# PRODUCTION OF SYNTHETIC HYDROCARBONS MIXTURE OF DIFFERENT COMPOSITION FROM CO AND $H_2$ VIA OXYGENATES

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**Abstract**

*The composition and technical characteristics of the synthetic hydrocarbons (HC) mixture produced from dimethyl ether (DME) are largely determined by properties of the zeolite catalyst. Great possibilities inherent in the zeolites nature allow purposefully change their physicochemical and catalytic properties. A directional modification of the zeolites of H-MFI type allows the preparation of a liquid synthetic product with a controlled composition. For the first time, when using the complex catalyst comprising the exchange forms of zeolites H-MFI and HY, the liquid synthetic product with a high content of triptane (with a yield of more than 15%) with an almost complete conversion of DME has been obtained in Topchiev Institute of Petrochemical Synthesis (RAS). The product contained no more than 1.5% aromatic hydrocarbon and 80% iso-paraffinic hydrocarbons $C_5$ -$C_8$. The octane number of the liquid product was comparable to the octane number of $C_{5+}$ hydrocarbons mixture with a high content of aromatic compounds.*

**Keywords:** *zeolite catalysts, dimethyl ether, liquid synthetic product, triptane*

## 1. INTRODUCTION

The production of hydrocarbons from synthesis gas gives a possibility to use any carbon-containing feedstock (coal, natural gas, associated petroleum gas, petrochemical residue, agricultural waste, urban trash, woods, etc.). The hydrocarbons manufacture from this kind of raw materials improves the ecology, because it gives the product not containing sulfur and other harmful substances (Phillips et al. 2011; Haro et al. 2013; Tunå 2014; Wang et al. 2015). Nowadays, innovative technologies of hydrocarbons production from synthesis gas via dimethyl ether and/or methanol are developed (Simonetti 2012; Bansode & Urakawa 2014). The composition and technical characteristics of the mixture of synthetic hydrocarbons are largely determined by properties of the zeolite catalyst. Great possibilities inherent in the zeolites nature allow purposefully change their physicochemical and catalytic properties. A directional modification of the zeolites of H-MFI type allows the preparation of a liquid synthetic product with a controlled composition.

Recently, in Topchiev Institute of Petrochemical Synthesis (RAS), there has been widely carried out the work concerned with the conversion of synthesis gas to dimethyl ether (DME) in one stage, that provided the basis for the development of the process of obtaining hydrocarbons from DME (Slivinsky et al. 2005; Kolesnichenko et al. 2006; Khadzhiev et al. 2012). For this process, a zinc-palladium containing zeolite catalyst has been prepared to obtain a high octane gasoline (RON 90) with the following composition (wt.%): *iso*-paraffins (60), *n*-paraffins (8), cyclic hydrocarbons (10-12), aromatic hydrocarbons (25-30), unsaturated hydrocarbons (~1), benzene and durene (~0).

At present, in Topchiev Institute of Petrochemical Synthesis (RAS), there is developing the innovative method of DME transformation into 2,2,3-trimethyl butane (triptane) which is environmentally friendly high-octane component (RON 112). In spite of the attractiveness of triptane as a high-octane additive of motor gasolines, a promising technology has been not yet created for the industrial implementation of this process. Now triptane is just formed in small amounts in industrial units of *iso*-butane alkylation with $C_3$-$C_4$ olefins (~ 10 wt. %, based on $C_7$ hydrocarbons).

It has been established that the quality of the hydrocarbons product obtained from DME could be varied depending on the synthesis gas composition, the catalyst composition and the process

conditions. In this article, we present the research data concerned with the effect of the above-mentioned parameters on the physicochemical and catalytic properties of catalysts.

## 2. MATERIALS AND METHODS

DME conversion was carried out in a micro-pilot unit supplied with a high-pressure circulating system. The reaction proceeded in the fixed bed reactor (a flow mode) over the heterogeneous stationary zeolite catalyst at 340°C under pressure up to 10 MPa. The experiments were conducted according to the following scheme. First, after charging the catalyst of gasoline synthesis into the reactor, it was subjected to reduction for 2 hours in hydrogen stream under pressure 0.1 MPa at temperature 380°C. Then the temperature was lowered to the operating temperature (340°C). After that, it started to flow DME mixed with synthesis gas through the reactor. The flow rate (V) was 5 l per hrs. The synthesis of hydrocarbons was realized continuously for 70-80 h in a synthesis gas stream. Detailed description of the installation, the conditions of preparing the catalysts, the conditions of their tests and the methodology for calculating the main process indicators are described in the papers (Markova et al. 2016; Ionin et al. 2015; Kolesnichenko et al. 2016).

## 3. RESULTS AND DISCUSSION

In the technology of synthetic hydrocarbons production from DME developed in Topchiev Institute of Petrochemical Synthesis (RAS), the content of aromatic hydrocarbons in the mixture of liquid hydrocarbons may change from 6 to 27 wt. %, depending on the process conditions and the composition of the synthesis gas. There is very low content of undesirable components, that means benzene and/or durene (≤ 2% by weight) and unsaturated hydrocarbons (≤1% by weight). The selectivity by liquid hydrocarbons is dependence on the synthesis gas composition very much. When changing synthesis gas with $H_2/CO \leq 2$ (molecular ratio) for the synthesis gas composition with the ratio of $H_2/CO \leq 3.5$ (that means the steam-gas mixture entering the gasoline production reactor contains an overwhelming amount of hydrogen), the yield of liquid hydrocarbons at the stage of gasoline production is decreasing. The results of the research concerned with the effect of different synthesis gas composition on the conversion of DME are present in Table 1.

**Table 1.** The effect of the concomitant synthesis gas composition on indicators of DME transformation (T =340ºC, P=10 MPa, $W_{DME}$=2.7 $hr^{-1}$, V= 5 l/hr)

| The composition of initial synthesis gas, % v. | | | | S, % wt. | The composition of liquid hydrocarbons mixture, % wt. | | | |
|---|---|---|---|---|---|---|---|---|
| $N_2$ | CO | $CO_2$ | $H_2$ | | *iso*-Alkanes | *n*-Alkanes | Cycloalkanes | Aromatic hydrocarbons (durene) |
| DME conversion is 99.0-99.8% | | | | | | | | |
| 6 | 34 | 3 | 57 | 80 | 57 | 7 | 7 | 29 (1.5) |
| 4 | 20 | 3 | 73 | 78 | 71 | 11 | 10 | 8 (0.5) |
| 0 | 0 | 0 | 100 | 62 | 73 | 11 | 7 | 8(0.2) |

*S – the selectivity by gasoline hydrocarbons.*

As seen from the data of Table 1, when increasing the hydrogen content in the synthesis gas, DME conversion remains practically unchanged, but the selectivity and the composition of the liquid hydrocarbons mixture change significantly. So, the content of aromatic hydrocarbons decreases, but the *iso*-alkanes content increases. Probably, the high partial pressure of hydrogen accelerates the hydrogenation light olefins to give *n*-alkane and *iso*-alkanes. Such a removal of the primary olefins products from the further transformations chain prevents the formation of aromatic hydrocarbons.

As shown either (Table 2), increasing the weight per hrs space velocity (WHSV) of DME leads to raising the selectivity by liquid hydrocarbons and gives increasing the aromatic hydrocarbons content in the gasoline composition.

Thus, synthesis gas composition and WHSV of DME influence significantly on the yield and the composition of liquid hydrocarbons produced.

**Table 2.** The effect of DME weight per hrs space velocity ($W_{DME}$) on the process indicators (at T=340ºC, P=10 MPa, V= 5 l/hr)

| $W_{DME}$, $hr^{-1}$ | S, % wt. | The composition of liquid hydrocarbons mixture, % wt. | | | |
|---|---|---|---|---|---|
| | | *iso*-Alkanes | *n*-Alkanes | Cycloalkanes | Aromatic hydrocarbons (durene) |
| Concomitant synthesis gas composition, % vol.: $N_2$– 6, CO – 34, $CO_2$ – 3, $H_2$ – 57 | | | | | |
| 1.3 | 78 | 58 | 7 | 8 | 27 (1,5) |
| 2.7 | 80 | 57 | 7 | 7 | 29 (1.5) |
| 5.3 | 84 | 55 | 5 | 7 | 33 (1.7) |
| Concomitant synthesis gas composition, % vol.: $N_2$– 4, CO – 20, $CO_2$ – 3, $H_2$ – 73 | | | | | |
| 1.3 | 72 | 71 | 11 | 11 | 7 (0.4) |
| 2.7 | 78 | 71 | 11 | 10 | 8 (0.5) |
| 5.3 | 81 | 68 | 9 | 9 | 14 (0.8) |

*$W_{DME}$ - WHSV of DME.*

*S – the selectivity by gasoline hydrocarbons*.

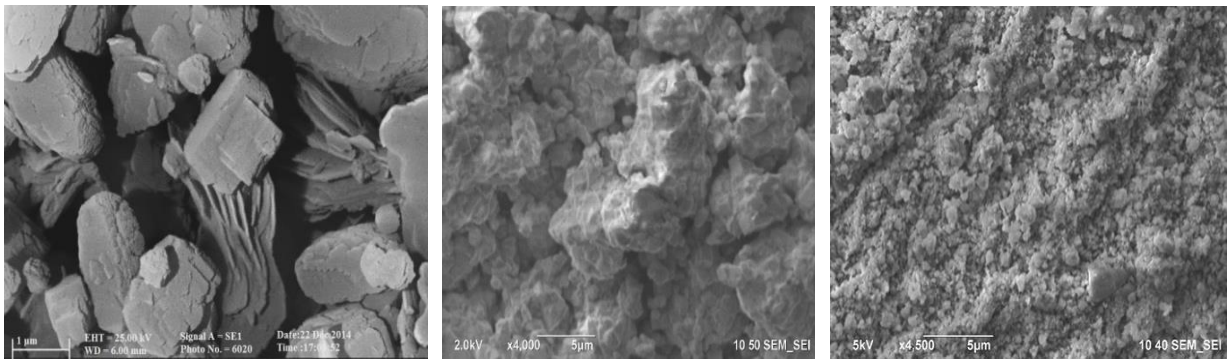
When creating a technology for the production of hydrocarbons from DME, it is very important to develop a catalyst with a long time-life. As known, the catalytic stability is dependent on the nature of the zeolite used for the catalyst preparation and on the methods of modifying zeolite (that means introducing an active element into the catalyst composition). So, we researched the influence of the nature of commercial samples of MFI zeolite (domestic and foreign manufactures) on the activity and selectivity of catalysts prepared on the base of them in the synthesis of $C_{5+}$ hydrocarbons from DME. As a result, the relationships between acid, spectral, morphological, textural characteristics and catalytic properties of the zeolite catalysts are established.

**Table 3.** Characteristics of the zeolite used for the preparation of palladium-zinc catalyst

| Zeolite sample | Manufacturer | $SiO_2/Al_2O_3$ | $S_{BET}$, $m^2/g$ | $V_{total}$ $cm^3/g$ | $V_{mocro-pores}$, $cm^3/g$ | $V_{meso-pores\ (BJH)}$, $cm^3/g$ | $a_{o\ (benzene)}$ μmol/g |
|---|---|---|---|---|---|---|---|
| Sample 1 | AZKiOS | 37 | 333 | 0.20 | 0.12 | 0.08 | 125 |
| Sample 2 | NZKhK | 40 | 293 | 0.19 | 0.11 | 0.08 | 124 |
| Sample 3 | Zeolyst | 30 | 323 | 0.26 | 0.12 | 0.14 | 151 |

For the preparation of the catalysts for DME conversion into $C_{5+}$ hydrocarbons, the following samples of commercial zeolites (with the MFI crystal structure) have been used: sample 1 (with the molar ratio of $SiO_2/Al_2O_3$ = 37) manufactured by the Angarsk Catalyst and Organic Synthesis Plant (AZKiOS), sample 2 (with $SiO_2/Al_2O_3$ = 40) supplied by the Novosibirsk Plant of Chemical Concentrates (NZKhK), sample 3 (with $SiO_2/Al_2O_3$ = 30) available from Zeolyst. These zeolites characteristics are shown in Table 3. The procedure of the catalysts preparation and the technique used for studying their physicochemical properties are described in detail in the paper (Kolesnichenko et al. 2016).

In Figure 1, the electron microscopic images (SEM) of these zeolite samples are shown. According to SEM images, the particles of the powdered zeolites differ in both shape (because of the presence of crystal aggregates) and crystal size. The micrograph of zeolite sample 2 shows that it is morphologically more uniform and comprised mainly of agglomerates of up to 2000 nm size. The greatest size of agglomerates was for sample 1, which is morphologically nonuniform, there are inclusions of the layered structures at 1000 nm magnification. It is based on the coarse particles of polygonal shape (over 3000 nm), but, along with them, there are ultrafine particles of 200-800 nm size. Sample 3 consists of uniformby size particles, the size below 1000 nm. All the zeolite samples have the crystallinity of no less than 85% according to XRD data.




Sample 1 Sample 2 Sample 3

**Figure 1.** The electron microscopic images (SEM) of commercial zeolite samples

In the table 3, there are shown the textural characteristics of the zeolites researched according to the data of the low–temperature adsorption of nitrogen (determined on a Micromeritics ASAP-2000). It follows from these data, that all zeolites have almost the same surface area, it is slightly lower for sample 2. The total volume of pores and mesopores for sample 3 is significantly higher than for samples 1 and 2.

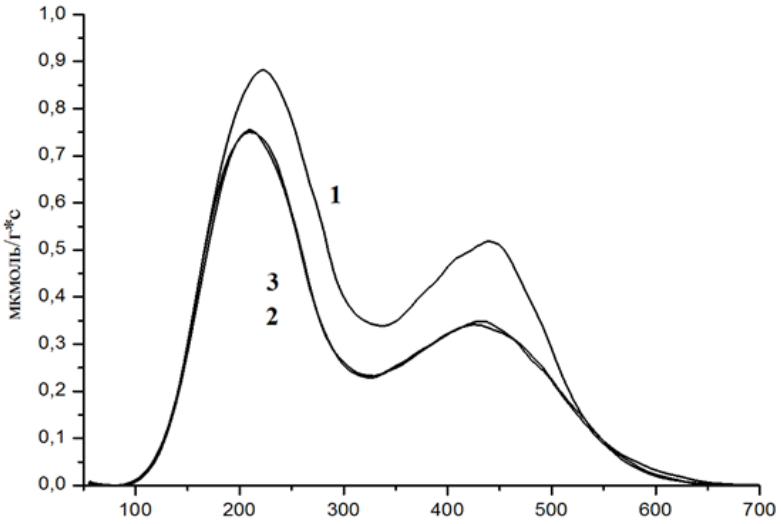



**Figure 2.** Ammonia thermodesorption curves for initial zeolite samples: (1) - sample 1, (2) - sample 2, (3) - sample 3.

The results of investigation of acidic properties of the initial zeolite samples by TPD-$NH_3$ method are present in Figure 2, based on which it is visible that all zeolite samples are characterized by the same shape of desorption peaks: low temperature peak in the region of 120-250°C with the temperature peak of peak maximum ($T_{max}$) 198°C, which correlates with the concentration of weak and medium acid centers and high-temperature peak in the region of 300-550°C with $T_{max}$= 400°C, referring to ammonia desorption from strong acid centers.

From the data present in Table 4, it is seen that sample 1 has the greatest number of acid sites, with the ratio of the amount of strong acid site to the total amount of medium and weak sites being the same of ~ 0.7 for all the samples.

**Table 4.** Distribution of acid sites (μmol/g) of zeolite samples by values of ammonia desorption activation energy ($E_d$, kJ/mol)

| Sample | Peak 1 | | Peak 2 | | Total amount of desorbed $NH_3$, μmol/g | Proportion of strong acid sites, % |
|---|---|---|---|---|---|---|
| | μmol/g | $T_{max}$, °C | μmol/g | $T_{max}$, °C | | |
| Sample 1 | 863 | 222 | 606 | 438 | 1469 (1.4) | 41.8 |
| Sample 2 | 670 | 209 | 457 | 424 | 1127 (1.4) | 40.6 |
| Sample 3 | 659 | 209 | 471 | 428 | 1130 (1.4) | 41.7 |

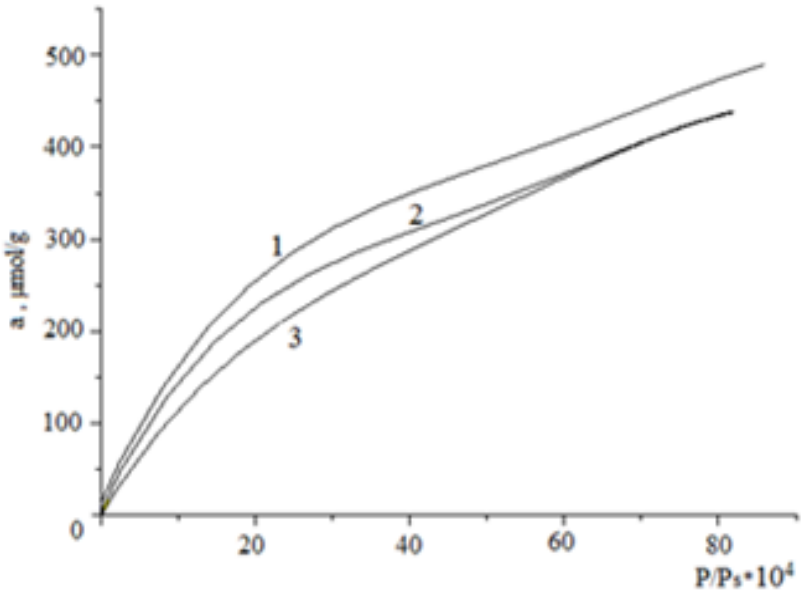



**Figure 3.** Isotherms of benzene adsorption of initial zeolite samples: (1) - sample 1, (2) - sample 2, (3) - sample 3.

Figure 3 shows the adsorption isotherms of benzene on the zeolite samples in the adsorption (μmol/g)–relative pressure $P/P_s$ coordinates, where $P_s$ is the saturated vapor pressure of benzene at 200°C calculated by the Antoine equation (Weissberger 1958). At the measurement temperature, it was possible to record only the initial parts of the isotherms. All of them are convex towards the ordinate axis, a shape that corresponds to the character of the chromatographic peaks with the vertical front and an extended tail. In the P/Ps range examined, the benzene adsorption on sample 1 exceeds the corresponding value for samples 2 and 3, correlating with the total amount of absorbed ammonia in TPD measurements, whereas the isotherms and amount of adsorbed ammonia are almost the same for the latter samples.

The limiting values of benzene adsorption were calculated by the Dubinin's equation ($a_o$) (Dubinin 1965), the values of which are given in Table 3. It is noteworthy that for all the test samples there is correlation between the limiting benzene adsorption by and the pores volume determined by nitrogen adsorption.

According to the data of diffuse reflectance IR (DRIR) spectra, the zeolite samples substantially differ in the type of OH groups making acid sites (Figure 4). The 3590 $cm^{-1}$ band due to Broensted acid sites (BAS) of the Al–OH(H) type (type 1), and the 36540 $cm^{-1}$ band (type 2) attributed to the bridging Al–O(H)–Si bond are strong BAS, and the 3733 $cm^{-1}$ band due to the isolated Al–OH (type 3) bond rather is a base site. Type 1 sites prevail in sample 1. There are bands of all three types of OH groups in the spectrum of sample 2, as well as a weak band due to the hydroxonium cation $H_3O^+$ (3250 and 3350 $cm^{-1}$) on the zeolite surface. Note that this band is well-resolved in the spectrum of sample 2 at 200 and 300°C and almost disappears at 450°C. There are bands of all three types of OH groups in the spectrum of sample 3. At the same time, the total intensity of absorption bands due to OH groups of different types is substantially higher for sample 3.

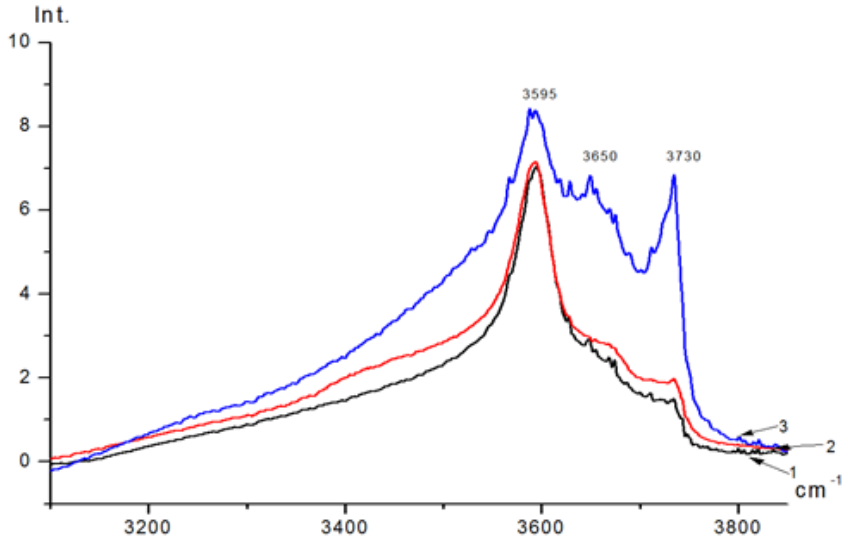



**Figure 4.** Diffuse reflectance IR (DRIR) spectra at 450°C in argon: (1) - sample 1, (2) sample 2, (3) - sample 3.

Table 5 shows the percentage distribution of acid sites of different types, based on the fact that the sum of all OH groups comprises 100%, under similar samples preparation condition. In samples 1 and 2, the proportion of BAS of different strengths is almost the same, but there are due to $H_3O^+$ hydroxonium cation sites in sample 2. In sample 3, the amounts of type 1 and 2 BAS and base sites of type 3 are almost the same. However in comparison with samples 1 and 2, the spectrum of sample 3 shows a noticeably lower proportion of acid sites of type 1 and a much higher amount of acid sites of types 2 and 3.

**Table 5.** Distribution of acid sites in zeolites

| Site type | Sample 1 | Sample 2 | Sample 3 |
|---|---|---|---|
| 1 (%) | 61 | 51 | 38 |
| 2(%) | 25,5 | 21 | 31 |
| 3(%) | 13,5 | 15 | 31 |
| $H_3O^+$ (3350 $cm^{-1}$ band) | - | 13 | - |

On the basis of these zeolite samples, catalysts for dimethyl ether conversion to hydrocarbons were prepared. The results of tests in the unit operated in the stand-alone mode are shown in Table 6. As seen, independently on the initial zeolite, the catalysts have increased activity in the DME conversion and good selectivity for $C_{5+}$ hydrocarbons. The greatest selectivity for gasoline was achieved on the catalyst based on sample 2. In this case, the final liquid product contains aromatic compounds in an amount of less than 7 wt %, including durene of no more than 0.2 wt %. This is apparently due to the presence $H_3O^+$ centers (Table 5) which promotes the hydrocarbons formation. Sample 3 shows the highest concentration of aromatic compounds in the product composition. This is most likely due to the presence of a larger volume of mesopores in this zeolite sample in the comparison with samples 1 and sample 2, and large size of pores allows the formation of large molecules.

**Table 6.** Dimethyl ether conversion to $C_{5+}$ hydrocarbons
(T =340ºC, P=10 MPa, $W_{DME}$=2.7 $hr^{-1}$, V= 5 l/hr. The concomitant synthesis gas composition, % vol.: $N_2$– 4, CO – 20, $CO_2$ – 3, $H_2$ – 73)

| Catalyst | DME conversion, % | S, % wt. | The composition of liquid hydrocarbons mixture, % wt. | | | |
|---|---|---|---|---|---|---|
| | | | *iso*-Alkanes | *n*-Alkanes | Cycloalkanes | Aromatic hydrocarbons (durene) |
| Sample 1 | 99.5 | 78 | 71 | 11 | 10 | 8 (0.5) |
| Sample 2 | 99.8 | 83 | 69 | 10 | 13 | 7 (0.2) |
| Sample 3 | 98.8 | 79 | 68 | 9 | 10 | 12 (1.0) |

Recent advances in the synthesis of hydrocarbons from DME have shown the possibility of obtaining 2,2,3-trimethylbutane (triptane) which is a very effective environmentally safe high-octane component (RON 112). As known (Kettering 1944), triptane additives (in amounts > 5% vol.) allows to increase the RON of fuel by 10-20 points. Based on the known data about possible routes of triptane formation from oxygenates (Ahn et al. 2009; Simonetti et al. 2012; Schaidle et al. 2015), we have developed a complex catalyst consisting of exchange forms of zeolites HZSM-5 (cat.1) and HY (cat. 2). In the presence of this combined catalyst, there was obtained a liquid synthetic product with a content of 2,2,3-trimethylbutane of more than 15% by weight and aromatic hydrocarbons of not more than 1.5% by weight (table 7). The reaction was carried out under a high pressure (10 MPa) at a high temperature (340°C) (that means quite severe conditions for triptane synthesis).

**Table 7.** Dimethyl ether conversion to $C_{5+}$ hydrocarbons
(T =340ºC, P=10 MPa, $W_{DME}$=2.7 $hr^{-1}$, V= 5 l/hr. The concomitant synthesis gas composition, % vol.: $N_2$– 4, CO – 20, $CO_2$ – 3, $H_2$ – 73)

| Catalyst | S, % wt. | Gasoline composition, % wt. | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | *iso*-Alkanes | Triptane | Triptane % in $\sum C_7$ | *n*-Alkanes | Cyclic alkanes | Olefins | Aromatic hydrocarbons (durene) |
| DME conversion is 98-99% | | | | | | | | |
| Cat. 1 | 86.0 | 57.5 | trace | trace | 10.1 | 12.1 | 4.3 | 16 (1,0) |
| Cat. 2 | 37.0 | 83.8 | 20.7 | 58 | 9.6 | 4.0 | 0.6 | 2 ( 0) |
| Cat.1+Cat.2 | 75.5 | 81.0 | 15.4 | 50 | 10.5 | 5.2 | 0.2 | 1.5 (trace) |

As seen from the data of table 7, the combination of catalysts with different functions (the catalyst for the preparation of olefins of Cat.1 and the alkylation catalyst of Cat.2) in their ratio of 1/3 gives a maximum triptane concentration about 15% wt. Proportion of triptane in the $C_7$ fraction is 50%. In this case, the product obtained is distinguished by the practical absence of olefins (0.2%). As when adding Cat.1 to Cat.2, the methanol content in the aqueous phase of the liquid product decreased sharply (from 42 to 14% wt.), it was assumed that the formation of triptane is most likely to realized via olefins methylation with DME and/or methanol and via *iso*- alkanes alkylation with light olefins. It was also found that with increasing contact time, the degree of formation of the triptane decreases.

The change in the distribution of $C_5$-$C_9$-alkanes in the composition of the synthetic gasoline lead to raising RON from 86.5 to 93.5, as a result of increasing a dimethyl substituted hydrocarbons proportion in three times and increasing a trimethyl substituted ones proportion in ten times.

## 4. CONCLUSIONS

1) The composition and technical characteristics of synthetic hydrocarbons mixture produced from DME are largely determined by the properties of the zeolite catalyst.
2) There has been shown the practical possibility of obtaining the triptane as a part of the framework of the developed process of the gasoline production from CO and $H_2$ under the rather severe conditions for the triptane synthesis. That means under the high pressure about 10 MPa at the high temperature about 340-360°C, in the presence of water continuously formed by the reaction from DME.
3) The gasoline composition obtained in the presence of a combined catalyst (consisting of exchange forms of zeolites HZSM-5 and HY) contains more 15% of triptane, when a total content of *iso*-alkanes being more 80%. In the product, unsaturated and aromatic compounds are practically absent.
4) Increasing the proportion of trimethyl substituted hydrocarbons in the composition of synthetic gasoline leads to raising octane number (RON) from 86.5 to 93.5.

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