Catalytic Synthesis of Liquid Hydrocarbons

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ABSTRACT

Introduction

Aromatic hydrocarbons, mainly benzene, toluene, ethylbenzene and xylene, are the most important chemicals in the petrochemical industry. Currently, aromatic compounds are obtained by catalytic reforming and cracking of petroleum fractions.

As oil reserves shrink, the demand for alternative sources of aromatics increases. One of the alternative sources of aromatic hydrocarbons are natural and biogases. Dehydroaromatization reactions under non-oxidizing conditions on bentonite catalysts containing modified intermediate metal ions is a promising method for using natural and petroleum gases [1-6].

Natural gas containing mainly methane is thermodynamically stable and resistant to many reagents. The binding energy C – H in a methane molecule is 439 kJ/mol. Direct synthesis of methane is difficult, but its derivatives are more active than methane, they enter into chemical reactions well [7-12].

The reactions proceed in the presence of a catalyst which accumulates zeolite. The oxidizing agent is not involved in this process. [13-15].

Based on the above, the purpose of this work is the synthesis of environmentally friendly liquid fuels by direct catalytic aromatization of natural gas.

Keywords: methane, aromatic hydrocarbons, catalyst, bentonite catalysts, textural characteristics, conversion, mechanism.

Experimental part

The conversion of methane (purity 99.9%) without the participation of oxidizing agents was carried out in a flow reactor at a temperature range of 600-8000C, P = 0.1 MPa, a methane:argon volume ratio = 1:1, a space velocity of 200-1000 h-1. Before the start of the experiment, the catalyst was heated in an argon flow at 7500C for 20 minutes.[16-22].

The reaction products were analyzed by chromatographic method every 40 minutes (Fig. 1). the states of the active sites of the catalyst, the structure and dispersion were studied using electron microscopy and electron diffraction.

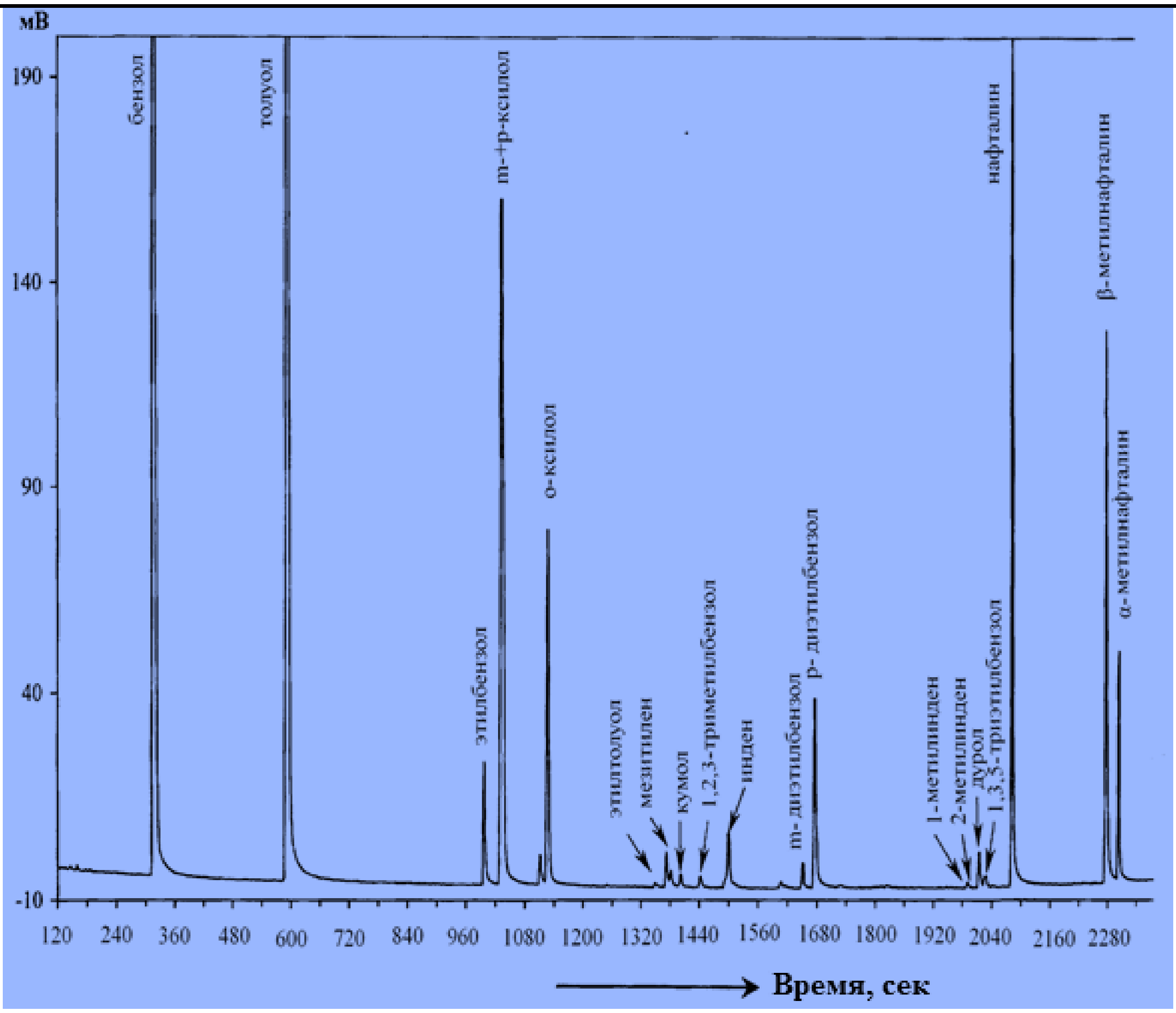


Fig.1.
Liquid chromatography of products of catalytic aromatization of methane with a selective catalyst.

The spatial composition of the obtained catalyst was studied on a «ДРОН – 3М»X-ray diffraction meter using a source of Си$К_{\alpha}$-rays.

One way to solve this problem is to perform the process in aerosol nanocatalysts. The active center is the nanoelectric core, which are xeloliths, and one of them is bentonite. The catalyst for the direct dehydroaromatization of methane was prepared by the «золь-гель» method. Aqueous solutions of salts$Zr(NO_3)_4$, $ZrO(NO_3)_2$, $Zr(NO_32$, for sol-gel synthesis of nanosized particles.

The necessary reagents were extracted and dissolved in bidistilled water by adding gelling additives, citric acid and ethylene glycol. The resulting mixture was thoroughly stirred at 8000C. Then heat treatment was carried out for 2 hours at 2000C and at 500-10000C for 3 hours. Scheme of the synthesis of the structure of the core layer of nanostructured particles

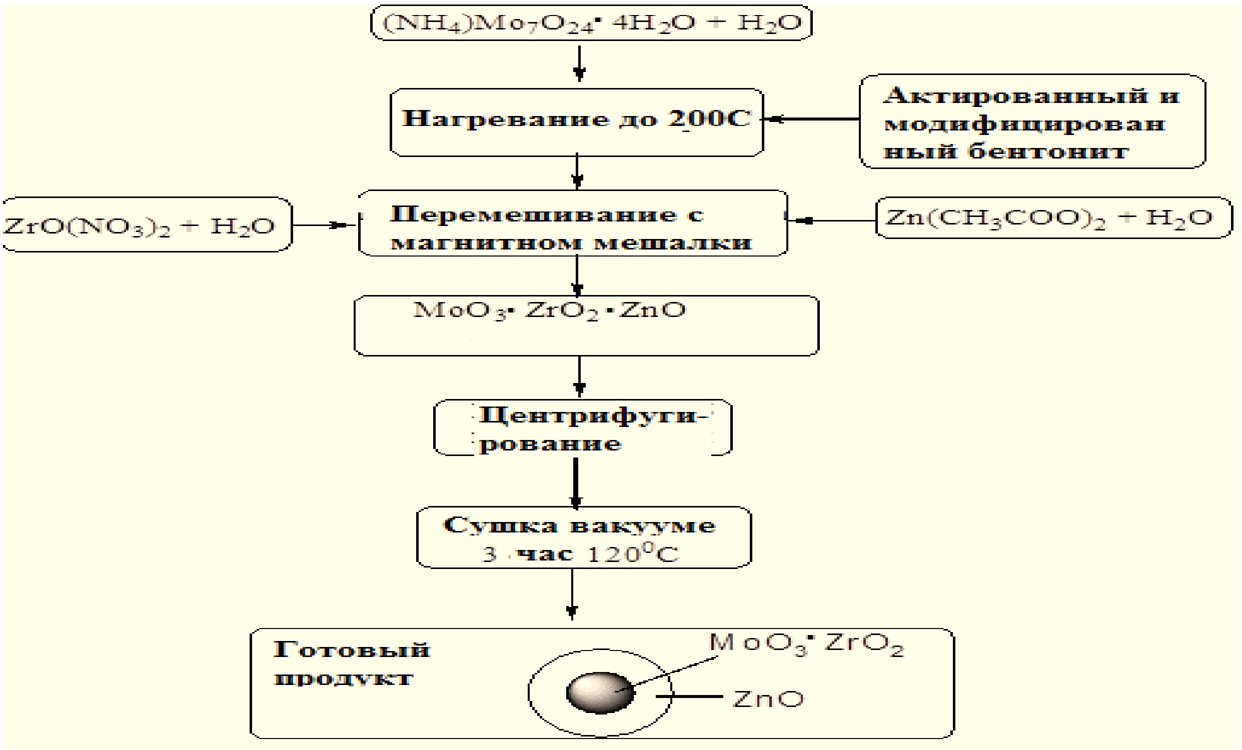


Fig.2.
Scheme for obtaining a nanostructured catalyst composition $(MoO_3)_x*(ZrO_2)_y*(ZnO)_z$

The high energy intensity and the use of existing technologies with heterogeneous catalysts force us to look for new ways to implement these processes. One way to solve this problem is to perform the process in aerosol nanocatalysts. The spatial composition of the resulting catalyst was studied on an X-ray diffraction meter «ДРОН-3М» using source СиК$_{\alpha}$-rays. The influence of the promoter of various metals on the yield, selectivity and conversion of aromatic hydrocarbons in the presence of selected high-performance catalysts was studied and the following results were obtained (see Fig. 3)

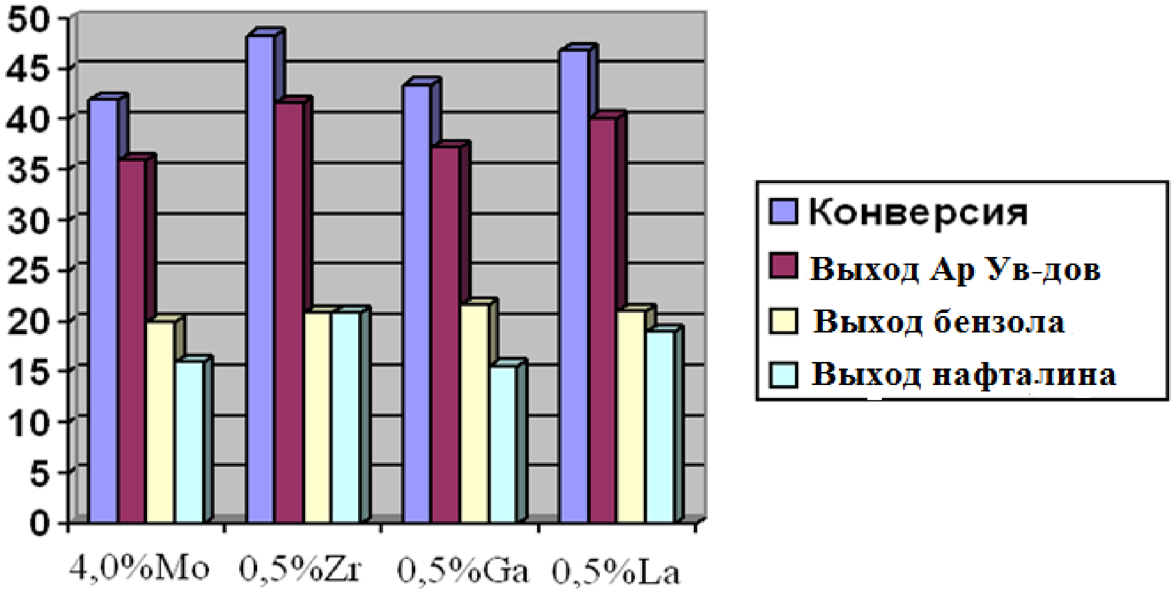
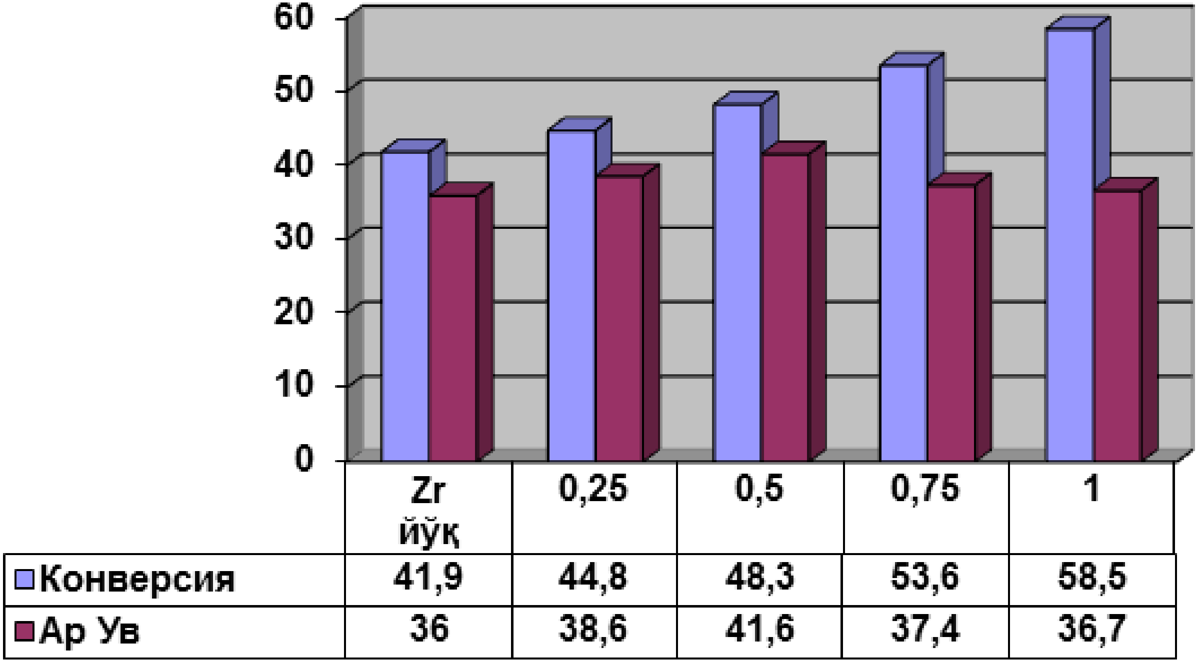


Fig 3.
Comparison of activity of Mo/bentonite and catalysts $(T=650^0C)$

Under optimal conditions, the conversion of the artificial mixture at 650^0C и $V_{смеси}=500$ $час^{-1}$ reaches 48,3%, and the yield of aromatic hydrocarbons was 86,1%.

As can be seen from Figure-3, the greatest results were obtained with a zirconium catalyst. Then we studied the effect of zirconium bentonite on the reaction yield and the selectivity of activation products.

Research has shown that when the content of zirconium in bentonite is 0.5%, the yield of the reaction, as well as the conversion of primary substances, have the highest values. With an increase in the zirconium content, the aromatizing properties of the catalyst decrease, and the cracking properties increase.



	Zr йуқ	0,25	0,5	0,75	1
■ Конверсия	41,9	44,8	48,3	53,6	58,5
■ Ар Ув	36	38,6	41,6	37,4	36,7

Fig 4.
The dependence of the concentration of zirconium in the catalyst 4.0% Mo/bentonite on the conversion of natural gas and the yield of reaction products *($T=650^0C$).*

The catalytic activity of a catalyst depends not only on its composition, but also on the thermomechanical conditions of its processing. During thermomechanical treatment of the catalyst, highly dispersed particles with excess energy are formed. The aromaticity of the catalyst containing 0.5% zirconium does not change at 500-6000C for 2-3 hours, with an increase in temperature to 700-7500C, an increase in the aromatic activity of the catalyst was observed. When the temperature reaches 5500C, relative to the initial yield of aromatic hydrocarbons increases by 5.2%.

At a temperature of 5500C and a space velocity of 300 h-1, the conversion of the initial substances reaches 99%, with a doubling of the space velocity, the yield of aromatic hydrocarbons decreases.

One of the important features of the catalyst, along with its activity and selectivity, is its ability to function for a long time without changing its high aromatic properties.

During the aromatization of hydrocarbons, coke is formed on the surface of the catalyst, which negatively affects the effective catalytic action of the catalyst and the gradual decrease in its activity. Therefore, catalyst regeneration is required. The catalyst was regenerated at 6500C in an air flow with a gradual increase in the volume of oxygen. In the air flow for 8 hours. After regeneration, the catalytic activity is restored again. The catalyst preparation technology also has a significant impact on the activity and productivity of the catalyst in the reactions of lower alkanes.

After the absorption of zirconium nitrate by bentonite, it was subjected to heat treatment at 500-6500C for 2 hours, and then its catalytic activity was studied. During this time, its catalytic activity remained practically unchanged. Heat treatment of the catalyst at 700-7500C for 3 hours showed a sharp increase in its aromatic activity. At a reaction temperature of 5500C, the yield of aromatic hydrocarbons increased by 5.2% compared to the initial condition, and at a space velocity of 300 h-1, the conversion of the starting material reached 99%. With a doubling of the space velocity, the yield of aromatic hydrocarbons decreases.

Studies show that with an increase in temperature and space velocity, the formation of coke and active centers increase, the catalyst is covered with coke, while the catalytic activity of the catalyst decreases. In order to prevent the formation of coke in Mo, containing bentonite was added to 0.2% cobalt, while a sharp reduction in coke formation was observed, and the catalyst operating time was increased.

As the space velocity of the primary substances increases, the rate of conversion of benzene and naphthalene into reaction products decreases quantitatively, and the yield C_2-C_4 olefins and alkylaromatic hydrocarbons increases.

With a decrease in the space velocity in the reactions of oligomerization and dehydrocyclization of olefins, as a result of an increase in the intensity of the reaction, their yield decreases, which leads to an increase in aromatic hydrocarbons. To study the kinetics and mechanism of the catalytic reaction of methane dehydroaromatization, the influence of various factors on the reaction rate was studied.

The effect of temperature and duration of the process on the non-oxidizing conversion of methane to aromatic hydrocarbons in the presence of a catalyst of the composition $(MoO_3)_x*(ZrO_2)_y*(ZnO)_z$ bentonite, and its effect on the composition and degree of conversion of the formed products. The data obtained are shown in Table 1.

Table 1
Effect of Methane Conversion on Reaction Time

Температура, ^0C	τ, мин	Конверсия метана, %	Выход продуктов, %		
			бензол	толуол	ксилол
650	120	36,5	6,2	-	-
	270	32,3	10,8	-	-
	360	27,0	19,9	0,87	1,15
	390	23,6	23,5	1,04	2,30
	420	18,2	15,4	1,67	2,10
	450	11,6	10,4	1,18	1,02
700	120	37,3	14,8	0,92	1,35
	240	36,2	19,3	1,08	1,70
	360	35,2	25,7	1,16	1,98
	420	32,2	27,5	1,40	1,88
	480	30,4	27,9	1,56	1,91
	510	28,9	26,5	1,48	1,78
	540	28,5	25,3	1,48	1,56
750	120	35,2	15,6	-	0,82
	240	50,8	25,4	-	1,78
	360	47,2	35,9	1,88	2,28
	390	52,5	31,5	1,12	2,12
	420	40,7	30,4	1,02	2,12
	450	40,0	29,5	0,96	2,02
	480	51,6	28,9	0,98	1,98

	510	51,8	27,6	0,82	1,90
	540	40,2	24,7	0,78	1,82
	570	50,6	23,2	0,71	1,78

As can be seen from the table. The highest conversion of methane at temperatures of 600-7000C was observed 120 minutes after the start of the reaction. during this time, the yield of aromatic hydrocarbons is the smallest. At 7500C, the highest conversion of methane is observed at a reaction time of 360 min.

The yield of aromatic hydrocarbons is the most significant at temperatures of 650-7500C and a reaction time of 360 minutes. As the contact time increases, the alkene yield decreases. The decrease in the yield of alkene with increasing contact time is explained by the fact that alkenes are more active than methane and are easily converted into aromatic hydrocarbons. As the contact time increases, the concentration of benzene almost doubles.

The decrease in the overall conversion of methane over time is due to the formation of coke on the catalyst surface and an increase in the yield of aromatic hydrocarbons due to an increase in the number of C_2H_y -fragments.

To improve the stability of the catalyst, promoters such as *Zr, La, Pt, Ni.* The task of metal promoters is related to their two functions: firstly, they control the degree of reduction MoO_3 in the $Me^{4+} + Mo^{6+} + Me^{4+} \rightarrow Mo^{+5}$ reaction, and secondly, they reduce the rate of coke formation due to its strongly hydrogenating properties

Studies have shown that the activity and selectivity of the catalyst depend on the properties of the catalyst and the method of its preparation.

The $(MoO_3)_x*(ZrO_2)_y*(ZnO)_z$ bentonite catalyst with the use of benttonite based on ammonium bicarbonate and hexamethylenediamine was synthesized with the highest activity in the reaction of methane dehydroaromatization. Table 2 shows the effect of temperature on the product composition and methane conversion in the methane aromatization reaction with the selected catalyst.

Table 2
Effect of Temperature on Methane Conversion and Product Composition in Modified Molybdenum Catalyst with Composition
1,0%-Zr, 1,0-Zn, 6,0% Mo($\tau = 360$ minutes)

T,⁰C	K%	Продуктов реакции							Вы-ход АрУ, %	$S_{АрУ}$, %
		H_2	Алкан C_1-C_4	Алкен C_2-C_4	C_6H_6	C_7H_8	C_8H_{10}	$C_{10}H_8$		
6,0% Мо/бентонит										
600	7,9	1,65	85,14	8,87	4,34	-	-	-	4,	54,9
650	17,7	2,22	80,96	5,74	10,72	0,15	0,21	-	11,1	62,7
700	26,4	4,12	75,00	3,18	15,78	0,28	0,68	0,46	17,2	65,2
750	35,8	5,08	68,90	2,86	20,83	0,40	0,84	0,62	22,7	63,4
1,0%Zr-6,0 % Мо/бентонит										
600	9,6	1,74	82,80	9,56	5,84	0,06	-	-	5,9	61,5
650	22,0	4,85	71,90	6,48	15,35	0,17	0,26	0,38	16,2	73,4
700	29,5	5,78	65,70	4,35	21,20	0,45	0,85	0,76	23,3	78,8
750	38,7	7,82	56,64	2,78	29,80	0,52	1,04	0,94	32,3	83,5
1,0%Zn - 1,0% Zr -6,0% Мо/бентонит										
600	10,9	2,18	80,36	8,78	6,80	0,18	0,94	0,76	8,7	80,5
650	27,0	6,08	65,12	5,92	19,86	0,87	1,15	1,02	22,9	84,8

700	35,2	6,98	58,50	3,78	25,74	1,16	1,98	1,84	30,7	87,3
750	47,2	7,78	48,92	1,02	35,98	1,88	2,28	2,14	42,3	89,6
1,0%Zn-6,0% Mo/бентонит										
600	10,2	2,68	81,36	9,35	6,08	0,08	0,18	0,26	6,1	64,7
650	24,2	5,23	70,18	6,13	16,96	0,69	0,98	0,51	18,3	75,6
700	33,2	6,52	62,61	3,94	23,87	1,02	1,22	0,62	26,7	80,6
750	41,0	7,74	55,08	1,98	30,52	1,34	1,76	1,08	34,7	84,6

As can be seen from table 2, with increasing temperature, the conversion of the source material and the yield of aromatic hydrocarbons increases.

The liquid reaction products are mainly benzene, toluene, xylene and naphthalene, which increase with increasing temperature. In the gaseous product, the amount of hydrogen increases with increasing temperature, but below C_2-C_4 alkanes.

Sample 6.0% Mo/bentonite has sufficient catalytic activity, while the conversion of methane and aromatic hydrocarbons at 7500C reach 35.8% and 22.7%, respectively.

Selectivity for aromatic hydrocarbons is from 54.9 to 63.4% at a temperature of 600-7500C. When adding 1.0% Zr to a sample of 6.0% Mo/bentonite, the total conversion of methane in the range of 600-7500C increased from 9.6 to 38.7%, the yield of aromatic hydrocarbons increased from 5.9% to 32.2%, and the selectivity of aromatic hydrocarbons from 6.5% to 83.5%; % to 47.2% with the yield of aromatic hydrocarbons from 8.68 to 48.28% and the selectivity of aromatic hydrocarbons increases from 80.5% to 89.6%.

Electron microscopic studies have shown that crystals obtained on catalysts from different structures have different shapes and sizes. Bentonite particles using hexamethylenediamine have polycrystalline spheroids and consist of single crystals. Spherical IDs range from 3 to 8 microns. Bentonite particles obtained using NH4HCO3 form hexagonal prisms. Thus, the catalytic activity depends on the morphology and size of the bentonite crystals.

Also, the catalytic activity depends on the acid sites of bentonites obtained from various structure-forming additives. Based on the study of the acid properties of H-shaped bentonites obtained by the method of temperature-programmed ammonia desorption, two active centers (strong and weak acid centers) were found on the surface. The maximum activity of the catalyst in the dehydrogenation of methane was observed at its space velocity of 1000 h-. The conversion of methane under these conditions reaches 52.5%, while the activity of the catalyst remains constant for 260 minutes. An increase in the volumetric flow rate of methane from 1000 h-1 to 1500 h-1 led to a decrease in its conversion and stable catalyst activity.

Based on the influence of the composition of the reaction products and process conditions on the yield of target products, the total amount of chemical reactions during the conversion of methane in the absence of oxidizing agents was determined: hydrogenation and dehydrogenation, oligomerization, dehydrocyclization, aromatization, alkylation and dealkylation, condensation. Based on experimentally determined participation data. Mo-containing catalysts, a reliable scheme for the conversion of methane to aromatic hydrocarbons was created: Methane → olefins → aromatic hydrocarbons

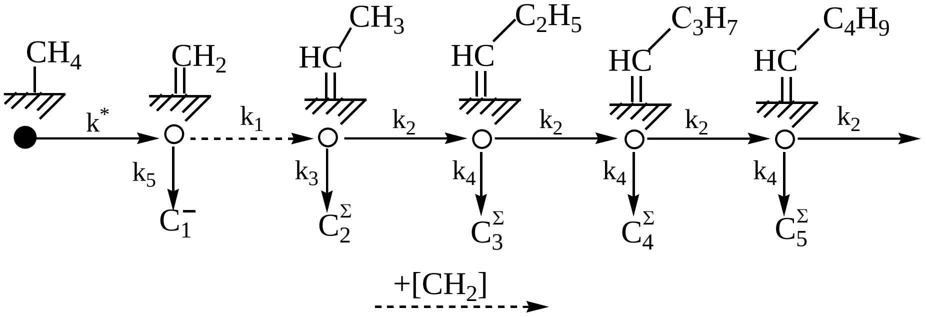
The scheme of the activation mechanism of the methane molecule is as follows:

$CH_4 + MoC_x/\ kat \rightarrow H_2C^{+}\text{-}\ MoC_x/\ kat + H_2$

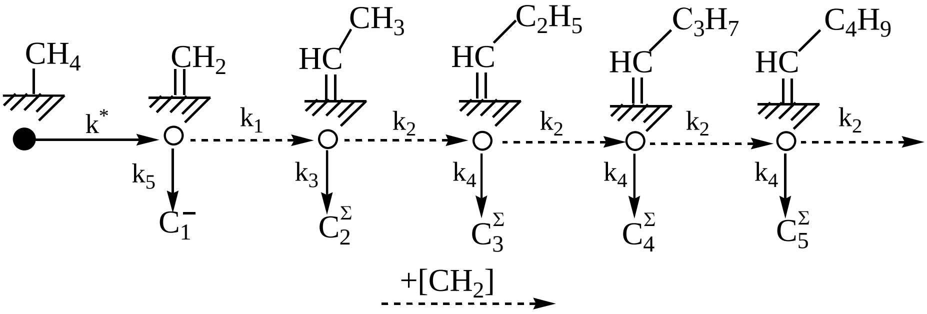
$CH_4\ + H_2C^{+}\ \text{-}MoC_x\ /\ kat \rightarrow H_2C^{+}\ \text{-}\ H_2C^{+}\ \text{-}\ MoC_x\ /\ kat$

$H_2C^{+}\ \text{-}\ H_2C^{+}\ \text{-}\ MoC_x\ /\ kat \rightarrow C_2H_4 + Mo^{+}C_x\ /\ kat$

Reaction scheme for dehydroaromatization of methane without an oxidizing agent:



Scheme of formation of [C_2H_4] in the interaction of 2 surface-active [CH_2] complexes:



In the catalytic methane dehydroaromatization reaction, small amounts of carbon monoxide and carbon dioxide are formed, which means that carbon-containing structures with different structures are formed on the surface of the catalyst. As a result of C_2-C_4 chemisorption into catalytically active sites, their molecules dissociate to form carbon and C_xH_y fragments. On the surface of molybdenum catalysts, carbon is present in several forms, some of which block catalytic centers, others return the active phases of metal clusters and are mainly localized on the outer surface of the catalyst, as a result, the overall methane conversion decreases, and the rate of formation of aromatic hydrocarbons increases.

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