

Conversion of Oxygenates to Aromatic Hydrocarbons on a Commercial Zeolite Catalyst: Comparison of Ethanol and Dimethyl Ether

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Abstract—Conversion of oxygenates to aromatic hydrocarbons in the syngas medium in the presence of a commercial zeolite-containing catalyst was studied. The influence of pressure on aromatization of dimethyl ether and ethanol was examined. At 400°C, an increase in the pressure from 0.1 to 3.0–10.0 MPa leads to a sharp increase in the yield of aromatic compounds. Dimethyl ether and ethanol, which are isomers belonging to different classes of compounds, were compared as substrates in conversion to aromatic hydrocarbons. At elevated pressure, dimethyl ether compared to ethanol exhibits higher selectivity in formation of the desired synthesis products, allowing synthesis of liquid hydrocarbons with increased content of arenes.

Keywords: oxygenates, ethanol, dimethyl ether, aromatic hydrocarbons, pressure, zeolite catalyst, selectivity

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Aromatic compounds are feedstock for producing a wide range of polymer materials for various purposes: plastics, synthetic fibers, rubbers, and other chemical products. Among commercially produced aromatic substances, lower arenes (benzene, toluene, xylenes) have found the widest use in chemical industry. On the other hand, aromatic compounds, including C₉₊ arenes and their hydrogenation products, allow production of environmentally clean jet fuels for various purposes with preset characteristics and high calorific value. In addition, C₉₊ aromatic hydrocarbons (AHs), primarily tri- and tetramethylbenzenes, are starting compounds for producing anhydrides, acids, and esters used in the synthesis of epoxy resins and plasticizers [1].

The AH production throughout the world increases by approximately 3% annually owing to the steadily growing demand; today it already exceeds 100 mln tons

annually, of which approximately 2 mln tons is annually produced in Russia [2]. The commercial production of arenes is now based on processing of petroleum fractions (reforming, pyrolysis) and coals (coking). However, these processes cannot completely meet the market demand, which leads to the deficit of commercially demanded aromatic hydrocarbons and to the growth of their prices. The growing competition and strengthening of environmental requirements make it necessary to search for alternative raw materials for AH production. Light (C₂–C₄) hydrocarbons [3, 4], syngas [5, 6], and oxygen-containing organic compounds [7, 8] can be considered as such raw materials. Such oxygenates as ethanol and other alcohols can be prepared from the biomass [9], and dimethyl ether (DME), directly from syngas under relatively mild conditions [10], which makes these compounds extremely attractive for aromatization from both environmental and process viewpoints.

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The possibility of using catalysts based on zeolites of MFI structure for converting ethanol and DME to AH concentrate was demonstrated previously [6, 7, 11, 12]. At atmospheric pressure, the ethanol conversion without inert medium and without syngas allows synthesis of aromatic hydrocarbons in approximately 20% yield based on the feed passed [6, 11]. The DME conversion on modified zeolite-containing catalytic systems yields mainly light olefins and a small amount of liquid hydrocarbons containing aromatic compounds [13–15]. However, at elevated pressure and moderate temperatures the DME conversion is accompanied by a sharp increase in the AH formation. The revealed problems stimulated studies of the conversion of the oxygenates in various media in a wide range of pressures and reactant concentrations. The influence of pressure on the conversion of a particular oxygenate can be evaluated by performing the experimental studies in the pressure range of 0.1–10.0 MPa. In this study, we examined the influence of pressure to gain deeper insight into specific features of ethanol and DME conversion on modified zeolite catalysts.

This study deals with the conversion of ethanol and DME, which are alternative raw materials and isomers belonging to different classes of compounds, to aromatic compounds. We examined the influence of pressure on the process parameters and specific features of aromatization of these oxygenates in the presence of syngas.

EXPERIMENTAL

The synthesis of aromatic hydrocarbons from oxygenates was performed using IK-17-M zeolite-containing catalyst intended for aromatization of the propane–butane fraction and produced on the semicommercial scale by the Novosibirsk Chemical Concentrates Plant (Novosibirsk, Russia). The catalyst was developed by the Institute of Catalysis, Siberian Branch, Russian Academy of Sciences [TU (Technical Specification) 2177-008-07622236–2006] on the basis of IK-17-1 zeolite of MFI type and Al_2O_3 binder (no more than 23 wt %); the catalyst was modified with zinc. According to the data of X-ray fluorescence analysis performed at the Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, the zinc content of the catalyst was 3 wt %.

Experiments on aromatization of oxygenates were performed on a small-scale flow-through pilot

installation in the presence of a fixed bed of the zeolite containing catalyst. A 3-g portion of the catalyst was mixed with an equal volume of quartz and loaded into the isothermal zone of the reactor. The oxygenates were fed to the reaction zone directly in a mixture with syngas ($\text{H}_2/\text{CO} = 2$ mol/mol). The concentration of the oxygenates at the reactor inlet was maintained on the level of 43–46 vol % in all the experiments. The synthesis was performed at 400°C, pressure of 0.1–10.0 MPa, and weight hourly space velocity (WHSV) of 3.0–30.0 h^{-1} .

The required amounts of ethanol and DME (in the liquefied state) were fed into the installation with an HPP 5001 high-pressure fluid-flow dosing pump (Czech Republic). The syngas flow rate was controlled with a Bronkhorst F-232M-RAD-33-V gas flow rate regulator (Netherlands). The flow rate of gaseous synthesis products was recorded with a Shinagawa DC-1C-M gas flow meter (Japan). The temperature in the reactor was controlled with OVEN TRM-210 automated temperature measurement and control devices (Russia). The pressure in the system was maintained with a Swagelok KPB1NOD412P200B0 mechanical back-pressure regulator (the United States).

After the experiment completion, the liquid products were discharged into receivers, the weights and volumes of the aqueous and organic phases were determined, and both phases were analyzed. The gases dissolved in liquid hydrocarbons were sampled into a special gas syringe and analyzed.

The reaction products were analyzed by gas chromatography. Chromatographic analysis of gas and liquid mixtures was performed as described in [16].

The main process parameters were determined from the material balance.

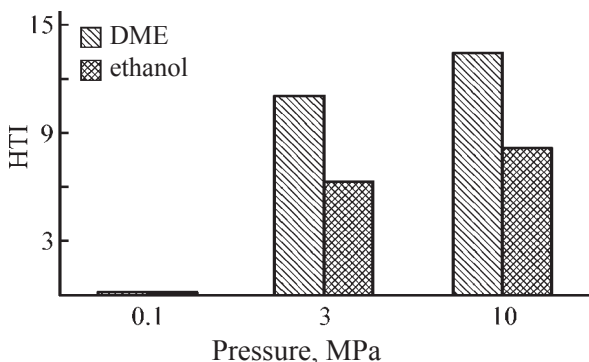
The oxygenate conversion (X) was calculated by Eq. (1)

$$X = \frac{m_0 - m}{m_0} \times 100\%, \quad (1)$$

where m_0 and m are the ethanol (or DME) weights at the reactor inlet and outlet, respectively (g).

The selectivity to liquid hydrocarbons (S_{liq}) was calculated by Eq. (2)

$$S_{\text{liq}} = \frac{m_{\text{liq}}}{m_{\text{liq}} + m_{\text{gas}}} \times 100 \text{ wt } \%, \quad (2)$$



Dependence of the hydrogen transfer index on the pressure and kind of oxygenate ($T = 400^\circ\text{C}$, $\text{WHSV} = 3.0 \text{ h}^{-1}$).

where m_{liq} and m_{gas} are the weights of the liquid and gaseous hydrocarbons, respectively (g).

The yield of aromatic hydrocarbons (Y_{AH}) was determined by Eq. (3)

$$Y_{\text{AH}} = \frac{X}{100} \frac{S_{\text{liq}}}{100} \frac{c_{\text{AH}}}{100} \times 100 \text{ wt } \%, \quad (3)$$

where c_{AH} is the AH concentration in liquid hydrocarbons (wt %).

The hydrogen transfer index (HTI) was calculated by Eq. (4)

$$\text{HTI} = \frac{m_{\text{alk}}}{m_{\text{olef}}}, \quad (4)$$

where m_{alk} and m_{olef} are the weights of the C_{2+} alkanes and olefins formed, respectively (g).

RESULTS AND DISCUSSION

The conversion of organic substrates to aromatic compounds occurs with high yield, as a rule, at temperatures above 400°C . However, the experience of ethanol and DME conversion in the presence of zeolitic catalysts of MFI structure shows that the conversion of oxygenates at 450°C is accompanied by increased gas evolution. This fact suggests intensification of the cleavage of the C–C bond, leading to a decrease in the selectivity to liquid hydrocarbons; as a result, the AH yield becomes low. Therefore, the experiments on ethanol and DME aromatization were performed at 400°C . The total AH yield was used as an overall

criterion for comparing the experimental data. The main results of the experiments are given in Table 1.

The experiments show that the pressure strongly influences the conversion of DME and ethanol to aromatic compounds. As seen from Table 1, an increase in the pressure in the syngas medium from 0.1 to 3.0 MPa leads to a sharp increase in the selectivity to liquid hydrocarbons and, correspondingly, in the yield of aromatic compounds (Y_{AH}). Attempted aromatization of oxygenates at atmospheric pressure mainly yields gaseous olefins and alkanes, and liquid hydrocarbon fractions are virtually fully absent. For example, at WHSV of 3.0 h^{-1} , the selectivity to liquid hydrocarbons and the AH yield were approximately 2%. As the feed space velocity is increased further, no aromatic compounds are formed at all. These trends are due to the fact that elevated pressure intensifies the intermediate steps of oligomerization and cyclization of olefins, which are primary synthesis products; the subsequent dehydrogenation of the product with hydrogen transfer, occurring under the synthesis conditions, favor the formation of arenes. The sequential character of the formation of aromatic compounds is also confirmed in experiments with WHSV variation: Its increase leads to a monotonic decrease in the AH yield.

It is important that the contribution of hydrogen transfer reactions to the formation of aromatic compounds is more significant compared to the dehydrogenation involving Zn sites, as indicated by high values of the hydrogen transfer index (HTI, see figure). The hydrogen transfer reactions occur in the presence of DME more intensely than in the presence of ethanol. As the pressure is increased from 3 to 10 MPa, HTI increases from 11.1 to 13.4 on DME and from 6.2 to 8.0 on ethanol. In both cases, the ArH yield decreases (Table 1). As the pressure is decreased to 0.1 MPa, HTI sharply decreases to 0.1.

It should be noted that the occurrence of the dehydrogenation follows from the formation of free hydrogen: Its amount increases by 10–15 wt % according to the material balance data.

An increase in the pressure from 3.0 to 10.0 MPa leads to a gradual decrease in the yield of the target synthesis products. The decrease is particularly noticeable at low WHSV values. The relative decrease in the AH yield at $\text{WHSV} = 3 \text{ h}^{-1}$ is 30% in the cases of both DME and ethanol. It should be noted that aromatization in the presence of DME occurs more intensely compared to ethanol. This relationship is observed virtually

Table 1. Conversion, selectivity to liquid hydrocarbons, and AH yield as functions of the pressure and kind of oxygenate ($T = 400^\circ\text{C}$)

WHSV, h ⁻¹	DME			Ethanol		
	X , %	S_{liq} , wt %	Y_{AH} , %	X , %	S_{liq} , wt %	Y_{AH} , %
10.0 MPa						
3.0	99.9	57.2	22.6	99.9	61.6	19.7
6.0	98.9	56.2	22.5	99.9	66.7	22.5
15.0	90.6	55.0	22.2	99.7	57.2	20.1
30.0	62.6	34.6	15.0	98.1	44.3	15.0
3.0 MPa						
3.0	99.0	51.0	32.7	100	66.8	28.4
6.0	98.7	41.7	24.5	99.8	66.8	25.9
15.0	98.4	58.0	23.7	99.8	53.3	19.3
30.0	88.0	46.6	21.8	98.9	34.8	14.7
0.1 MPa						
3.0	99.9	2.0	1.8	99.9	2.3	1.8
6.0	99.9	0.0	0.0	99.9	0.0	0.0
15.0	99.9	0.0	0.0	99.9	0.0	0.0
30.0	97.4	0.0	0.0	97.4	0.0	0.0

throughout the ranges of the varied process parameters. As seen from Table 1, the highest AH yield in the case of DME is observed at a pressure of 3.0 MPa and reaches 32.7%. However, ethanol shows higher selectivity to liquid hydrocarbons: The maximal selectivity reaches 67 wt % against 58 wt % for DME.

It should be noted that the aromatization on the commercial zeolite-containing catalyst occurs throughout the examined pressure range with exhaustive conversion of the feed, exceeding 90%. The DME conversion at high feed space velocities and pressures of 10 and 3 MPa appreciably decreases (to 62 and 88%, respectively), whereas in the case of ethanol the conversion remains on the level of 98%. This fact may be due to increased ability of DME, compared to ethanol, for coking on acid sites of the zeolite.

The experimental studies on the synthesis of aromatic hydrocarbons from DME and ethanol in the presence of a zeolitic catalyst demonstrate an increase in the content of aromatic compounds (c_{AH}) in the liquid hydrocarbons with decreasing pressure. Because the practical value of

arenes is different depending on their chemical structure, for more detailed generalization of the results they were subdivided into two fractions, C_6 – C_8 and C_{9+} . The AH distribution in the liquid reaction products is given in Table 2.

As shown in Table 2, the total amount of AHs in liquid hydrocarbons increases, on the average, by 15–30 rel. % as the pressure is decreased from 10.0 to 3.0 MPa. The use of DME, compared to ethanol, as a feedstock allows preparation of a mixture of liquid hydrocarbons with higher AH concentration. In particular, in the presence of DME the total amount of arenes present in liquid synthesis products at a pressure of 3.0 MPa exceeds 50 wt % and reaches 71.8 wt % at $\text{WHSV} = 3.0 \text{ h}^{-1}$, whereas with ethanol under similar conditions the total AH concentration is in the range of 42–48 wt %. When performing aromatization of the oxygenates at a pressure close to atmospheric, the content of aromatic components considerably increases, reaching 91–95 wt %. Owing to molecular-sieve properties of the MFI structure zeolite catalyst, monocyclic alkylaromatic hydro-

Table 2. Content of aromatic hydrocarbons in liquid hydrocarbons ($T = 400^\circ\text{C}$)

WHSV, h ⁻¹	Content, wt %					
	DME			Ethanol		
	C ₆ -C ₈	C ₉₊	AHs	C ₆ -C ₈	C ₉₊	AHs
10.0 MPa						
3.0	9.3	45.0	54.3	11.0	32.0	43.0
6.0	9.2	35.2	44.4	11.1	30.5	41.6
15.0	14.3	28.6	42.9	8.6	27.4	36.0
30.0	17.3	33.7	51.0	10.6	27.0	37.6
3.0 MPa						
3.0	13.6	58.2	71.8	19.2	29.3	48.5
6.0	14.8	37.3	52.1	13.8	27.9	41.7
15.0	23.1	28.2	51.3	15.0	27.1	42.1
30.0	25.7	24.9	50.6	17.8	24.5	42.3
0.1 MPa						
3.0	27.0	68.0	95.0	33.0	58.2	91.2
6.0	0.0	0.0	0.0	0.0	0.0	0.0
15.0	0.0	0.0	0.0	0.0	0.0	0.0
30.0	0.0	0.0	0.0	0.0	0.0	0.0

carbons containing from 6 to 12 carbon atoms prevail among aromatic compounds. The aromatic concentrate mainly consists of C₉₊ arenes; their weight fraction among aromatic compounds is 50–80% depending on the weight hourly space velocity.

CONCLUSIONS

Our experimental data show that the pressure largely influences the conversion of dimethyl ether and ethanol to aromatic hydrocarbons and the distribution of the synthesis products. The pressure elevation from 0.1 to 3.0–10.0 MPa positively influences the selectivity of the formation of liquid hydrocarbons containing aromatic compounds, which is reflected in an increase in the total yield of aromatic hydrocarbons. Dimethyl ether exhibits the highest selectivity in aromatization in the syngas medium on the zeolite-containing catalyst, giving the hydrocarbon concentrate containing more than 70 wt % arenes with the target product yield of 32.7%. The ethanol conversion to aromatic hydrocarbons is characterized

by increased selectivity to liquid hydrocarbons and decreased arene content; therefore, the yield of aromatic hydrocarbons is relatively low.

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CONFLICT OF INTEREST

One of coauthors, A.L. Maksimov, is the Editor-in-Chief of *Zhurnal Prikladnoi Khimii* (*Russian Journal of Applied Chemistry*); the other authors have no conflict of interest.

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