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# Kinetics and Mechanism of the Reaction of Catalytic Dehydroaromatization of Methane

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**Abstract:** In the work the influence of various parameters on methane conversion and reaction yield of the reaction of methane dehydroaromatization was studied. Based on obtained results the mechanisms of activation of the methane molecule and proceeding of the process were offered. Kinetic equations of formation reactions of coke, benzene, toluene, xylene were improved and expressed in terms of the Langmuir-Hinshelwood equation.

**Keywords:** Methane, Dehydroaromatization, Catalyst, Activation Mechanism, Kinetic Equation

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## 1. Introduction

Aromatic hydrocarbons, namely (basically) benzene, toluene, ethylbenzene and xylene are important chemical products in chemical industry.

At present aromatic compounds are obtained by catalytic reforming and cracking oil fractions [1-4].

But while oil reserves are decreasing the demand for finding alternative sources of aromatic hydrocarbons is increasing. One of the alternative sources for obtaining aromatic hydrocarbons is natural gas and biogas [5-7].

In Mo-containing bentonite catalysts modified with the ions of transition metals the dehydroaromatization reaction of natural and associated oil gases in condition without oxidants is a perspective method [8-13].

## 2. Experimental Part

Methane (degree of purity is 99,9%) conversion without oxidants has been carried out in running reactor changing the temperature in the interval of 600-800°C, in P=0.1 MPa, in methan: argon=1:1 ratio, in value of volumetric rate of 200-1000 hour<sup>-1</sup>. In quartz reactor (the reactor diameter is 12 mm) the catalyst volume made 1cm<sup>3</sup>. Size of the catalyst particles

was 0.5-1.0 mm. before beginning the experiment the catalyst has been heated at 750°C in helium flow for 20 minutes. The state of active centers, dispersion and structure of the catalyst have been examined by electron microscope and electrons diffraction. The composition of initial and compounds formed was analyzed by chromatographic method.

## 3. Results and Their Discussion

To study kinetics and mechanism of the reaction of catalytic dehydroaromatizing methane the influence of various factors to reaction rate has been examined. Methane conversion to aromatic hydrocarbons without oxidants in the presence of a catalyst with the composition (MoO<sub>3</sub>)<sub>x</sub>·(ZrO<sub>2</sub>)<sub>y</sub>·(ZnO<sub>2</sub>)<sub>z</sub>/bentonite the influence of temperature and process duration to conversion degree and composition of the compounds formed was studied. The obtained results are presented in table 1.

It is shown from table 1 that in temperature of 650-700°C the highest conversion of methane is observed after 120 minutes from the reaction start. At this time the yield of aromatic hydrocarbons has little value. The highest conversion of methane is observed at 750°C, when the reaction has continued for 390 minutes. At 650-750°C, when the reaction continues for 360 minutes aromatic

hydrocarbons are formed with the highest yield. In time the decrease of total conversion of methane is explained with the formation of coke in the catalyst surface and the increase of aromatic hydrocarbons output with the increase of C<sub>2</sub>H<sub>4</sub>-

fragments amount. With the rise in temperature and the increase in reaction time the decrease of methane conversion and aromatic hydrocarbons output is explained with the scheme in figure 4.

**Table 1.** Influence of process duration to conversion degree of methane and composition of the compounds formed.

Temperature, °C	$\tau$ , min	Methane conversion, %	Product output, %		
			benzene	toluene	xylene
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
750	540	28,5	25,3	1,48	1,56
	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	

To increase stable work of the catalyst promoters like Zr, La, Pt and Ni were added to it. Task of metal-promoters depends on their following two functions: firstly, they control reductive degree of MoO<sub>3</sub> on the reaction of Me<sup>m+</sup> + Mo<sup>6+</sup> → Me<sup>m+</sup> + Mo<sup>+5</sup>, secondly, they decrease a coke formation speed with their high hydrogenation feature.

Researchers have shown dependence of activity and selectivity of the catalyst on carrier substance property and

on its preparation method.

In dehydroaromatization reaction of methane the catalyst (MoO<sub>3</sub>)<sub>x</sub>·(ZrO<sub>2</sub>)<sub>y</sub>·(ZnO<sub>2</sub>)<sub>z</sub>/bentonite synthesized based on bentonite using ammonium bicarbonate and hexamethylenediamine has shown the highest activity. Results of temperature influence to products composition of aromatization reaction of methane on chosen catalysts and methane conversion are presented in table 2.

**Table 2.** Results of temperature influence to methane conversion on modified 1,0% Zn · 1,0% Zr · 6,0% Mo catalyst and products composition ( $\tau = 360$  minutes).

T, °C	K%	Reaction products							ArHy output, %	S <sub>ArHy</sub> , %
		H <sub>2</sub>	Alkane C <sub>1</sub> -C <sub>4</sub>	Alkene C <sub>2</sub> -C <sub>4</sub>	C <sub>6</sub> H <sub>6</sub>	C <sub>7</sub> H <sub>8</sub>	C <sub>8</sub> H <sub>10</sub>	C <sub>10</sub> H <sub>8</sub>		
6,0% Mo/bentonite										
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% Mo/ bentonite										
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% Mo/ bentonite										
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/ bentonite										
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

It is shown from table 2 that with temperature rise the initial substance conversion and the yield of aromatic hydrocarbons increase. Liquid products of the reaction basically are benzene, toluene, xylene and naphthalene, their amount increases with temperature rise. With temperature rise amount of hydrogen in composition of gas product increases, but amount of low C<sub>2</sub>-C<sub>4</sub> alkanes and alkenes decreases. 6% Mo/bentonite sample has enough catalytic activity and at 750°C methane conversion and yield of aromatic hydrocarbons reach to 35.8% and 22.7% respectively. Selectivity with respect to aromatic hydrocarbons in 600-750°C varies from 54.9% to 63.4%. When 1% Zr was added to 6% Mo/bentonite sample in interval of 600-750°C, total conversion of methane increased from 9.6% to 38.7%, the yield of aromatic hydrocarbons from 5.9% to 32.2%, formation selectivity of aromatic hydrocarbons from 61.5% to 83.5%. In the presence of a catalyst with the composition of 1,0% Zn 1,0% Zr 6,0% Mo/bentonite in interval of 600-750°C total conversion of methane increases from 10.9% to 47.2%, the yield of aromatic hydrocarbons from 8.68 to 48.28% and formation selectivity of aromatic hydrocarbons from 80.5% to 89.6%.

As electron microscopic investigations show the shape and size of the crystals formed from the catalysts obtained from different structure formers are different. The particles of bentonite obtained using hexamethylenediamine have polycrystal spheroidal shape and composed of monocrystals. Spheroids size varies from 3 to 8 mkm. The particles of bentonite obtained using NH<sub>4</sub>HCO<sub>3</sub> form hexagonal prisms. Thus, catalytic activity of catalysts depends on morphology and size of bentonite crystals. Catalytic activity depends also on acidity centers on bentonite obtained from different admixtures forming structure. Based on studying acidity properties of H-form bentonites by temperature-programmed desorption of ammonia two types of active centers (strong and weak acid centers) on surface have been determined. Acidity centers of the bentonite obtained using ammonium bicarbonate is strong with respect to those of the bentonite obtained using hexamethylenediamine. The more strong the acidity centers of bentonite is the fast a catalyst loses its activity. Based on experimental data received on various conditions for conducting the process the kinetic objective laws of converting methane to aromatic hydrocarbons have been analyzed. Research results of the influence of volumetric rate and reaction time to methane conversion are shown on figure 1. In dehydroaromatization process of methane the maximal activity of the catalyst was observed in its volumetric rate 1000 hour<sup>-1</sup>. In this condition methane conversion reaches to 52.5%, the catalyst activity is not changed during 260 minutes. Increasing methane flow speed from 1000 to 1500 hour<sup>-1</sup> leads to the decrease of its conversion and duration of the catalyst stable work.

Dependence between the yield of methane conversion main products and contact time is presented in figure 2. With the increase of contact time alkenes yield decreases. When contact time increases decrease of alkenes yield is explained

with alkenes activity in comparison with methane and easy conversion to aromatic hydrocarbons. Benzene concentration increases almost two times with contact time increase.

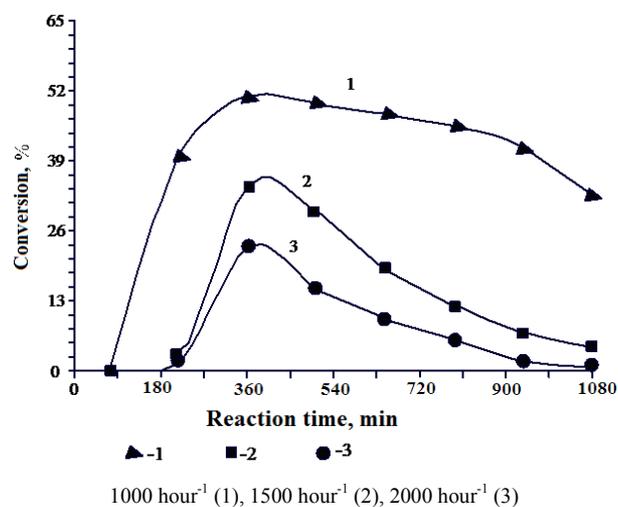


Figure 1. Dependence of volumetric rate and reaction time on methane conversion.

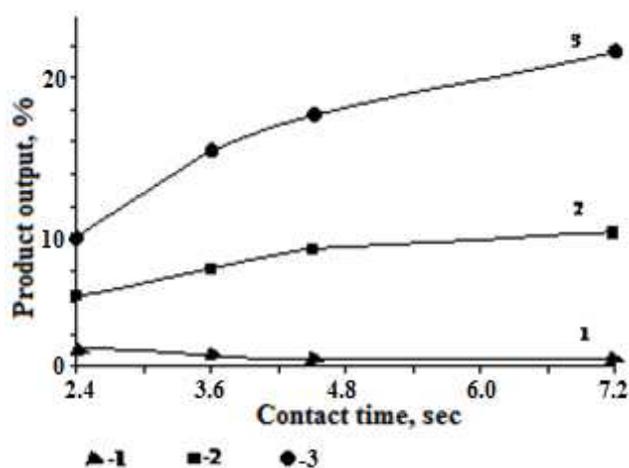
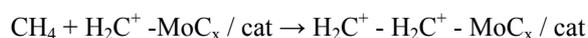
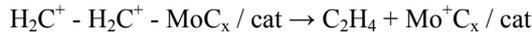


Figure 2. Dependence of the output of alkenes (1), benzene (2), naphthalene (3) on contact time.

Based on the influence of composition of obtained reaction products and process condition to the yield of target products, the sum of chemical reactions proceeding in methane conversion on a condition without oxidants has been determined: hydrogenation and dehydrogenation, oligomerization, dehydrocyclization; aromatization, alkylation and dealkylation; condensation. Proceeding from kinetic data determined experimentally, a reliable way for conversion of methane to aromatic hydrocarbons on Mo-containing catalysts has been proposed: methane → olefines → aromatic hydrocarbons. Activation mechanism scheme of methane molecule:





methane without oxidants is generally presented in Figure 3:

Mechanism of the dehydroaromatization reaction of

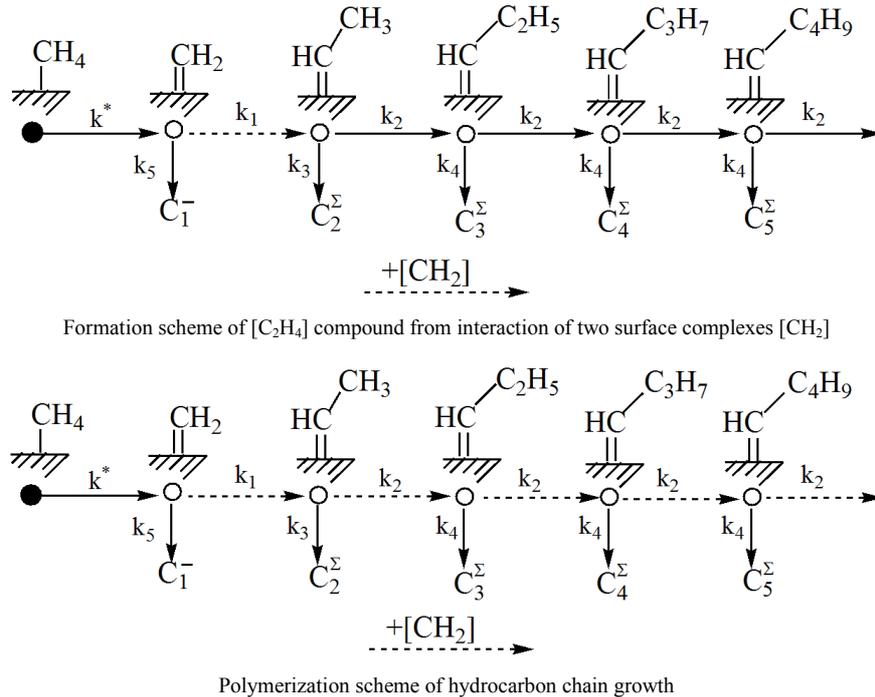
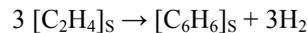
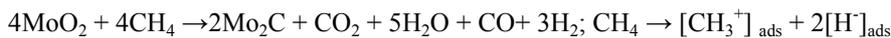
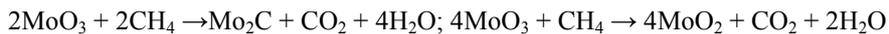


Figure 3. Scheme for reliable mechanism of hydrocarbon chain growth in catalytic aromatization reaction of methane.

Carbon dioxide gas and carbon dioxide form in a little amount in the reaction of catalytic dehydroaromatization of methane. This informs formation of carbon-containing structures with different structure on the catalyst surface. As a result of chemical sorption of C<sub>2</sub>-C<sub>4</sub>-hydrocarbons on the catalyst active centers their molecules form carbon and C<sub>x</sub>H<sub>y</sub>-fragments and are dissociated. On the surface of molybdenum-containing catalysts carbon is in several forms

and a part of them blocks the catalytic centers, the other part reduces active phases of metal clusters and is basically localized on external surface of a catalyst. As a result total conversion of methane decreases and formation speed of aromatic hydrocarbons increase.

In general the process mechanism could be presented as following:



The reaction of catalytic aromatization of methane and coking process of the catalyst active centers could be expressed by the following scheme:

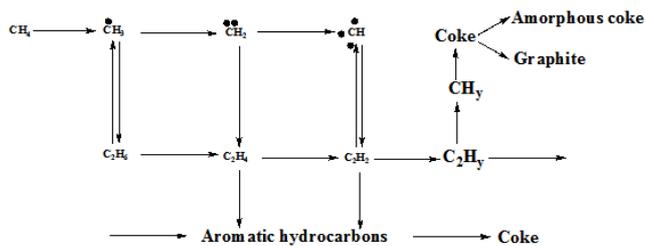


Figure 4. Coking process of the catalyst active centers.

Coke formed on the catalyst surface could be an amorphous or graphite form on its structure depending on C/H ratio.

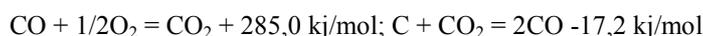
Knowing the structure of coke formed allows to choose an optimal condition for catalyst regeneration. If the C/H ratio is from 1.5 to 2, the formed coke is graphitized on its structure and heating it is performed in enough high temperature (about 800-900°C). If the C/H ratio is between 0.2 and 1 amorphous coke forms.

The main combustible component of coke in the catalyst is graphite and in general its combustion is characterised by the following processes:

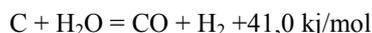
- 1) When carbon reacts with oxygen Co and CO<sub>2</sub> form:



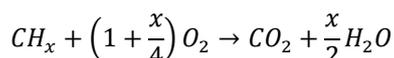
2) Further changes of formed oxides:



3) Reaction of carbon with water steams in reaction zone:



In general combustion reaction of coke could be expressed as follows:



Amount of oxygen spent for the reaction and that of carbon dioxide formed as a result of the reaction is determined as follows:

$$n_{O_2} = \frac{G_{air}(C_{O_2}^0 - C_{O_2})}{100V_m} \text{ and } n_{CO_2} = \frac{G_{air}(C_{CO_2} - C_{CO_2}^0)}{100V_m}$$

here,  $n_{O_2}$  and  $n_{CO_2}$  - amount of oxygen spent and formed carbon dioxide, kmol/hour;  $G_{air}$  - air expenditure, nm<sup>3</sup>/hour,  $C_{O_2}^0$ ,  $C_{O_2}$  and  $C_{CO_2}$ ,  $C_{CO_2}^0$  - concentrations of oxygen given

and carbon dioxide going out, in volume%;  $V_m$  - gas volume in normal condition, m<sup>3</sup>/kmol.

Amount of hydrogen in coke composition is determined from the difference between amounts of spent oxygen and formed carbon dioxide:

$$n_H = 4(n_{O_2} - n_{CO_2})$$

here,  $n_H$  - amount of hydrogen atoms in coke, kmol.

Thus, by the given method the structure of coke (graphitized or amorphous) could be determined. When the results obtained by this method compared with that of derivatographic analysis method (figure 5), it was determined that an error makes  $\pm 3\%$ .

Size of the catalyst pores and specific surface determines an inclination to coking, therefore the method of physical adsorption of nitrogen was used to determine the catalyst surface, size and volume of pore.

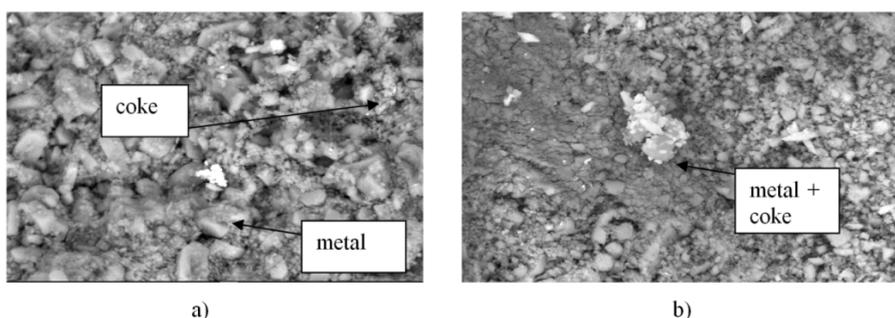


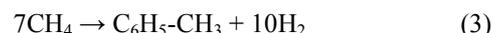
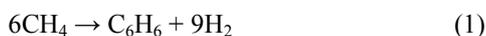
Figure 5. Micrograph of coked catalyst (enlarged by 5000 times).

The large the specific surface of the catalyst is the high its activity is. Coke formation on active surface of the catalyst leads to worsening of condition parameters of catalytic processes. To restore the catalyst activity oxidative regeneration is used.

Conducting regeneration process depends on the stability and activity if the catalyst. Therefore an optimal conducting regeneration process has a great importance in many organic syntheses.

Amount of coke in the catalyst has been determined on the difference between the masses before and after heating in open air. For this the catalyst was heated at 110°C in air and mass was measured, then it was burnt at 800°C in oven. After 1 hour its mass was measured again and amount of coke determined.

In the presence of  $(MoO_3)_x \cdot (ZrO_2)_y \cdot (ZnO_2)_z$ /bentonite catalyst the following 4 main reactions proceed in catalytic aromatization process of methane:



Reaction (b) could be neglected, this reaction is necessary to study coke formation potential effect only.

The reaction rate equations of abovementioned 4 reactions have been optimized from 700 to 750°C according to experimental data and expressed by the Langmuir-Hinshelwood equation:

$$W_1 = \frac{k_1 f_{CH_4}^6 \left(1 - \frac{f_{C_6H_6} f_{H_2}^9}{K_{R1} f_{CH_4}^6}\right)}{(1 + K_{CH_4} f_{CH_4} + K_{H_2} f_{H_2} + K_{C_6H_6} f_{C_6H_6})^6} \quad (1)$$

$$W_2 = \frac{k_2 f_{CH_4} \left(1 - \frac{f_{H_2}^2}{K_{R2} f_{CH_4}}\right)}{(1 + K_{CH_4} f_{CH_4} + K_{H_2} f_{H_2} + K_{C_6H_6} f_{C_6H_6})^6} \quad (2)$$

$$W_3 = \frac{k_3 f_{CH_4}^7 \left(1 - \frac{f_{C_7H_8} f_{H_2}^{10}}{K_{R3} f_{CH_4}^7}\right)}{(1 + K_{CH_4} f_{CH_4} + K_{H_2} f_{H_2} + K_{C_7H_8} f_{C_7H_8})^7} \quad (3)$$

$$W_4 = \frac{k_4 f_{CH_4}^8 \left(1 - \frac{f_{C_8H_{10}} f_{H_2}^2}{K_{R3} f_{CH_4}^7}\right)}{(1 + K_{CH_4} f_{CH_4} + K_{H_2} f_{H_2} + K_{C_8H_{10}} f_{C_8H_{10}})^8} \quad (4)$$

here,  $f_i$  – volatility of  $i$  component;  $K_{R_1}$  and  $K_{R_2}$  – equilibrium constants of reactions 1 and 2, which could be calculated on thermodynamic terms;  $k_1$  and  $k_2$  – rate constants of reactions of 1 and 2;  $k_i$  – equilibrium adsorption constant of component  $i$ .

In modeling the following kinetic parameters were used:

$$k_1 = 8,1283 \cdot 10^{-3} \exp\left(-\frac{2,0909 \cdot 10^5}{R} \left(\frac{1}{T} - \frac{1}{943,15}\right)\right) \quad (5)$$

$$k_2 = 2,3252 \cdot 10^{-3} \exp\left(-\frac{1,2096 \cdot 10^5}{R} \left(\frac{1}{T} - \frac{1}{943,15}\right)\right) \quad (6)$$

$$K_{CH_4} = \exp\left(-1,1963 - 1,3209 \cdot 10^2 \left(\frac{1}{T} - \frac{1}{943,15}\right)\right) \quad (7)$$

$$K_{H_2} = \exp\left(-1,6736 - 1,5796 \cdot 10^3 \left(\frac{1}{T} - \frac{1}{943,15}\right)\right) \quad (8)$$

$$K_{C_6H_6} = \exp\left(-9,09 - 1,177 \cdot 10^5 \left(\frac{1}{T} - \frac{1}{943,15}\right)\right) \quad (9)$$

$$K_{C_7H_8} = \exp\left(-11,32 - 1,786 \cdot 10^6 \left(\frac{1}{T} - \frac{1}{943,15}\right)\right) \quad (10)$$

$$K_{C_8H_{10}} = \exp\left(-15,46 - 1,982 \cdot 10^8 \left(\frac{1}{T} - \frac{1}{943,15}\right)\right) \quad (11)$$

## 4. Conclusion

1. In dehydroaromatizing methane in the presence of a catalyst with composition of  $(MoO_3)_x \cdot (ZrO_2)_y \cdot (ZnO)_z$  / bentonite the influence of the temperature and duration of the process to conversion degree and composition of compounds formed has been investigated.
2. Based on studying the influence of various factors to the yield of aromatic hydrocarbons the activation mechanism of methane molecule, general mechanism of process proceeding were offered.
3. Rate equations for formation reactions of coke, benzene, toluene and xylene have been optimized from 700 to 750°C accordingly to experimental data and expressed by the Langmuir-Hishelwood equation.

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