

Methanol Conversion on Pentasils: The Order of Product Formation

O. A. Ponomareva, I. F. Moskovskaya, and B. V. Romanovskii

Department of Chemistry, Moscow State University, Vorob'evy gory, Moscow, 119899 Russia

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Abstract—The products of methanol conversion to hydrocarbons over a modified pentasil zeolite catalyst are classified by the Wojciechowski method of kinetic analysis as primary/secondary and stable/unstable. A general scheme of reaction pathways in methanol conversion to hydrocarbons over the pentasil-type zeolites is proposed.

INTRODUCTION

Over the past 25 years, methanol conversion over pentasil zeolites has been studied in detail. However, the mechanism of formation of the primary C–C bond [1–4] and the order of formation of aromatic reaction products [5, 6] are not fully understood. One of the debatable issues is whether dimethyl ether is a necessary intermediate in the C–C bond formation, what is the nature of the adsorption complex of methanol and the Brønsted acid site, and whether the methanol molecule is hydrogen-bonded or protonated [7]. It also remains unclear whether *m*- and *o*-xylenes are the products of *p*-xylene isomerization or if they are formed via parallel pathways. The formation of higher aromatic and aliphatic hydrocarbons remains an open question, and it is unclear whether they are the products of direct cyclization of lower olefins C₂–C₄ or formed by alkylation–disproportionation. Data on the sequence of transformation are necessary for selectivity control and improvement in the processes. It is interesting to elucidate the order of the formation of aromatic compounds, which are the main products of methanol conversion and valuable chemicals, in order to enhance the productivity in the formation of C₈–C₁₀ hydrocarbons.

Upon the conversion of methanol, ethanol, and lower olefins, aromatic compounds comprise more than 30–35% of the total yield of hydrocarbons with a high selectivity to C₇ and C₈ hydrocarbons. Attempts at a detailed analysis of the mechanism of formation of aromatic hydrocarbons were made in [5, 6, 8, 9]. Based on the data on product distribution as a function of the conversion of methanol, dimethyl ether, ethylene, propylene, butene, and 3,3-dimethylbutene-1 over HZSM-5 found by ¹³C NMR, IR spectroscopy, ESR, and calorimetry, it was suggested that higher aliphatic and aromatic hydrocarbons are formed by the additive cyclization of olefins C₂–C₄ and their carbenium ions [5]. For instance, methanol converts successively to dimethyl ether and surface carbonoid species C₂, from which ethylene can be formed. Then, the surface C₂ species can

be transformed into C₃ and C₄ surface species in a reaction with methanol or gas-phase ethylene. C₃ and C₄ surface species can undergo oligomerization, isomerization, cyclization, and dehydrogenation to form aromatic products and can be hydrogenated to form saturated aliphatic compounds. Alkylation with the CH₃⁺ and C₂H₅⁺ species also occurs along with the formation of aromatic compounds. Alkylation with the carbenium ions C₃H₇⁺ and C₄H₉⁺ does not occur because of the limitations caused by the ZSM-5 structure. Therefore, the mechanism of methanol conversion as the complex multiroute reaction still attracts the interest of researchers.

In this work we used the method of kinetic analysis developed by Wojciechowski [10–13], which was expected to elucidate the macroscopic process mechanism, to determine the order of formation and transformation of aromatic products. This method allows one to investigate complex multiroute reactions with the fast deactivation of a catalyst and to determine whether the product is primary (1) or secondary (2). Unlike Rozovskii's method of relative selectivities [14], the approach used by us allows one to categorize products as stable (S) or unstable (U) and to evaluate the primary selectivity to each of them. The Wojciechowski method has been developed and used for complex one-substrate reactions such as cracking, redistribution of hydrogen [15–18], and isomerization [19]. Its application to the two-substrate reaction of styrene alkylation by methanol, studied by us [20, 21], proved to be successful.

The mathematical apparatus of the method for a simplified scheme of the catalytic cracking A → B → C, where A is gas oil, B is a target product, and C is a by-product, was presented in [11, 12]. The Wojciechowski method is based on constructing so-called “selectivity curves,” i.e., the plots for the time-averaged yields of the *i* reaction product (Y_{*i*}) vs. the total conversion of the initial material (X). This depen-

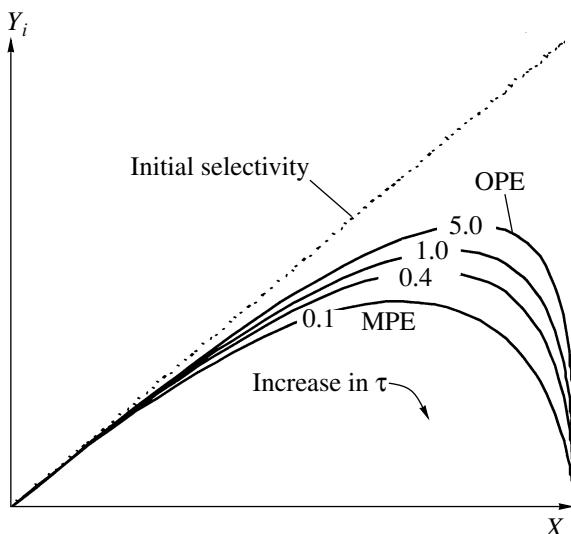


Fig. 1. Selectivity curves for “slowly aging” catalyst at $P = 0.1, 0.4, 1.0$, and 5.0 with increase in the contact time (τ).

dence is estimated by varying the contact time at a fixed ratio between the catalyst weighed portion (P) and the amount of the starting material supplied. These conditions are fulfilled by choosing appropriate run durations. For example, runs of various durations were carried out at a chosen minimal contact time and several values of the parameter P were obtained as well as the average values of the product yield and conversion for these time periods. Then, the contact time was increased in each subsequent experiment so that the values of the P parameter remained unchanged at various durations of runs.

For a set of the P values we obtained families of experimental points for various contact times (τ) as curves with maxima or open loops depending on the class of deactivation to which the catalyst under study belongs [18].

Wojciechowski called the lines enveloping all these loops at the top and the bottom [10] the optimal (OPE) and minimal (MPE) enveloping curves. They characterize the catalyst selectivity in the absence of deactivation and at the maximal deactivation, respectively.

Hence, the OPE curve determines the conditions for the maximal yield of the primary reaction product, and its slope at the beginning of the coordinates determines the initial selectivity of its formation over a fresh catalyst (Fig. 1). Secondary reaction products have a zero slope of OPE [13]. The products whose OPE curves are concave toward the conversion axis are unstable; in the opposite case, they relate to the stable products. An example of the typical OPE curves for all types of reaction products is shown in Fig. 2.

In this work, we determined the order of formation of the products of methanol conversion to hydrocarbons and proposed a general scheme for the reaction routes on the basis of kinetic experiments and the above approach.

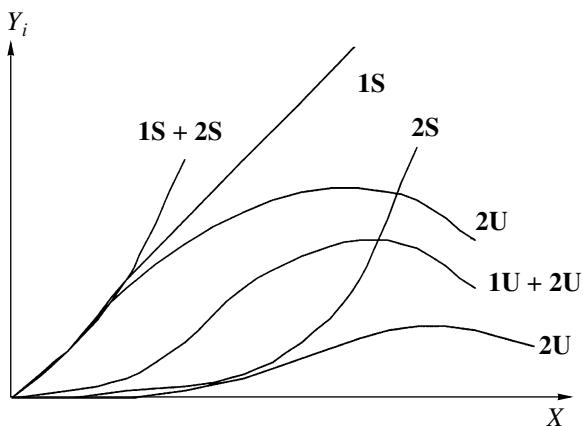


Fig. 2. OPE curves for various products [12]: **1**, primary product; **2**, secondary product; **S**, stable product; **U**, unstable product.

EXPERIMENTAL

The initial high-silica zeolite HTsVN with a ratio $\text{SiO}_2/\text{Al}_2\text{O}_3 = 43$ was synthesized at VNII NP using monoethanolamine as a template. The size of zeolite needle-like crystals was $2\text{--}6 \times 10\text{--}20 \mu\text{m}$, and the Na_2O concentration was 1.0 wt %. Catalytic experiments were carried out over this zeolite after its treatment with 100% steam at 600°C for 4 h. The reaction was performed at 440°C in a flow setup under atmospheric pressure. The conditional contact time (the value reverse to a mass feed flow rate) was varied from 0.01 to 0.44 h; the run duration was varied from 5 min to 1.5 h, and the parameter P was changed from 0.028 to 0.5.

Liquid hydrocarbons were analyzed on a CHROM-5 chromatograph with a quartz capillary 25-m column and supported phase Carbowax 20M in the temperature programming regime from 62 to 200°C with a heating rate of $6^\circ\text{C}/\text{min}$. An aqueous fraction and gases were analyzed on an LKhM-8MD chromatograph with a column packed with a Porapac Q sorbent at temperatures 120 and 108°C , respectively.

RESULTS AND DISCUSSION

A plot of the total methanol conversion vs. contact time is common (Fig. 3) for all points with various values of the parameter P . Hence, the catalyst under study can be categorized, according to Wojciechowski [10–12], as a “slowly aging” catalyst. In our case, the OPE curve is common for all values of the parameter P and can be obtained experimentally as a function of the conversion and yield of the product vs. contact time for all P values (Table 1).

Experimental data shown in Fig. 4a for dimethyl ether (DME) fall on the OPE curve with a maximum that is concave to the conversion axis; that is, these data are typical of a primary unstable product. This shows that under the conditions of methanol conversion, DME

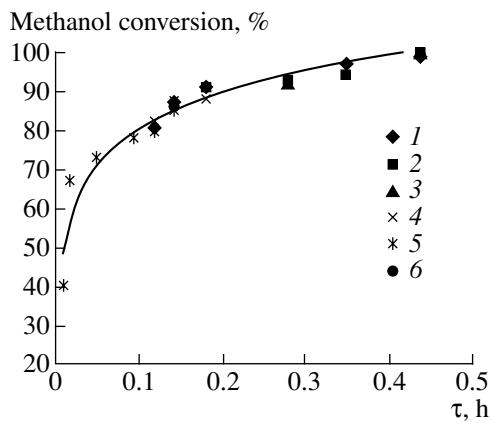


Fig. 3. Methanol conversion vs. contact time at various values of parameter P : 1, 0.50; 2, 0.30; 3, 0.20; 4, 0.15; 5, 0.10; 6, 0.01.

is formed via alcohol dehydration and then undergoes further transformations.

The shape of the OPE curve for water presented in Fig. 4b allows us to assign it to products that are formed in both primary and secondary reactions. Water is formed as a primary product at the first step of methanol conversion to form DME and as a secondary product upon DME dehydration to ethylene.

Figure 4c shows the OPE curve for *p*-xylene, which is typical of secondary unstable products (zero initial slope and concavity toward the conversion axis). The

selectivity curves for *p*-methylethylbenzene, ethylene, propylene, butenes, and aliphatic C₅–C₈ hydrocarbons have a similar shape. All these products are secondary and undergo further transformations.

The shapes of the selectivity curves for *m*-xylene (Fig. 4d) and *o*-xylene, toluene, ethylbenzene, *m*- and *o*-methylethylbenzenes, pseudocumene, durene, as well as for methane, ethane, propane, and butanes allow us to assign them to secondary stable products (zero initial slope and upward concavity). One can conclude that alkanes (secondary stable products) are formed from the corresponding alkenes (secondary unstable products) by hydrogen redistribution reactions and do not participate in further transformations; that is, they are stable products.

Several possible routes exist for the formation of aromatic compounds by methanol conversion over pentasil. First, they can be formed by the additive polymerization of olefins [5]. The carbenium ion and olefin form an olefin with a high molecular weight, which is cyclized with hydrogen redistribution to form an aromatic hydrocarbon. For example,



Second, aromatic hydrocarbons can be formed as a result of disproportionation, isomerization, alkylation, dealkylation, or cracking of the initially formed arenes. It was suggested in [8, 9] that *p*-xylene and *p*-methyl-

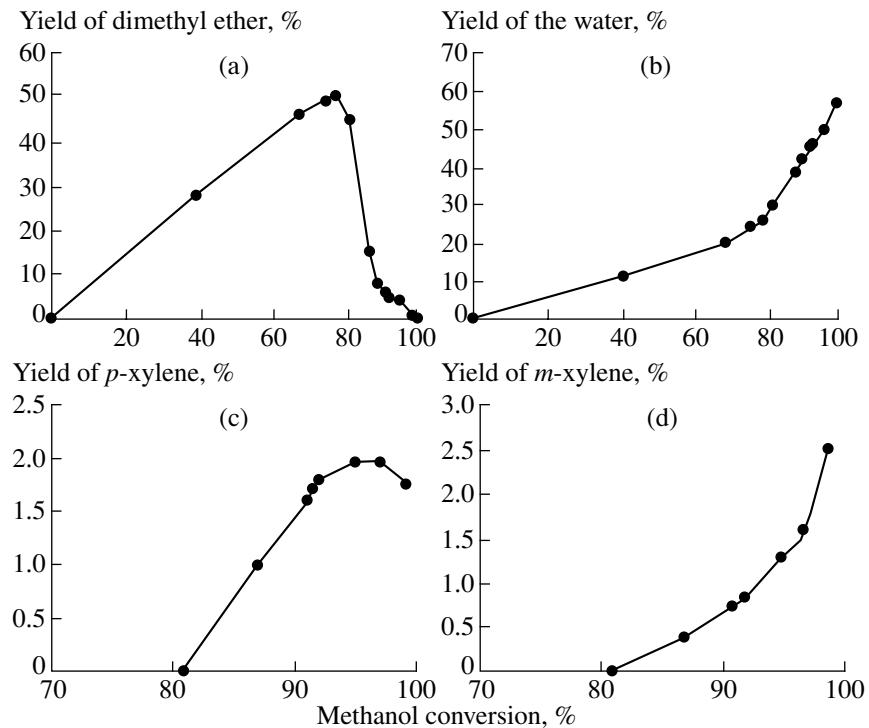


Fig. 4. OPE curves for (a) dimethyl ether, (b) water, (c) *p*-xylene, and (d) *m*-xylene.

Table 1. Characteristics of methanol conversion over catalyst HTsVN at 440°C

Weight of catalyst, g	τ , h	t , min	P , g/g	X , %	Y_i , %
methanol \longrightarrow dimethyl ether					
2.0	0.44	50.0	0.50	98.6	0.30
2.0	0.35	30.0	0.50	97.1	1.70
1.0	0.18	10.0	0.50	91.7	9.30
1.0	0.14	30.0	0.20	87.1	15.4
2.0	0.12	8.0	0.50	80.9	45.8
2.0	0.01	8.0	0.38	79.0	50.7
1.0	0.02	5.0	0.10	67.6	46.4
1.0	0.01	10.0	0.28	40.0	28.2
methanol \longrightarrow water					
2.0	0.44	10.0	1.40	100	60.6
2.0	0.44	10.0	1.40	98.5	55.9
1.0	0.18	10.0	0.50	91.1	48.2
1.0	0.14	10.0	0.45	87.3	40.4
2.0	0.12	8.0	0.50	80.9	30.8
1.0	0.02	5.0	0.10	67.6	20.7
1.0	0.01	10.0	0.03	40.0	11.2
methanol \longrightarrow <i>p</i> -xylene					
2.0	0.44	10.0	1.40	98.5	1.76
2.0	0.35	10.0	1.10	97.5	1.93
2.0	0.35	70.0	0.27	94.6	1.92
2.0	0.28	9.6	0.90	92.0	1.73
1.0	0.22	10.0	0.74	91.6	1.89
1.0	0.18	10.0	0.50	91.1	1.72
1.0	0.14	10.0	0.45	87.3	1.00
1.0	0.04	12.6	0.10	81.1	0.00
methanol \longrightarrow <i>m</i> -xylene					
2.0	0.44	10.0	1.40	98.5	2.20
2.0	0.35	10.0	1.10	97.5	1.51
2.0	0.28	9.6	0.90	92.0	1.06
1.0	0.18	10.0	0.50	91.1	0.75
1.0	0.14	30.0	0.20	87.1	0.48
1.0	0.04	12.6	0.10	81.1	0.00

Note: τ is the contact time, t is the duration of reaction.

ethylbenzene are the initial arenes, which then transform to other arenes.

The above findings (see scheme) allow us to suggest that all aromatic compounds are formed by the cyclization of olefins, which are the secondary and unstable intermediates. Of the aromatic products, only *p*-xylene and *p*-methylethylbenzene are unstable, whereas their isomers are stable. Hence, these compounds are initially formed among the aromatic products and easily

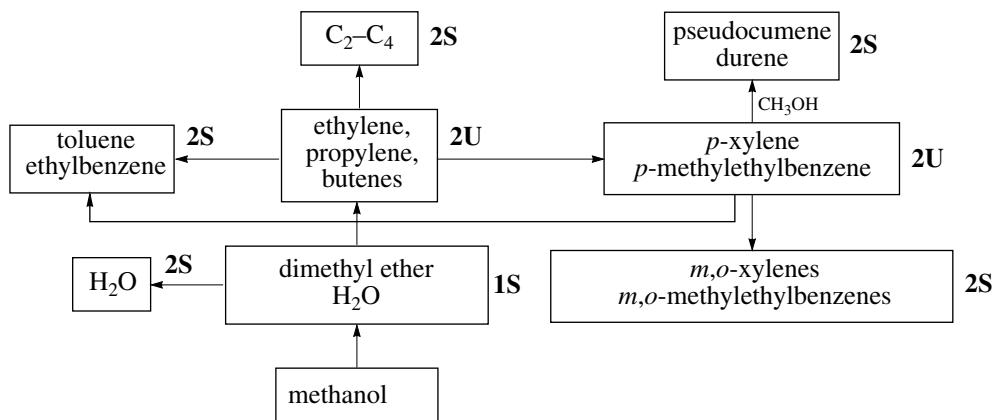
isomerize to the *m*- and *o*-isomers, which are more thermodynamically stable.

Since the rest of the arenes are stable, they either do not participate in further reactions of disproportionation, alkylation, dealkylation etc. or these processes mutually equilibrate each other and do not affect the final yields of aromatic hydrocarbons. *p*-Xylene and *p*-methylethylbenzene are unstable products and can participate in other transformations along with isomeriza-

tion, for instance, in methylation. However, it is difficult to assume that all other aromatic hydrocarbons are only formed from these products because in this case, at high contact times, all of the *p*-methylethylbenzene and *p*-xylene would transform to other arenes, but this has not been found. Hence, the aromatic hydrocarbons are likely formed via reactions (I) and (II) and participate in the reactions of alkylation, disproportionation, and dealkylation to a minor extent. Note that the cracking of aromatic compounds over the HTsVN catalyst

occurs to a low extent because only traces of benzene are present in the reaction products.

Table 2 presents the classification of all products in methanol conversion to hydrocarbons and the initial selectivities to the primary products evaluated from the slopes of the OPE curves. On the basis of the results obtained, one can present the following scheme of the reaction routes of methanol conversion to hydrocarbons and the formation of primary and secondary reaction products:



Scheme.

Hence the study of methanol conversion by the Wojciechowski method allowed us to confirm the intermediate nature of dimethyl ether and the C₂–C₄ olefins,

Table 2. Classification of the products of methanol conversion over zeolite HTsVN at 440°C

Products	Type of product
Dimethyl ether	1U
H ₂ O	1S + 2S
CH ₄	2S
Ethylene, propylene, butenes	2U
C ₂ –C ₄	2S
C ₅ –C ₈	2U
Toluene	2S
Ethylbenzene	2S
<i>p</i> -Xylene	2U
<i>m</i> -Xylene	2S
<i>o</i> -Xylene	2S
<i>p</i> -Methylethylbenzene	2U
<i>m</i> -Methylethylbenzene	2S
<i>o</i> -Methylethylbenzene	2S
Pseudocumene	2S
Durene	2S

Note: Initial selectivity of the formation of dimethyl ether is 0.7 and that of water formation is 0.3, the rest is 0.0.

which participate in cyclization and the formation of higher aromatic and aliphatic products of conversion, as well as to prove the initial formation of *p*-xylene and *p*-methylethylbenzene, which isomerize to *m*- and *o*-isomers and are methylated to pseudocumene and durene.

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