

## Generation of Liquid Products from Natural Gas over Zeolite Catalysts

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### Abstract

The main component of the natural gas is methane, whose molecules are characterized by a high chemical and thermal stability. It is impossible to perform the chemical transformation of natural gas into liquid organic compounds without applying highly active polyfunctional catalysts. Natural gas might be converted into liquid products in the presence of zeolite catalysts of pentasil family. Zeolite catalysts of ZSM-5 type were prepared to realize the process. They contained various amounts of Zn and Ga promoters introduced by ion exchange and impregnation. It has been shown that in the presence of small amounts of C<sub>2</sub>-C<sub>5</sub> alkanes in the feedstock the methane is converted into aromatic hydrocarbons much more readily and in softer conditions than pure methane. At optimum process conditions reached is a high conversion of the natural gas into a mixture of aromatic hydrocarbons. This mixture mainly consists of benzene and naphthalene and small amounts of their derivatives – toluene, C<sub>8</sub> and C<sub>9+</sub> alkylbenzenes, methyl- and dimethylnaphthalenes. An optimum composition of zeolite matrix and the amount of the modifier in the catalyst have been established.

### Introduction

Due to a gradual depletion of oil reserves the problem of more complete use of natural and associate gases as a feedstock for chemical and petrochemical industry is urgent and should take priority. As for now the worldwide resources of natural gas are immense. Its processing using conventional technologies is not economic, because it is performed through some power-consuming stages: production of the synthesis-gas followed by methanol synthesis and higher alcohols or hydrocarbons mixture via Fisher-Tropsch process. At present the main part of the gaseous hydrocarbons is used as a fuel to produce electric and heat energy, an insignificant amount being used efficiently to synthesize the petrochemical products. In this connection novel process of methane conversion into liquid fuels or petrochemical feedstock is important for an efficient and rational use of the resources of natural and associate gas. Recently the research aiming at a direct conversion of low alkanes, first of all methane, into the hydrocarbons with a larger molecular mass is carried out in many countries. Different variants of the catalytic methane

conversion are envisaged [1-8]: into low olefins used as the feedstock for chemical industry, *e.g.*, ethylene, to produce the gasoline fraction; into an ecologically pure motor fuel (a joint conversion of methane and methanol); into a mixture of aromatic hydrocarbons followed by the isolation of benzene and naphthalene.

The processes of chemical processing of gaseous hydrocarbons acquire a special appeal and efficiency if they are performed immediately at the oil-gas fields because they allow converting large gas amount into liquid products. These products may be used *in-situ* or transported to the oil refineries using the existing pipelines. That is why research in this field must go on.

Natural and associate gases, a wide fraction of light hydrocarbons (WFLH) and refinery gases might be converted into liquid products using the zeolite catalysts of pentasil family possessing unique molecular-sieve, adsorption and acidic properties. The main advantages of the catalysts developed and the processes on their base are as follows: insensitivity of catalytic systems to various catalytic poisons contained in the stock; application of a fixed bed catalyst layer; a high selectivity of the product forma-

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tion; technology versatility allowing one to use both the wide fraction of light hydrocarbons and natural and associate gases as the feedstock. The liquid products obtained may be used as a high-octane blending compound to enhance the octane number of gasolines; after the separation into individual hydrocarbons they represent a valuable feedstock for petrochemical industry. The processes of aromatic hydrocarbons synthesis in the presence of zeolite-containing catalysts allows one to use the gaseous hydrocarbons produced or recovered with oil more rationally, in this way one have additional oil to produce the aromatics. Moreover, the environment in oil-and-gas producing regions is improved.

## Experimental

To produce the catalysts, high-silicate zeolites (HSZ) with the silicate modulus (M) 30 and 40 without organic additives were synthesized. Gallium was introduced into the zeolites via ion exchange, zinc – via impregnation by its nitrate solution. The samples modified were dried at 110°C and calcined in air-flow at 550°C for 6 hours. The amounts of the gallium and zinc oxides introduced were, respectively, 0.5; 1.0; 2.0 and 3.0 wt.%.

X-ray analysis of the samples was carried out using DRON-3 X-ray instrument (Ni-filtered, Cu  $K_{\alpha}$  irradiation). Zeolites diffractograms were treated by determining the interplanar spacings and the intensities of the lines of the samples studied followed by the comparison of their position and relative intensity to the reference. X-ray study of the initial zeolites with different silicate modulus has shown that all of them are of high crystallinity degree and do not contain foreign admixture phases. Their structure is closer to the structure of ZSM-5 zeolite. IR-spectra of the zeolites studied were recorded on "Specord-75 IR" spectrophotometer in pellets with KBr (1.2 mg of zeolite per 300 mg of KBr). IR-spectroscopy data evidence that the adsorption bands of the samples are at 450 and 550  $\text{cm}^{-1}$  identical to the spectra of ZSM-5 zeolites. The ratio between the intensities of the adsorption bands in the region from 550 to 450  $\text{cm}^{-1}$  allows assessing the purity of the samples synthesized and their degree of crystallinity. The absence of the adsorption bands at 960  $\text{cm}^{-1}$  verifies a high degree of crystallinity of the samples and the absence of the amorphous phase admixture in their composition.

Catalytic experiments were carried out at atmo-

spheric pressure of natural gas in a flow system with a quartz reactor (14 mm i.d.) where we loaded 1  $\text{cm}^3$  of 0.25-0.50 mm fraction of the crushed catalyst pellets. The pipe at the output of the reactor and gas-sampling valve had the temperatures of 225°C, which prevents the condensation or strong adsorption of higher hydrocarbons. Upon the nitrogen flow-through (40 ml/min) of the reactor containing the catalyst for 30 min at 500°C a temperature necessary to carry out the reaction was set. Then the nitrogen flow was replaced with the initial gas mixture consisting of 81.60%  $\text{CH}_4$ ; 6.46%  $\text{C}_2\text{H}_6$ ; 7.40%  $\text{C}_3\text{H}_8$ ; 4.04%  $\text{C}_4\text{H}_{10}$  and 0.47%  $\text{C}_5\text{H}_{12}$ . The reactor was blown through with nitrogen in preset reaction conditions before every experiment. The tests were carried out at the reaction temperatures of 500-700°C, gas hourly space velocity (GHSV) of 250-2500  $\text{h}^{-1}$  and atmospheric pressure. The reaction products were analysed using a gas chromatograph equipped with a flame ionisation detector. To separate the hydrocarbons, a capillary column with OV-101 (100 m  $\times$  0.25 mm  $\times$  0.5 mm) was used; carrier gas was nitrogen. To assess the catalytic activity of the samples in the process of natural gas conversion, we determined the conversion degree of the components of the initial gas and calculated the yield of the gaseous and liquid reaction products and selectivity of aromatic hydrocarbons formation.

## Results and Discussion

Figure 1 shows the influence of the process temperature on the composition of natural gas conversion over a zeolite with M = 40 containing 0.5% ZnO, GHSV is 500  $\text{h}^{-1}$ .

With the reaction temperature increase the degree of the feedstock conversion and the yield of aromatic hydrocarbons increase. At 700°C they reach, respectively, 39.7 and 32.9%. The liquid products contain more benzene and naphthalene and less toluene and  $\text{C}_8$ - $\text{C}_9$  alkylbenzenes, the concentration of the alkyl-naphthalenes passing through maximum at 600°C. The gaseous products have an increased hydrogen concentration and a decreased amount of alkanes and alkenes with temperature increase. The selectivity of aromatic hydrocarbons formation within the temperature range of 500-700°C over 0.5% Zn/HSZM = 40 is 72.0-82.9%. Therefore, over a modified zeolite catalyst the natural gas is converted into aromatic hydrocarbons at a high selectivity.

Figure 2 shows the influence of the GHSV on

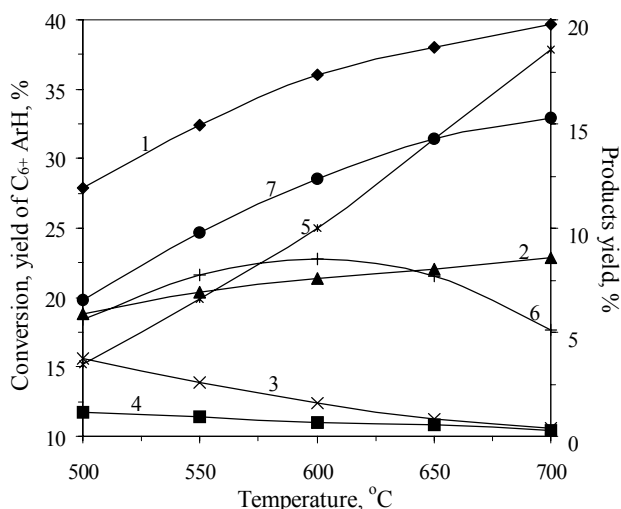


Fig. 1. Natural gas conversion (1) and the yields of benzene (2), toluene (3), C<sub>8</sub>-C<sub>9</sub> ArH (4), naphthalene (5), C<sub>11</sub>-C<sub>12</sub> ArH (6) and C<sub>6+</sub> ArH (7) vs. the temperature of natural gas conversion over 0.5% Zn/HSZM = 40 (GHSV = 500 h<sup>-1</sup>).

natural gas conversion and composition of the products of its conversion over 0.5% Zn/HSZM = 40 at 550°C. The reduction of the contact time from 7.2 to 1.44 s results in a decrease in conversion and yield of aromatic hydrocarbons by 5.0 and 5.8%, respectively. The aromatic hydrocarbons contain less benzene, naphthalene and alkyl naphthalenes and more toluene and C<sub>8</sub>-C<sub>9</sub> alkylbenzenes with increasing GHSV. Gaseous products have a decreased hydrogen concentration and contain an increased amount of alkanes and alkenes. The selectivity of aromatic hydrocarbons formation over 0.5% Zn/HSZM = 40 decreases by 7.2% when GHSV rises from 500 to 2500 h<sup>-1</sup>.

Thus, a clear relationship between the yield of certain hydrocarbons and the conditions of the process of natural gas conversion is observed. At high temperatures and relatively high contact time, *i.e.*, in more severe conditions, the formation of preferentially non-saturated aromatic hydrocarbons (benzene, naphthalene) occurs, and at relatively low temperatures and low contact times alkylsubstituted aromatic hydrocarbons are formed in significant amounts. This is obviously connected to a reduced rate of arenes dealkylation process.

Similar dependences of the conversion and the yield of the products of natural gas conversion on the process temperature and GHSV are observed over the zeolites containing a large amount of zinc oxide. It is interesting to follow the influence of zinc oxide on the yield and composition of the liquid and gaseous products formed. As seen from the data of Fig.

3, the increase in Zn content in a zeolite from 0.5 to 1.0 wt.% does not significantly influence its catalytic activity and the yield of aromatic hydrocarbons.

The aromatic hydrocarbons contain mainly naphthalene and smaller amounts of benzene and C<sub>11</sub>-C<sub>12</sub> arenes. Further increase in zinc concentration leads to a decrease in general and aromatising zeolite activity and to a significant change in the composition of the products formed. The concentrations of toluene and alkylaromatic hydrocarbons declines and the naphthalene content rises. Moreover, the naphtha-

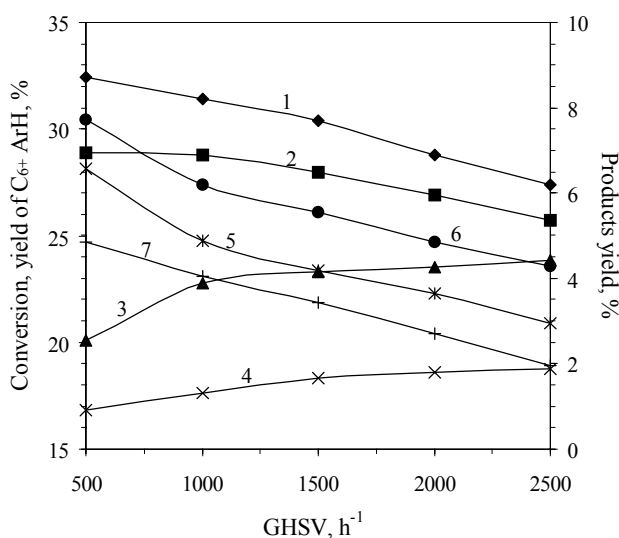


Fig. 2. Natural gas conversion (1) and the yields of benzene (2), toluene (3), C<sub>8</sub>-C<sub>9</sub> ArH (4), naphthalene (5), C<sub>11</sub>-C<sub>12</sub> ArH (6) and C<sub>6+</sub> ArH (7) over 0.5% Zn/HSZM = 40 vs. GHSV (T = 550°C).

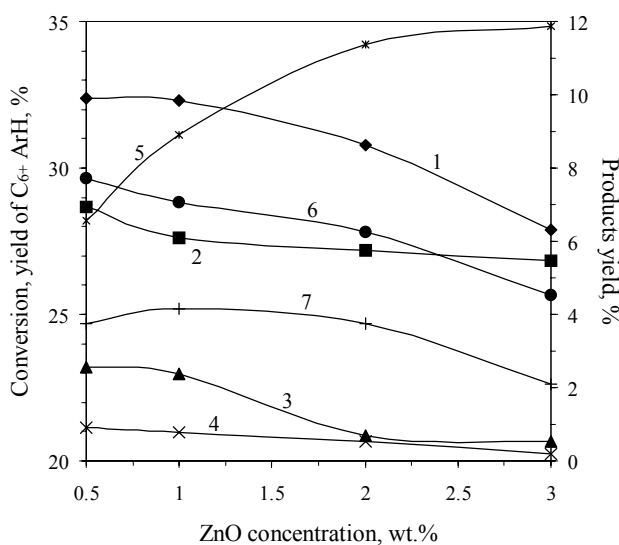


Fig. 3. Natural gas conversion (1) and the yields of benzene (2), toluene (3), C<sub>8</sub>-C<sub>9</sub> ArH (4), naphthalene (5), C<sub>11</sub>-C<sub>12</sub> ArH (6) and C<sub>6+</sub> ArH (7) vs. ZnO concentration in a zeolite with M=40 (T = 550°C; GHSV = 500 h<sup>-1</sup>).

lene fraction in aromatic products increases with the increase in zinc content in a zeolite despite of the reduction in total amount of the arenes formed. The gaseous products contain more alkanes and less alkenes and hydrogen.

Thus, not only the closest methane homologues contained in natural gas are converted over a zinc-modified zeolite with  $M = 40$  but also methane. In addition, methane is involved in the process at a temperature which is sufficiently low for its conversion (500°C). At 550-650°C methane conversion over 0.5-1.0 wt.% Zn/HSZM = 40 reaches 14-20%, in this case the yield of aromatic hydrocarbons is more than 20%. Benzene, naphthalene, methyl- and dimethylnaphthalenes are main liquid products of natural gas conversion over Zn-containing zeolite with  $M = 40$ , the amount of naphthalene formed increasing with Zn concentration in a zeolite and that of benzene decreasing. It should be noted that the selectivity of aromatic hydrocarbons formation does not significantly depend on zinc concentration in a zeolite, whereas maximum arenes amount is formed over a zeolite containing 0.5-1.0 wt.% ZnO. The composition of the products obtained may be varied both by changing the reaction conditions, first of all, the temperature, and the feedstock discharge as well as Zn content in a zeolite.

Figure 4 shows the influence of the process temperature on the composition of the products of natural gas conversion over a zeolite with  $M = 40$  containing 1.0 wt.% of  $\text{Ga}_2\text{O}_3$ , GHSV is 2000  $\text{h}^{-1}$ . With process temperature increase observed is an increase in feedstock conversion degree and in the yield of aromatic hydrocarbons. In the composition of liquid products the fraction of naphthalene and methylnaphthalenes increases and the concentration of toluene and  $\text{C}_8\text{-C}_9$  alkylbenzenes decrease. Benzene yield in the reaction products within all the range of the temperatures studied changes insignificantly.

With the temperature rise the hydrogen concentration increases and alkanes and alkenes amounts in gaseous products decrease. The selectivity of aromatic hydrocarbons formation over 1.0 wt.% Ga/HSZM = 40 is 70.6-78.0% at 500-650°C.

Figure 5 represents the data showing the GHSV influence on natural gas conversion and the composition of the products of its conversion over 1.0 wt.% Ga/HSZM = 40 at 600°C.

If the GHSV increases from 250 to 2500  $\text{h}^{-1}$ , a decrease in conversion and yield of aromatic hydrocarbons is observed. The concentrations of toluene,

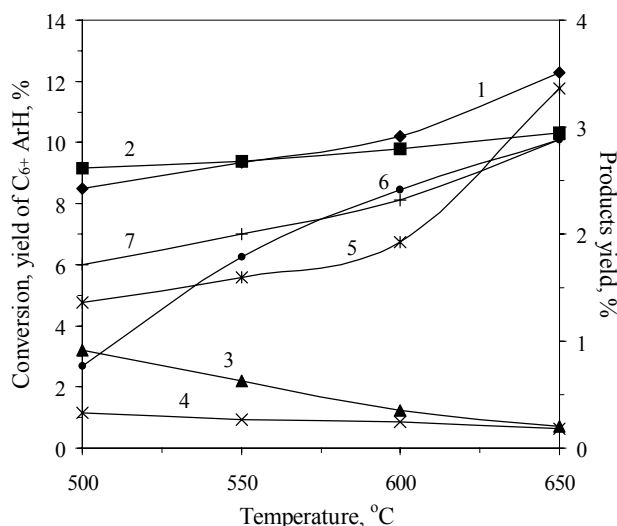


Fig. 4. Conversion (1) and the yields of benzene (2), toluene (3),  $\text{C}_8\text{-C}_9$  ArH (4), naphthalene (5),  $\text{C}_{11}\text{-C}_{12}$  ArH (6) and  $\text{C}_{6+}$  ArH (7) over 1.0% Ga/HSZM = 40 vs. the temperature of natural gas conversion process (GHSV = 2000  $\text{h}^{-1}$ ).

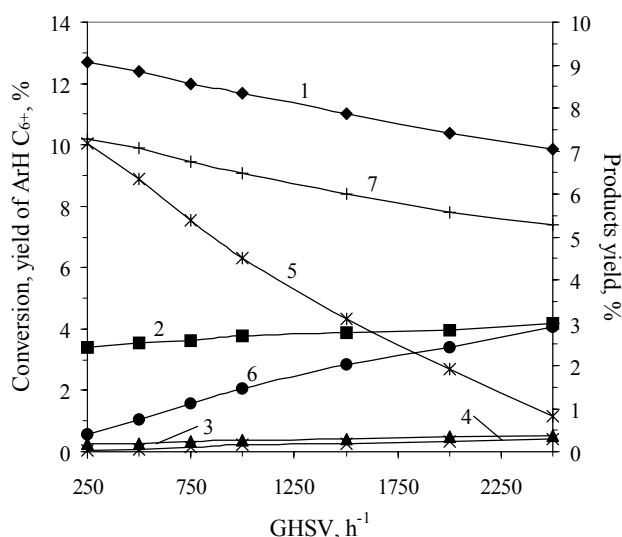


Fig. 5. Natural gas conversion (1) and the yields of benzene (2), toluene (3),  $\text{C}_8\text{-C}_9$  ArH (4), naphthalene (5),  $\text{C}_{11}\text{-C}_{12}$  ArH (6) and  $\text{C}_{6+}$  ArH (7) over 1.0% Ga/HSZM = 40 vs. gas hourly space velocity ( $T = 600^\circ\text{C}$ ).

$\text{C}_8\text{-C}_9$  alkylbenzenes and methylnaphthalenes increase, naphthalene concentration decreases, benzene concentration changes insignificantly. When the contact time is decreased, the selectivity of aromatic hydrocarbons formation over 1.0 wt.% Ga/HSZM = 40 drops from 80.3 to 74.0%. The gaseous products contain less hydrogen and more alkanes and alkenes.

Similar dependences of the conversion degree of natural gas and the products yield on the process temperature and GHSV are observed over the zeolites containing 0.5; 2.0 and 3.0 wt.% of gallium oxide.

As seen from the data of Fig. 6, with the increase in gallium concentration in the zeolite a rise in total and aromatising activities of the zeolite takes place. The conversion and the selectivity of aromatic hydrocarbons formation over 3.0 wt.% Ga/HSZM = 40 at 600°C and 2000 h<sup>-1</sup> are 11.7 and 77.8%, respectively. In addition, the zeolites containing 2.0 and 3.0 wt.% of gallium oxide are characterised by a higher catalytic activity at lower temperatures than for the samples containing less gallium oxide. The selectivity of aromatic hydrocarbons formation over these zeolites surpasses 70% even at 500°C and a GHSV of 2000 h<sup>-1</sup>, reaching 76.0% over 3.0 wt.% Ga/HSZM = 40 under these process conditions.

Thus, on the basis of the results obtained one may conclude that the largest amount of aromatic hydrocarbons are formed over a zeolite with silicate modulus 40 at gallium oxide content in the catalyst not lower than 3.0 wt.%.

By comparing the results obtained over the zeolites with the silicate modulus 40 containing Zn and Ga, one may note that Zn-containing catalysts exhibit a higher activity in the reaction of natural gas conversion. The concentration of aromatic hydrocarbons formed is significantly higher.

Similar dependences of the conversion and the yield of the products on the process temperature and the GHSV are observed over a zeolite with the silicate modulus 30 containing various amount of gallium oxide (Tables 1 and 2).

An increase in the degree of the feedstock conver-

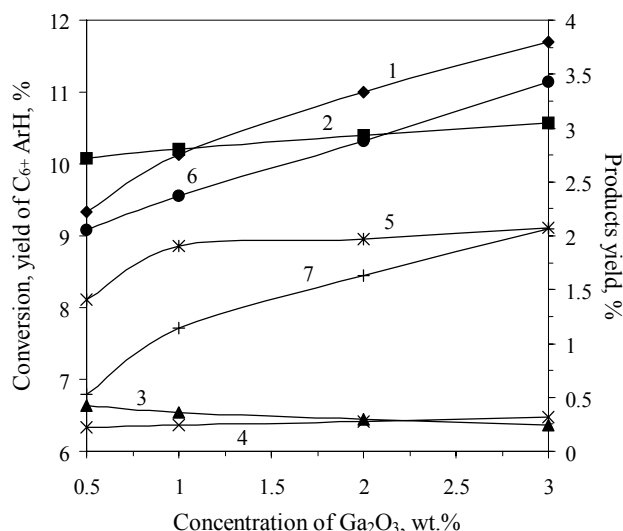


Fig. 6. Natural gas conversion (1) and the yields of benzene (2), toluene (3), C<sub>8</sub>-C<sub>9</sub> ArH (4), naphthalene (5), C<sub>11</sub>-C<sub>12</sub> ArH (6) and C<sub>6+</sub> ArH (7) vs. Ga<sub>2</sub>O<sub>3</sub> concentration in a zeolite with M = 40 (T = 600°C; GHSV = 2000 h<sup>-1</sup>).

sion and yield of the aromatic hydrocarbons is observed over the sample 3.0 wt.% Ga/HSZM = 40 with the temperature rise (the concentrations of naphthalene and alkyl naphthalenes increase and that of toluene drops). The selectivity of aromatic hydrocarbons formation reaches 81.6% at the reaction temperature of 650°C. In this case the conversion of the natural gas is 16.3%, which is by 2.5% higher than that over 3.0 wt.% Ga/HSZM = 40 catalyst under the similar process conditions.

Both over 3.0 wt.% Ga/HSZM = 30 and 3.0 wt.%

**Table 1**

The influence of the process temperature on the composition of the products of natural gas conversion over a zeolite (M = 30) containing Ga<sub>2</sub>O<sub>3</sub> (GHSV = 2000 h<sup>-1</sup>)

T, (°C)	X, (%)	Reaction products (wt.%)								Y <sub>Ar</sub> , (%)	S <sub>Ar</sub> , (%)
		H <sub>2</sub>	alkanes	alkenes	C <sub>6</sub> H <sub>6</sub>	C <sub>7</sub> H <sub>8</sub>	C <sub>8-9</sub>	C <sub>10</sub> H <sub>8</sub>	C <sub>11-12</sub>		
0.5% Ga <sub>2</sub> O <sub>3</sub> /HSZM = 30											
500	9.0	0.68	90.96	1.46	3.57	1.09	0.36	1.46	0.42	6.9	76.7
550	11.4	1.21	88.62	1.37	3.68	0.54	0.32	2.84	1.42	8.8	77.2
600	12.0	1.45	87.99	1.26	3.71	0.34	0.28	3.24	1.73	9.3	77.5
650	12.9	1.58	87.13	1.18	3.81	0.18	0.24	3.88	1.99	10.1	78.3
1.0% Ga <sub>2</sub> O <sub>3</sub> /HSZM = 30											
500	9.9	0.80	90.08	1.42	3.63	0.99	0.39	1.75	0.94	7.7	77.8
550	12.9	1.56	87.15	1.29	3.70	0.48	0.35	3.13	2.34	10.0	77.5
600	13.7	1.70	86.35	1.15	3.76	0.26	0.30	3.85	2.63	10.8	78.8
650	14.6	1.94	85.39	1.07	3.83	0.15	0.26	4.54	2.82	11.6	79.5

**Table 1**  
Continued

T, (°C)	X, (%)	Reaction products (wt.%)								Y <sub>Ar</sub> , (%)	S <sub>Ar</sub> , (%)
		H <sub>2</sub>	alkanes	alkenes	C <sub>6</sub> H <sub>6</sub>	C <sub>7</sub> H <sub>8</sub>	C <sub>8-9</sub>	C <sub>10</sub> H <sub>8</sub>	C <sub>11-12</sub>		
2.0% Ga <sub>2</sub> O <sub>3</sub> /HSZM = 30											
500	10.7	1.07	89.34	1.39	3.65	0.94	0.41	1.97	1.23	8.2	76.6
550	13.4	1.65	86.57	1.18	3.79	0.42	0.38	3.56	2.45	10.6	79.1
600	14.7	1.99	85.27	1.04	3.83	0.23	0.32	4.57	2.75	11.7	79.6
650	15.6	2.09	84.45	0.96	3.89	0.13	0.20	4.92	3.36	12.5	80.1
3.0% Ga <sub>2</sub> O <sub>3</sub> /HSZM = 30											
500	11.3	1.20	88.70	1.20	3.68	0.89	0.43	2.09	1.81	8.9	78.8
550	14.1	1.83	85.95	1.12	3.81	0.38	0.38	4.00	2.53	11.1	78.7
600	15.5	2.10	84.46	0.94	3.88	0.20	0.34	5.05	3.03	12.5	80.6
650	16.3	2.21	83.66	0.83	3.90	0.11	0.22	5.60	3.47	13.3	81.6

Note. T is reaction temperature; X is conversion degree; Y<sub>Ar</sub> is yield of aromatic hydrocarbons; S<sub>Ar</sub> is selectivity of aromatic hydrocarbons formation.

Ga/HSZM = 40 catalyts a decrease in the degree of natural gas conversion and yield of aromatic hydrocarbons is observed with GHSV increase, the reduction in corresponding indices reaching 2.2%. As far as it concerns the gaseous products, the hydrogen concentration decreases and the contents of alkanes and alkenes increase (Table 2). As seen from the data of the Tables 1 and 2, a similar relationship exists between the temperature and GHSV and the properties of the zeolite catalysts containing a smaller amount of gallium oxide.

Figure 7 shows the dependence of the natural gas conversion and products yield on gallium oxide concentration in a zeolite with the silicate modulus 30 at 600°C and 2000 h<sup>-1</sup>. The conversion degree of the initial feedstock increases with the gallium concentration in the catalyst and reaches 15.5% over a sample containing 3.0 wt.% of gallium oxide. The selectivity of aromatic hydrocarbons formation increases with the increase of the concentration of gallium oxide in the catalyst, preferentially due to the formation of naphthalene hydrocarbons. Benzene and toluene concentrations change insignificantly with changes of the Ga<sub>2</sub>O<sub>3</sub> content in a zeolite with M = 30.

Thus, one may conclude that the maximal conversion of natural gas and the highest yield of aromatic hydrocarbons are reached over a zeolite containing 3.0 wt.% of gallium oxide. It should be noted that the similar results were obtained over a zeolite with the silicate modulus 40. Obviously, the opti-

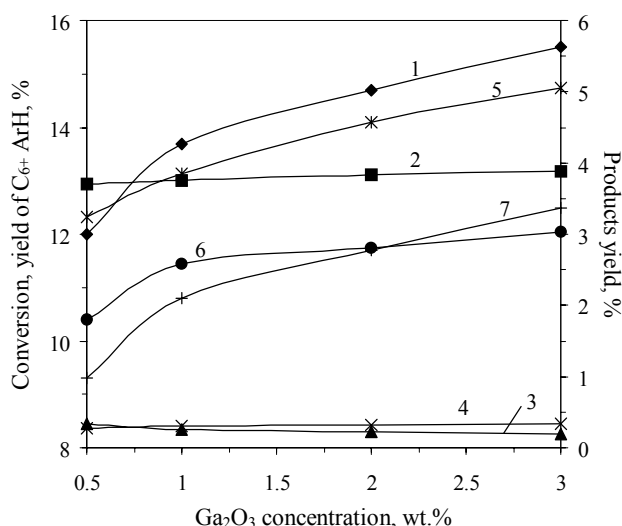


Fig. 7. Natural gas conversion (1) and the yields of benzene (2), toluene (3), C<sub>8</sub>-C<sub>9</sub> ArH (4), naphthalene (5), C<sub>11</sub>-C<sub>12</sub> ArH (6) and C<sub>6+</sub> ArH (7) vs. Ga<sub>2</sub>O<sub>3</sub> concentration in a zeolite with M = 30 (T = 600°C; GHSV = 2000 h<sup>-1</sup>).

imum ratio between Brönsted and Lewis acidic sites is established at this concentration of gallium oxide in zeolites of corresponding compositions.

Figure 8 shows the catalytic activity of zeolites containing the equal amounts of gallium oxide vs. SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> molar ratio in the process of natural gas conversion. The analysis of the data obtained demonstrates that the modified zeolites with the silicate modulus 30 exhibit a higher catalytic activity in natural gas conversion and a larger amount of aromatic

**Table 2**  
The influence of the gas hourly space velocity on the composition of the products of natural gas conversion over Ga<sub>2</sub>O<sub>3</sub>/HSZM = 30 (T = 600°C)

GHSV, (h <sup>-1</sup> )	X, (%)	Reaction products (wt.%)								Y <sub>Ar</sub> , (%)	S <sub>Ar</sub> , (%)
		H <sub>2</sub>	alkanes	alkenes	C <sub>6</sub> H <sub>6</sub>	C <sub>7</sub> H <sub>8</sub>	C <sub>8-9</sub>	C <sub>10</sub> H <sub>8</sub>	C <sub>11-12</sub>		
0.5% Ga <sub>2</sub> O <sub>3</sub> /HSZM = 30											
500	15.4	2.07	84.61	0.92	3.44	0.22	0.12	7.33	1.29	12.4	80.5
1000	14.6	1.94	85.41	1.05	3.57	0.26	0.15	6.16	1.46	11.6	79.5
1500	13.1	1.55	86.93	1.12	3.64	0.29	0.18	4.70	1.59	10.4	79.3
2000	12.0	1.45	87.99	1.26	3.71	0.34	0.28	3.24	1.73	9.3	77.5
1.0% Ga <sub>2</sub> O <sub>3</sub> /HSZM = 30											
500	16.3	2.20	83.71	0.79	3.51	0.20	0.12	7.67	1.80	13.3	81.6
1000	15.1	2.03	84.94	0.93	3.62	0.22	0.18	6.21	1.87	12.1	80.1
1500	14.5	1.98	85.49	1.03	3.69	0.24	0.24	5.22	2.11	11.5	79.3
2000	13.7	1.70	86.35	1.15	3.76	0.26	0.30	3.85	2.63	10.8	78.8
2.0% Ga <sub>2</sub> O <sub>3</sub> /HSZM = 30											
500	16.8	2.34	83.24	0.72	3.57	0.17	0.15	7.90	1.91	13.7	81.5
1000	16.2	2.17	83.82	0.81	3.65	0.19	0.19	6.98	2.19	13.2	81.5
1500	15.6	2.10	84.45	0.95	3.77	0.21	0.25	5.78	2.49	12.5	80.1
2000	14.7	1.99	85.27	1.04	3.83	0.23	0.32	4.57	2.75	11.7	79.6
3.0% Ga <sub>2</sub> O <sub>3</sub> /HSZM = 30											
500	17.8	2.51	82.33	0.56	3.63	0.11	0.17	8.35	2.31	14.6	82.0
1000	17.1	2.39	82.93	0.68	3.72	0.14	0.24	7.30	2.60	14.0	81.9
1500	16.4	2.24	83.56	0.80	3.81	0.17	0.29	6.17	2.96	13.4	81.7
2000	15.5	2.10	84.46	0.94	3.88	0.20	0.34	5.05	3.03	12.5	80.6

Note. GHSV is gas hourly space velocity; X is conversion degree; Y<sub>Ar</sub> is yield of aromatic hydrocarbons; S<sub>Ar</sub> is selectivity of aromatic hydrocarbons formation.

hydrocarbons is formed over such catalysts.

## Conclusions

On the basis of the results obtained one may infer the following: i) catalytic systems containing 1.0% ZnO and 3.0% Ga<sub>2</sub>O<sub>3</sub> possess the highest activity and selectivity in the conversion of the gaseous hydrocarbons into liquid products; ii) the optimal zeolite matrices for the production of such catalysts are zeolites with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> of 30-40; iii) it is possible to convert more than 35% of gaseous hydrocarbons and to obtain 30% and more of the liquid products at optimum process conditions in the presence of active catalysts. Nevertheless, to develop the technologies of natural and associate gases con-

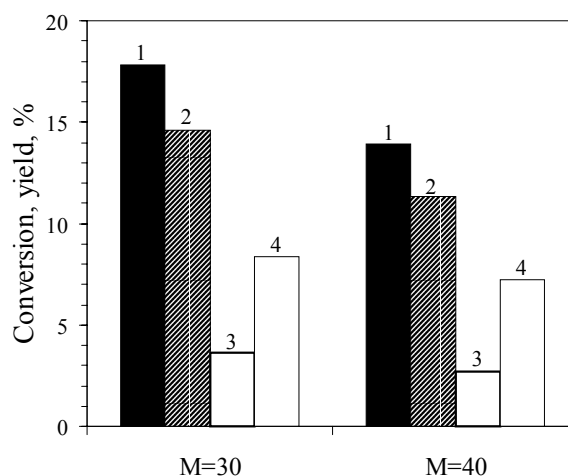


Fig. 8. Conversion (1) and C<sub>6+</sub> arenes yield (2), benzene (3) and naphthalene (4) vs. the silicate modulus of a zeolite containing 3.0% of Ga<sub>2</sub>O<sub>3</sub> (T = 600°C, GHSV = 500 h<sup>-1</sup>).

version, it is necessary to check the efficiency of their application for a specific feedstock and under specified process conditions.

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