME on rhodium-modified samples (Table 6). For example, an increase in the temperature from 270 to 340°C leads to an increase in the DME conversion over the Rh/HZSM-5/Al₂O₃ catalyst from 20.4 to 100 wt %; the selectivity for $\Sigma\text{C}_2^--\text{C}_4^--$ olefins remains almost unchanged. By contrast, the DME conversion on La/Zr/Rh/HZSM/Al₂O₃ increases only up to 73% and the selectivity for C₂–C₄ olefins increases from

Table 4. Conversion of MeOH on an Rh(0.1)/HZSM/Al₂O₃ catalyst

$T, ^\circ\text{C}$	Conversion, %	Product composition, wt %							
		CH ₄	C ₂ ⁼	C ₃ ⁼	C ₄ ⁼	C ₅ ⁼	ΣC_{2+}	DME	EtOH
240	9.4	1.2	2.7	2.8	—	—	2.1	90.6	0.6
270	78.3	11.9	8.2	16.3	—	0.4	37.9	21.3	4.0

Note: $P = 0.1$ MPa; original mixture: 10% MeOH + 30% CO + 60% H₂; $v_0 = 2000$ h⁻¹.

Table 5. Conversion of DME and MeOH on La-Zr-Rh(0.1)/HZSM/Al₂O₃

Feed mixture	<i>T</i> , °C	Conver- sion, %	Product composition, wt %								
			CH ₄	C ₂ ⁼	C ₃ ⁼	C ₄ ⁼	C ₅ ⁼	SC ₂₊	MeOH	EtOH	DME
DME + He	240	0.5	0.9	4.6	14.2	0.3	0.2	0.8	79.0	—	—
	270	1.7	0.4	7.1	30.8	1.2	0.6	1.3	57.1	1.5	—
MeOH + CO + H ₂	240	45.0	1.3	—	—	—	—	tr.	—	tr.	98.7
	270	55.4	1.3	tr.	—	—	—	tr.	—	tr.	98.7
DME + CO + H ₂	240	0.6	0.9	8.8	28.4	—	—	3.8	56.9	1.2	—
	270	1.9	0.6	13.9	39.2	—	—	3.4	41.6	1.3	—

P = 0.1 MPa, *v*₀ = 2000 h^{−1}.**Table 6.** Conversion of DME and MeOH in conditions of olefin synthesis

Catalyst	Feed mixture	Conver- sion, %	Product composition, wt %							
			CH ₄	C ₂ ⁼	C ₃ ⁼	C ₄ ⁼	C ₅ ⁼	ΣC ₂₊	ΣC ₂ ⁼ − C ₄ ⁼	
Rh/HZSM/Al ₂ O ₃	DME (10%) + He	99.9	0.2	24.3	19.4	6.3	2.7	47.1	50.0	
La-Zr/HZSM/Al ₂ O ₃	DME (10%) + He	70.0	2.5	26.0	44.4	6.4	3.6	17.1	76.8	
La-Zr-Rh/HZSM/Al ₂ O ₃	DME (10%) + He	73.0	0.2	30.4	37.9	18.7	0.8	12.0	87.0	
	MeOH (10%) + CO (30%) + H ₂ (60%)	100	2.4	28.1	22.2	7.0	—	40.3	57.3	
	DME (10%) + CO (30%) + H ₂ (60%)	96.0	0.5	32.0	48.0	10.1	0.9	8.5	90.1	

Note: (*T* = 340°C, *P* = 0.1 MPa, *v*₀ = 2000 h^{−1}).**Table 7.** Parameters of the synthesis of lower olefins from DME and methanol according to data of the different companies

Parameters	Process			
	company 1	company 2	company 3	Topchiev Inst., Russ. Acad. Sci.
Catalyst	SAPO-34	SAPO-34	ZSM-5	La-Zr-Rh/HZSM-5
Temperature, °C	500	450	450	340
Pressure, atm.	1.5	1.0	1.0	1.0
Feedstock:				
DME/methanol, vol %	50/50	50/50	50/50	100/0
<i>v</i> ₀ , h ^{−1}	3000	2000	—	2000
DME/methanol conversion, %	97	100	98	96
Product composition %:				
ethylene	33	40	4	32
propylene	47	34	68	48
butylene	9	8	1.5	10
methane	1.5	—	1.5	0.5
C ₂ –C ₅ alkanes	9.5	—	25	9.5
Selectivity for C ₂ –C ₄ olefins				
olefins, %	89	82	74	90
Yield of olefins, %	87	82	72	87
Catalyst on-stream time, h	1–2	1–2	700	700

39.7 to 87 wt %. In the case of methanol, the selectivity for olefins is 57.3 wt % with a conversion of 100%.

Thus, the introduction of rhodium into La/Zr/HZSM/Al₂O₃ leads to an insignificant increase in the activity in the conversion of DME and to a considerable increase in the selectivity for C₂=C₄ olefins (an increment of more than 10 wt %). Simultaneously, a redistribution of the composition of resulting olefins toward an increase in the yield of ethylene and butylenes and a decrease in the yield of propylene takes place. These data show that it is, in principle, possible to vary the composition of resulting olefins over a fairly wide range. The occurrence of the DME conversion reaction in a syngas instead of a helium stream leads to a sharp increase in the conversion and to a change in the composition of olefins in the direction of increasing propylene with an almost unchanged total yield of C₂=C₄ olefins at a level of 87–90 wt %.

Table 7 collates our data with the published data obtained at main engineering centers that have designed their own processes.

The technology and the catalyst designed by the Topchiev Institute make it possible to synthesize lower olefins from DME with the same high yield as in the commercialized “methanol” processes and, moreover, at a lower temperature and using a more stable catalyst.

In summary, the direct production of DME from syngas and its subsequent conversion to C₂=C₄ olefins on rhodium-containing zeolite catalysts provide a high feedstock conversion and a high selectivity for olefins (up to 90 wt %), opens an opportunity for varying the composition of olefins according to the manufacturing requirements, and significantly simplifies the process technology.

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