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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

SCIENTIFIC BASIS OF OPTIMAL DESIGN OF SELECTIVE OXIDATIVE DEHYDROGENATION REACTION OF METHYLCYCLOHEXANE TO METHYLCYCLOHEXADIENE ON MODIFIED ZEOLITES

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CHARACTERISTICS OF THE WORK

Relevance of the topic and the degree of elaboration. Industrialization of effective synthesis processes of unsaturated organic compounds based on readily available materials is considered one of the important problems of modern chemical technology. A special place in this class of compounds belongs to alicyclic diene hydrocarbons. Alicyclic diene hydrocarbons are considered the main starting materials for the synthesis of various classes of polyfunctional compounds. Due to their active double bonds, functional derivatives of these compounds are used in the purposeful synthesis of special-purpose polymer and composite materials, physiologically active substances and at the same time analogues of natural compounds and medicinal preparations.

Alicyclic diene hydrocarbons, especially 1,3-methylcyclo-hexadiene are used as primary raw materials for the production of high-density components for jet engine fuels, as a hardener for epoxy resins and for the synthesis of important substances used in industry and national economy.

Currently, methylcyclohexadiene is mainly obtained by dehydrohalogenation of halogenated derivatives of the corresponding olefins in the liquid phase. However, the main shortcomings of these methods are related to the process being carried out in the liquid phase, low selectivity for the target product and difficulty in separating the reaction products.

Synthesis of alicyclic diene hydrocarbons by oxidative dehydrogenation of naphthenic hydrocarbons, which are abundant resources in oil and its processing products, is considered an important direction in oxidative heterogeneous catalysis. From this point of view, the synthesis of the valuable product - methylcyclohexadiene-1,3 by means of oxidative dehydrogenation of methylcyclohexane is of great theoretical and practical importance.

[1]At present, catalytic dehydrogenation reactions of more

[1] Meng, J. A Review of Catalysts for Methylcyclohexane Dehydrogenation / Meng, J., Zhou, F., Ma, H. [et al.] // Top Catal, – 2021. 64, – p.509-520. https://doi.org/10.1007/s11244-021-01465-6

naphthenic hydrocarbons under oxygen-free conditions have been studied[1]. It is known that these reactions are thermodynamically limited, lead to resinification and aromatization of some of the hydrocarbon fractions under harsh conditions and also lead to deactivation and rapid coking of the used catalyst. The use of molecular oxygen as a hydrogen acceptor allows these processes to be carried out in milder conditions and avoid the above-mentioned complications.

The use of zeolite catalysts in obtaining highly active and selective catalysts is of great interest for the purpose of effective implementation of catalytic oxidative dehydrogenation processes of naphthenic hydrocarbons. However, there are insufficient literature data on the catalytic oxidative dehydrogenation reactions of methylcyclohexane to 1,3-methylcyclohexadiene over zeolite-based catalysts. Oxidative dehydrogenation reaction of methylcyclohexane over existing catalysts proceeds mainly in the direction of obtaining toluene.[2,3]

In this regard, the development of zeolite-based catalysts with high stability, catalytic activity and selectivity for the oxidative dehydrogenation of methylcyclohexane to 1,3-methylcyclohexadiene at low temperature and atmospheric pressure, the study of the kinetic laws of this reaction, the probable stepwise mechanism, and the optimal type of reactor based on the kinetic model selection, theoretical optimization, calculation of the optimal structural dimensions of the reactor element according to the given productivity and the creation of a complete mathematical model of the process are quite relevant and are the main issues of the industrialization of the dehydrogenation process of methylcyclohexane.

Object and subject of the research. Metalzeolite catalysts

[2] Cromwell, D.K. Enhanced methylcyclohexane dehydrogenation to toluene over Ir/USY catalyst / D.K.Cromwell, P.T.Vasudevan, B.Pawelec [et al.] // Catalysis Today, - 2016. Vol. 259, - p.119-129. https://doi.org/10.1016/j.cattod.2015.05.030.

[3] Сулейманова, Э.Т. Развитие исследований в области получения и использования алициклических углеводородов и их функциональных производных / Э.Т. Сулейманова, Х.М. Алимарданов, М.Ф. Аббасов [и др.] // Процессы нефтехимии и нефтепереработки. – 2008. №3-4, – с.35-36.

modified by ion-exchange method with cations of various transition elements were taken as the object of research in the thesis work. The subject of the research was the study of the oxidative dehydrogenation reaction of methylcyclohexane to the appropriate alicyclic diene on modified metal-zeolite catalysts, kinetic and mathematical modeling of the process, selection of the optimal reactor type and construction of the principle technological schem.

Goals and objectives of the study. In order to industrialize the process of oxidative dehydrogenation of methylcyclohexane to 1,3-methylcyclohexadiene in the presence of molecular oxygen on zeolite-containing catalytic systems, it consists of developing an active metal zeolite catalyst for this process, elucidating the mechanism of the reaction, building kinetic and mathematical models and the principle technological scheme of the device.

For this purpose, the following tasks were set and solved in the research work:

- Synthesis of metal zeolite modified with cations of transition elements, study of the relationship between physicochemical properties, structural properties and catalytic activity of metal zeolite catalysts in the oxidative dehydrogenation reaction of methylcyclohexane;
- Selection of a highly efficient and selective catalyst for the oxidative dehydrogenation of methylcyclohexane to 1,3-methylcyclohexadiene in the vapor phase;
- Experimental study of the kinetic regularities of this reaction on the selected active catalyst;
- Selection of the probable phase scheme of the reaction mechanism;
- Development of a theoretically based kinetic model of the process;
- Creating a complete mathematical model of the process and carrying out theoretical optimization;
- Choosing the optimal type of reactor and drawing up the basic technological scheme.

Research methods. Complex studies and works were carried out with the use of modern methods of physico-chemical analysis (AAS,

ICP, GC, GC-MS, etc.), application of computer technologies, taking into account the important regularities of heterogeneous catalysis. During the experiments, modern devices, equipment, instruments and measuring tools were used. The objectivity, accuracy and correctness of the results of the works conducted by experimental and theoretical tests were determined.

The main provisions of the defense:

−Results of studies for the selection of an active metal zeolite catalyst for the partial oxidative dehydrogenation reaction of methylcyclohexane to 1,3-methylcyclohexadiene;

−A new highly efficient metal zeolite catalyst selected for the selective oxidative dehydrogenation reaction of methylcyclohexane to 1,3-methylcyclohexadiene;

−A general kinetic model of the oxidative dehydrogenation of methylcyclohexane over zeolite catalysts describing the rate of formation and consumption of the main and secondary reaction products;

−A general mathematical model of the oxidative dehydrogenation of methylcyclohexane;

−Results of the theoretical optimization of the partial oxidative dehydrogenation reaction of methylcyclohexane to methylcyclohexadiene.

Scientific novelty of the research:

- The reaction of selective oxidative dehydrogenation of methylcyclohexane to 1,3-methylcyclohexadiene over metal zeolite catalysts modified with cations of transition elements was studied.
- The effect of individual components of catalysts on their activity was revealed. It has been shown that transition metal-free zeolites are characterized by low activity in the selective oxidative dehydrogenation reaction of methylcyclohexane to 1,3-methylcyclohexadiene.
- As a result of complex studies of the physico-chemical and catalytic properties of polycomponent zeolite-containing systems, a clinoptilolite zeolite-based metal zeolite catalyst modified with cobalt (Co^{2+}) and chromium (Cr^{3+}) cations was selected for the

selective oxidative dehydrogenation reaction of methylcyclohexane to 1,3-methylcyclohexadiene.

- The kinetic regularities of the oxidative dehydrogenation of methylcyclohexane in the presence of molecular oxygen over the selected highly effective modified zeolite catalyst were studied and the probable mechanism of the reaction was clarified.
- A theoretically based kinetic model describing the main routes of chemical transformations on the zeolite surface of the oxidative dehydrogenation reaction of methylcyclohexane over modified metal zeolite catalysts was developed.
- The theoretical optimization of the process was carried out, the optimal reactor type was selected based on the kinetic model, the optimal structural dimensions of the reactor element were calculated according to the given productivity and a complete mathematical model of the process was created.
- The principle technological scheme of the unit was developed for the industrial implementation of the process of selective oxidative dehydrogenation of methylcyclohexane to 1,3-methylcyclohexadiene.

Theoretical and practical significance of the research. For the first time in conducting the work, theoretical ideas were created for the formation of the principles of selecting highly effective catalytic systems for the process of selective oxidative dehydrogenation of methylcyclohexane to suitable alicyclic diene-1,3 methylcyclohexadiene. Based on theoretical and experimental studies, highly efficient polycomponent ultradispersed zeolite-containing catalytic systems were developed for the selective oxidative dehydrogenation reaction of methylcyclohexane to 1,3-methylcyclohexadiene. Instead of expensive synthetic zeolites, the possibility of using their natural analogues in the processes of oxidative conversion of hydrocarbons has been theoretically and experimentally substantiated.

Based on the experimental results, the kinetic regularities of the reaction were studied and the optimal type of reactor was selected for the purpose of application to production and the principle technological scheme of the process was prepared and proposed.

The optimal catalyst composition selected for the selective

oxidative dehydrogenation reaction of methylcyclohexane to 1,3-methylcyclohexadiene is patented.

The results of the published dissertation work can be used by specialists engaged in research in the field of oxidative heterogeneous catalysis and modeling of oxidative conversion processes.

Approbation and application. 18 scientific works on the dissertation, including 9 articles (2 without co-authors), 8 theses of reports were published and 1 patent of the Republic of Azerbaijan was obtained.

The main scientific results of the dissertation work were published in the journals named below: Journal "Oil Refining and Petrochemistry" (Russia), Azerbaijan Chemical Journal, Chemical Problems Journal (Azerbaijan), Journal of applied chemistry (Russia), Journal of scientific works of Azerbaijan Technical University.

The main results of the dissertation were discussed and reported at the following national and international conferences:

1st International Scientific Conference of young scientists and specialists “The role of multidisplinary approach in solution of actual problems of fundamental and applied sciences (Earth, Technical and Chemical)” (Baku, 2014); 7th All-Russian Zeolite Conference "Zeolites and Mesoporous Materials: Achievements and Prospects", (Zvenigorod, 2015); 1st International Turkic World Conferenece on Chemical Sciences and Technologies, (28 october-1 november, Sarayevo, 2015); International scientific and technical conference “Petrochemical synthesis and catalysis in complex condensed systems” dedicated to the 100th anniversary of academician B.K. Zeynalov, (Baku, 2017); Republican scientific conference dedicated to the 90th anniversary of Academician Toghrul Shahtakhtinsky, abstracts of reports, (Baku-2015); Azerbaijan national academy of sciences council of young scientists and specialists. ANAS-70, (Baku, 02-04 november, 2015); Materials of the republican scientific conference dedicated to the 80th anniversary of the Institute of Catalysis and Inorganic Chemistry named after M. Naghiyev (Baku-2015).

Author's personal participation.

The author independently participated in the implementation of

the dissertation work - planning the work, collecting literature materials, conducting basic experimental studies, mathematical calculations, including personally participating in the writing of the article, thesis and dissertation. The author's share in published scientific works is decisive.

The organization where the dissertation work was performed. The dissertation work was carried out in the "Zeolite catalysis" laboratory of the Institute of Catalysis and Inorganic Chemistry named after Academician M. Naghiyev of the Ministry of Science and Education of the Republic of Azerbaijan.

The scope and structure of the work. The dissertation consists of an introduction containing the approach to the problem, the purpose and issues of the work, the main scientific and practical results (12700 marks), 5 chapters (Chapter I - 71655, Chapter II - 33500, Chapter III-48318, Chapter IV - 25258, Chapter V - 17878), summary, results and a list of literature published on the dissertation. The dissertation contains 150 pages, 12 tables, 10 pictures, and 124 names of cited literature.

In the introductory part of the dissertation, the relevance of the topic of the research is substantiated, the purpose and tasks of the work are formulated, the object and subject of the research are defined, the main results defended are described, the scientific novelty and practical importance of the performed works, as well as information on the approval of the research results and publications are given.

In the first chapter, a brief overview of the current state of the problem was given, existing works were critically reviewed, known catalysts, kinetics and mechanisms of oxidative dehydrogenation reactions of naphthenic hydrocarbons, and information related to the optimization of these processes were shown.

Description of the apparatus, methods of conducting experiments and analysis of reaction products are shown **in the second chapter**. In this chapter, the scheme of the flow-type laboratory experiment device is described, methods of conducting experiments on oxidative dehydrogenation of methylcyclohexane, analysis of reagents and reaction products, preparation of catalysts, and preliminary processing of experimental materials are given.

The third chapter is devoted to the results of research on the selection of highly active and effective catalysts for the oxidative dehydrogenation of methylcyclohexane. The general concept of solving the problem was summarized and carried out, the relationship between the activity, preparation method and physico-chemical characteristics of individual catalytic systems was reviewed.

The fourth chapter shows the results of the study of the kinetics and mechanism of the oxidative dehydrogenation reaction of methylcyclohexane on an active catalyst.

In the fifth chapter, information on the theoretical optimization of the selective oxidative dehydrogenation reaction of methylcyclohexane to methylcyclohexadiene and the selection of a suitable reactor based on the kinetic model was reflected.

As a summary of the dissertation work, the general results, the main achievements of the obtained and conducted researches were formed in the **final and results**. A list of cited literature sources is given at the end.

THE MAIN CONTENT OF THE WORK

Analysis of raw materials and reaction products, reaction methodology and description of the equipment used.

For the study of the oxidative dehydrogenation of methylcyclohexane, a laboratory experimental unit consisting of 3 parts - a preparatory part, a catalytic part and an analytical part was assembled. The preparation part includes a system for cleaning gases (nitrogen, oxygen and helium). The catalytic part consisted of a U-shaped quartz reactor with an immobile catalyst layer. The analytical section consists of a chromatograph directly connected to the catalytic section. The reaction products were first qualitatively identified on GC-MS (Agilent 7890 GC, Agilent 5975 MS) and analyzed on an Agilent 7890 GC gas chromatograph equipped with TCD and FID (flame ionization detector).

During the research, synthetic NaA (SiO_2/Al_2O_3=2.0), NaX (SiO_2/Al_2O_3=2.9), NaY (SiO_2/Al_2O_3=4.2), as well as natural

clinoptilolite from the Aidagh deposit of the Republic of Azerbaijan (SiO_2/Al^2O_3=8,68), mordenite from the Chananab deposit (SiO_2/Al_2O_3=9.6), as well as their modified forms with H+ and cations of transition elements were used.

In order to obtain H^+ forms of zeolites, NH_4^+ forms were obtained by mixing zeolites dried at 120-150^{o}C with 2N NH_4Cl (or NH_4NO_3) solution in a three-necked flask and heating them at 80-90^{o}C for two hours each time. Then these samples were washed from Cl- and (NO_3^-) ions and dried in a drying cabinet at 80-120^{o}C for five hours, and their H^+ forms were obtained by carrying out the process at 350-400^{o}C and 500-550^{o}C for 3-5 hours.

Before synthesizing metalzeolite catalysts based on natural zeolites, natural zeolites were dealuminated. For this purpose, 50 g of the fraction whose grain size is 0.25-0.63 mm was taken, kept in a liter flask with 1N HCl solution at 95-96^{o}C twice for two hours each time, successively washed, dried and thermally treated by the above method. has been done.

Catalysts were prepared by the following method: a certain amount of zeolite sample dried in a drying cabinet at 100-120^{o}C was pounded and placed in a liter flask, then solutions of salts of transition elements were added drop by drop until the mixed cations were completely exchanged. It was stirred for 5-10 hours. Determination of the amount of metals included in the composition of zeolite was determined on an Agilent 7700 ICP-MS device by means of ion spectral analysis. After the end of the ion exchange, the catalyst was washed with distilled water, dried at 80-120^{o}C, pressed, and then separated into a fraction with a grain size of 0.25-0.63 mm. The received fraction was thermally processed at 400^{o}C for 3 hours.

The same volume (2 cm^3) of the catalyst sample was filled into the reactor and activated at a temperature of 400^{o}C for 2 hours in an air flow (V=3000 $hour^{-1}$).

The activity of the catalysts in the oxidative dehydrogenation reaction of methylcyclohexane was carried out in the range of 280-380^{o}C, the volume velocities of the reaction mixture were 1000-3000 h^{-1} and different molar ratios of reagents and gas diluent.

Selection of active catalysts for oxidative dehydrogenation of methylcyclohexane

A highly efficient polycomponent ultradisperse metal zeolite catalyst was selected for the oxidative dehydrogenation reaction of methylcyclohexane to 1,3-methylcyclohexadine.

The results of the research conducted on the oxidative dehydrogenation of methylcyclohexane on metal zeolite catalysts have shown that, depending on various factors - the type of zeolite, the structural properties, the reaction conditions, methylcyclohexadiene, toluene, xylenes and carbon dioxide are formed as a result of the reaction, along with the target product - methylcyclohexadiene. The yield of reaction products is influenced by the porous structure of zeolite, its physicochemical properties, as well as the nature and concentration of cations included in zeolite and the reaction conditions.

First, the catalytic activity of primary zeolites in oxidative dehydrogenation reactions of methylcyclohexane was studied and the research results are shown in table 1.

The obtained results proved that the Na-forms of fojasite-type zeolites, whose internal cavities are accessible to methylcyclohexane molecules are active only during deep oxidation and these zeolites do not activate the oxidative dehydrogenation of methylcyclohexane to methylcyclohexene and methylcyclohexadiene. This is explained by the strong adsorption of methylcyclohexane in phojasites. Unlike wide-pore zeolites (NaX, NaY), narrow-pore zeolites with a small surface area (8.0-20.0 m^2/g) and small pore size (4.2-4.9 A) lead to the selective conversion of methylcyclohexane to methylcyclohexene.

Table 1

Results of oxidative dehydrogenation of methylcyclohexane on initial forms of zeolites (T=380°C, V=2000 h^{-1}, methylcyclohexane:O_2 = 1:1)

Zeolite	X, %	S,%	Yield of reaction products, %					
			$C_6H_9CH_3$	$C_6H_7CH_3$	$C_6H_5CH_3$	C_6H_6	$C_6H_4(CH_3)_2$	CO_2
NaX	42,4	-	-	-	35,5	-	-	6,9
NaY	46,3	-	-	-	38,2	0,5	-	7,6
HY	62,1	-	-	-	32,8	3,5	22,3	3,5
Mor.	23,6	0,8	7,3	0,2	13,9	-	-	2,2
H-Mor.	44,4	-	0,5	-	28,9	0,9	13,3	0,8
Clin.	28,2	3,9	13,2	1,1	12,3	-	-	1,6
H-Clin.	36,4	-	2,3	-	25,5	0,3	7,8	0,5

Table 1 shows that the alkaline cation forms of clinoptilolite and mordenite are more active and selective in the formation reaction of methylcyclohexene.

Among the cationic forms of porous zeolites, a relatively high yield of methylcyclohexadiene is observed on natural clinoptilolite. In subsequent studies, modification of clinoptilolite with metal cations (Ni, Co, Cr, Zn, Cu, Mn, Mo) included in known dehydrogenation catalysts leads to changes in the activity of these catalysts (table 2.). It was determined that the effect of these metal cations is not the same and that individually these cations exhibit relatively low catalytic activity for the yield of methylcyclohexadiene.

Table 2

Oxidative dehydrogenation of methylcyclohexane over modified natural clinoptilolite (T=380°C, V_h=2000 h^{-1}, $C_6H_{11}CH_3:O_2:N_2$=1:1:5,3)

№	Composition, mass %	X, %	S, %	Yield of reaction products, %			
				$C_6H_9CH_3$	$C_6H_7CH_3$	$C_6H_5CH_3$	CO_2
1	Zn (0,2)	7,6	7,9	0,9	0,6	5,2	0,9
2	Cu (0,5)	28,9	1,03	3,8	0,3	8,5	16,3
3	Cr (0,1)	21,4	21,0	5,9	4,5	9,5	1,5
4	Co (0,1)	19,4	19,6	6,2	3,8	7,4	2,0
5	Fe (0,25)	21,4	-	1,5	-	6,7	13,2
6	Ni (0,1)	50,2		-	-	40,3	9,9
7	CuFe (0,5:0,25)	34,6	6,4	3,2	2,2	10,3	18,9
8	CuCo (0,5:0,1)	32,5	10,8	5,8	3,5	15,7	7,5
9	CuCr (0,5:0,1)	28,6	7,7	3,9	2,2	19,8	2,7
10	ZnCr (0,2:0,1)	18,8	4,3	1,9	0,8	14,5	1,6
11	CoCr (0,1:0,1)	32,7	30,3	3,6	9,9	13,9	5,3
12	CoCr (0,5:0,1)	37,4	28,9	5,8	10,8	12,3	8,5
13	CoCr (1,0:0,1)	41,1	23,4	5,2	9,6	13,8	12,5
14	CoCr (0,5:0,25)	49,8	28,9	7,2	14,4	15,6	12,6
15	CoCr (0,5:0,5)	53,9	12,1	1,9	6,5	35,7	9,8
16	ZnCoCr(0,2:0,5:0,25)	45,9	23,3	12,5	10,7	10,9	11,8
17	ZnCoCr (0,2:0,5:0,5)	49,4	13,9	13,5	6,9	21,5	7,5
18	CuZnCoCr(0,5:0,2:0,1:0,1)	37,4	22,7	5,3	8,5	9,9	13,7

As a result of research, it was determined that 1,3-methylcyclohexadiene can be obtained from oxidative dehydrogenation of methylcyclohexane by changing the composition and structure of zeolite. The optimal concentration of cations included

in the composition of clinoptilolite (Co^{2+}- 0.5%; Cr^{3+}- 0.25%) and the optimal conditions for the reaction (T=380°C, V_h=2000 hours^{-1}, C_6H_{12}:O_2:N_2=1:1:5.3) were determined. Under these conditions, the yield of methylcyclohexadiene is 14.4% at 49.8% conversion of methylcyclohexane.

The introduction of 0.5% Co^{2+} and 0.25% Cr^{3+} cations into the natural clinoptilolite zeolite of the Republic of Azerbaijan forms an effective catalytic system for the oxidative dehydrogenation of methylcyclohexane to 1,3-methylcyclohexadiene, which indicates that metal ions are directly involved in the studied reaction.

Mechanism and kinetic model of oxidative dehydrogenation reactions of naphthenic hydrocarbons over modified zeolite catalysts

The results of experimental studies on the selection of an active catalyst for oxidative dehydrogenation reactions of methylcyclohexane showed that it was synthesized by ion exchange on the basis of natural zeolite - clinoptilolite, containing Co^{2+} - 0.5%; The metal zeolite catalyst with Cr^{3+}-0.25% cations exhibits relatively higher activity in the oxidative dehydrogenation reaction of methylcyclohexane to 1,3-methylcyclohexadiene. Taking this into account, the kinetic regularities of reactions with the presence of that catalyst were studied, and the results of the study are shown in Tables 3-5.

Kinetic experiments were carried out in a flow-type laboratory device in the temperature range of 320-380 °C, volume rates of 500-3000 h^{-1}, partial pressures of reagents $P_{C6H11CH3}$=0.06-0.25 atm, P_{O2}=0.04-0.20 atm. In order to determine the reaction area, a number of experiments were conducted with different sizes of catalyst grains (from 0.25 to 2 mm) and different linear velocities of the initial raw materials. Based on the conducted studies, it was determined that internal and external diffusion factors do not affect the speed of the process. Thus, the reaction takes place in the kinetic field, where all the diffusion stages occur faster than all the chemical stages that make up the reaction mechanism.

Table 3

Effect of oxygen partial pressure on oxidative dehydrogenation of methylcyclohexane over CoCr-clinoptilolite catalyst: V_h=2500 h^{-1}; V_{C7H14} =0.69 l/h; P_{C7H14}= 0.11 atm.; G_{cat}=1.78 g

№	T,^{0}C	$P_{C_7H_{14}}$	P_{O_2}	P_{N_2}	X,%	$C_6H_9CH_3$	$C_6H_7CH_3$	$C_6H_5CH_3$	CO_2
1	320	0.11	0.04	0.84	4.25	1.5	0.6	2.1	0.05
2		0.11	0.09	0.79	9.2	1.9	2.8	4.2	0.3
3		0.11	0.14	0.75	10.7	2.2	3.1	4.6	0.8
4		0.11	0.20	0.69	13.9	2.0	2.9	6.8	2.2
5	340	0.11	0.04	0.84	11.4	3.2	2.6	3.8	1.8
6		0.11	0.09	0.79	19.4	3.9	6.2	6.8	2.5
7		0.11	0.14	0.75	21.2	4.4	6.5	7.0	3.3
8		0.11	0.20	0.69	24.2	3.7	5.9	9.5	5.1
9	360	0.11	0.04	0.84	23.7	5.8	6.6	6.4	4.9
10		0.11	0.09	0.79	31.1	6.2	10.5	8.6	5.8
11		0.11	0.14	0.75	33.8	6.7	11.1	9.3	6.7
12		0.11	0.20	0.69	38.3	6.4	10.7	12.3	8.9

As can be seen from Table 3, an increase in P_{O2} from 0.04 to 0.17 atm leads to an increase in the yield of methylcyclohexadiene, which is explained by an increase in the concentration of surface oxygen, while the yield practically does not change at a further increase in P_{O2} to 0.20 atm. The conversion of methylcyclohexane increases with the increase of partial pressure of oxygen in the entire studied interval.

Table 4

Effect of partial pressure of methylcyclohexane on oxidative dehydrogenation of methylcyclohexane over CoCr-clinoptilolite catalyst: V_h=2000 h^{-1}; V_{O2} = 0.69 l/h; P_{O2}= 0.14 atm.; G_{cat}=1.78 g

№	T,^{0}C	$P_{C_7H_{14}}$	P_{O_2}	P_{N_2}	X,%	$C_6H_9CH_3$	$C_6H_7CH_3$	$C_6H_5CH_3$	CO_2
1	320	0.06	0.14	0.80	11.4	0.8	1.9	7.5	1.2
2		0.11	0.14	0.75	10.7	2.2	3.1	4.6	0.8
3		0.17	0.14	0.68	9.9	3.4	2.9	3.1	0.5
4		0.25	0.14	0.61	8.5	4.1	2.0	2.2	0.2
5	340	0.06	0.14	0.80	22.6	3.6	5.2	9.3	4.5
6		0.11	0.14	0.75	21.2	4.4	6.5	7.0	3.3
7		0.17	0.14	0.68	18.4	5.2	6.0	5.4	1.8
8		0.25	0.14	0.61	15.4	6.0	3.9	4.5	1.0
9	360	0.06	0.14	0.80	35.1	6.2	9.8	11.5	7.6
10		0.11	0.14	0.75	33.8	6.7	11.1	9.3	6.7
11		0.17	0.14	0.68	30.8	8.0	10.8	7.8	4.2
12		0.25	0.14	0.61	27.4	8.7	8.5	6.9	3.3

As can be seen from Table 4, the yield of methylcyclohexadiene increases with the increase of the partial pressure of methylcyclohexane from 0.06 to 0.12 atm. At this time, the yield of methylcyclohexene increases, and the yield of toluene decreases. The decrease in the conversion of carbon dioxide and methylcyclohexane with an increase in the partial pressure of methylcyclohexane is explained by the fact that the relatively high partial pressure of methylcyclohexane at a given partial pressure of oxygen prevents the coordination of oxygen with the active centers of the metal-zeolite catalyst.

The effect of temperature and volume velocity on the course of the reaction was studied in optimal P_{C7H14} and P_{O2}.

Table 5.

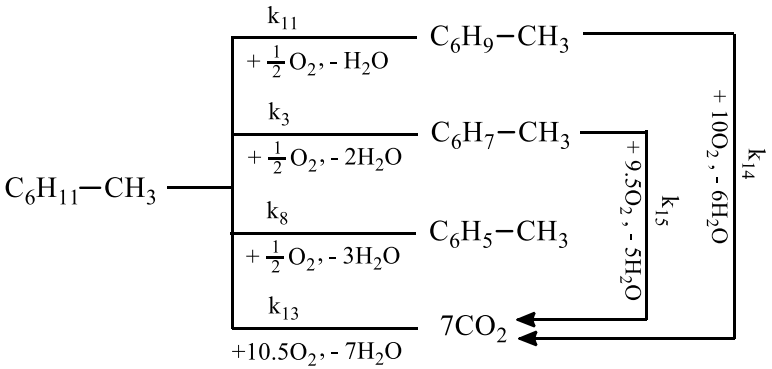
Effect of temperature and volume rate on oxidative dehydrogenation of methylcyclohexane over CoCr-clinoptilolite catalyst in $C_6H_{11}CH_3$:O_2:N_2=1.00:1.00:5.3 mol ratio; G_{kat}=1.78 q; V_{cat}=2 sm^3

№	V_h, h^{-1}	T,^{0}C	X,%	$C_6H_9CH_3$	$C_6H_7CH_3$	$C_6H_5CH_3$	CO_2
1		320	16.45	0.05	0.6	11.9	3.9
2		340	26.59	0.09	1.9	16.8	7.8
3	1000	360	35.2	1.1	3.4	20.9	9.8
4		380	47.2	1.5	5.0	23.8	16.9
5		400	51.7	1.3	4.8	25.9	19.7
6		320	12.9	0.9	1.5	8.7	1.8
7		340	23.1	1.9	3.6	12.7	4.9
8	2000	360	34.9	3.7	5.7	17.2	8.3
9		380	46.2	4.6	8.2	20.3	13.1
10		400	50.8	4.2	7.8	23.5	15.3
11		320	10.7	2.2	3.1	4.6	0.8
12		340	21.2	4.4	6.5	7.0	3.3
13	2500	360	33.8	6.7	11.1	9.3	6.7
14		380	46.6	7.2	15.7	12.2	11.5
15		400	49.9	7.2	14.4	15.6	12.7
16		320	10.3	5.2	3.2	1.6	0.3
17		340	19.9	6.9	6.9	3.7	2.4
18	3000	360	31.7	10.1	11.3	6.1	4.2
19		380	43.7	12.0	15.9	9.6	6.2
20		400	47.1	11.2	14.3	12.8	8.8

As can be seen from Table 5, when the temperature rises from 320°C to 380°C, the yield of methylcyclohexadiene increases continuously and the yield reaches a maximum at 380°C, while at higher temperatures (380-400°C) almost no practical change is observed. The increase in the yield of toluene in all investigated temperature ranges is due to the easy conversion of methylcyclohexene and methylcyclohexadiene, which are highly reactive, into toluene.

The decrease in the conversion of methylcyclohexane with the increase of the volumetric rate from 1000 to 3000 h^{-1} is due to the lower contact time (table 5). The increase in the yield of methylcyclohexene and methylcyclohexadiene, the decrease in contact time is due to the fact that these products prevent the deep conversion of these products into toluene.

Based on the experimental results obtained from the oxidative dehydrogenation reaction of methylcyclohexane over CoCr-clinoptilolite metal zeolite catalyst, the following kinetic scheme is given.



Choosing the optimal reactor type for the considered process can be realized by comparing the volumes needed to obtain a given conversion rate in different reactors based on its kinetic model.

Fixed catalyst bed and heated catalyst bed reactors are widely used in industry. In reactors of the first type, the hydrodynamic regime of the flow is close to the ideal compression-type regime, and in the

reactors of the second type, the hydrodynamic regime of the flow is close to the ideal mixing regime.

Taking into account the above, the course of the mentioned process was studied in 2 types of reactors: ideal compression and ideal mixing reactors. The kinetic model of the oxidative dehydrogenation process of methylcyclohexane to methylcyclohexadiene on modified zeolites can be written as follows for an ideal compression type reactor:

$$\frac{dA_1}{d\left(\frac{G_k}{n^0_{C_7H_{14}}}\right)} = k_{11}P_{C_7H_{14}}\left\{\frac{-\sqrt{\frac{k_{11}P_{C_7H_{14}}}{k_{10}P_{O_2}}}+\sqrt{\left(\sqrt{\frac{k_{11}P_{C_7H_{14}}}{k_{10}P_{O_2}}}\right)^2+4\left(\frac{k_{11}P_{C_7H_{14}}}{k_{12}}+1\right)}}{2\left(\frac{k_{11}P_{C_7H_{14}}}{k_{12}}+1\right)}\right\}^2 \quad (1)$$

$$\frac{dA_2}{d\left(\frac{G_k}{n^0_{C_7H_{14}}}\right)} = k_3P_{C_7H_{14}}\left\{\frac{-\left(\sqrt{\frac{k_3P_{C_7H_{14}}}{k_1P_{O_2}}}+\sqrt{\frac{k_3P_{C_7H_{14}}}{k_2P_{O_2}}}\right)+\sqrt{\left(\sqrt{\frac{k_3P_{C_7H_{14}}}{k_1P_{O_2}}}+\sqrt{\frac{k_3P_{C_7H_{14}}}{k_2P_{O_2}}}\right)^2+4\frac{k_3P_{C_7H_{14}}}{k_4}}}{2\frac{k_3P_{C_7H_{14}}}{k_4}}\right\}^2 \quad (2)$$

$$\frac{dA_3}{d\left(\frac{G_k}{n^0_{C_7H_{14}}}\right)} = k_8P_{C_7H_{14}}\left\{\frac{-\left(\sqrt{\frac{k_8P_{C_7H_{14}}}{k_5P_{O_2}}}+\sqrt{\frac{k_8P_{C_7H_{14}}}{k_6P_{O_2}}}+\sqrt{\frac{k_8P_{C_7H_{14}}}{k_7P_{O_2}}}\right)+\sqrt{\left(\sqrt{\frac{k_8P_{C_7H_{14}}}{k_5P_{O_2}}}+\sqrt{\frac{k_8P_{C_7H_{14}}}{k_6P_{O_2}}}+\sqrt{\frac{k_8P_{C_7H_{14}}}{k_7P_{O_2}}}\right)^2+4\frac{k_8P_{C_7H_{14}}}{k_9}}}{2\frac{k_8P_{C_7H_{14}}}{k_9}}\right\}^2 \quad (3)$$

$$\frac{dA_4}{d\left(\frac{G_k}{n^0_{C_7H_{14}}}\right)} = \frac{k_{13}K_1P_1K_6P_2}{\left(1+K_1P_1+\sqrt{K_2P_2}+K_3P_3+K_4P_4+K_5P_5+K_6P_2\right)^2} + \\ + \frac{k_{14}K_3P_3K_6P_2}{\left(1+K_1P_1+\sqrt{K_2P_2}+K_3P_3+K_4P_4+K_5P_5+K_6P_2\right)^2} + \frac{k_{15}K_4P_4K_6P_2}{\left(1+K_1P_1+\sqrt{K_2P_2}+K_3P_3+K_4P_4+K_5P_5+K_6P_2\right)^2} \quad (4)$$

Here $P_1 = P_{C_7H_{14}}$, $P_2 = P_{O_2}$, $P_3 = P_{C_7H_{12}}$, $P_4 = P_{C_7H_{10}}$, $P_5 = P_{C_7H_8}$, $P_6 = H_2O$; A_1, A_2, A_3 and A_4 are derivatives of C_7H_{12}, C_7H_{10}, C_7H_8 and CO_2-respectively. The partial pressures of the components are calculated by the following formula:

$$P_i = \frac{n_i}{\sum n_i}P \quad (5)$$

Here P_i – *i*- partial pressure of i-component, atm; P – is the total

pressure of the system (1 atm).

The material balance is as follows:

$$\left.\begin{aligned}
n_{C_7H_{14}} &= n^0_{C_7H_{14}} - (A_1 n^0_{C_7H_{14}} - A_2 n^0_{C_7H_{14}} - A_3 n^0_{C_7H_{14}} - A_4 n^0_{C_7H_{14}})/100 \\
n_{H_2O} &= (A_1 n^0_{C_7H_{14}} + A_2 n^0_{C_7H_{14}} + A_3 n^0_{C_7H_{14}} + 5A_4 n^0_{C_6H_{12}})/100 \\
n_{O_2} &= n^0_{O_2} - (\frac{1}{2} A_1 n^0_{C_7H_{14}} - \frac{1}{2} A_2 n^0_{C_7H_{14}} - 10.5A_4 n^0_{C_7H_{14}})/100 \\
n_{C_7H_{12}} &= A_1 n^0_{C_7H_{14}}/100 \\
n_{C_7H_{10}} &= A_2 n^0_{C_7H_{14}}/100 \\
n_{C_7H_8} &= A_3 n^0_{C_7H_{14}}/100 \\
n_{CO_2} &= 7A_4 n^0_{C_7H_{14}}/100
\end{aligned}\right\} \quad (6)$$

The developed kinetic model of the reaction was subjected to statistical analysis based on kinetic evidence. Calculating the values of exponential multiplication of reaction constants $ln\, k_i^0$ ($ln\, K_i^0$), activation energy (E_i^0) and heat of adsorption (Q_i^0) using "Variable boundaries" and "Search" software systems. It was done by Powell methods, where the objective function was as follows:

$$F = \min \sum_{j=1}^{m} \sum_{i=1}^{n} \left(\frac{A_{ji}^{eks} - A_{ji}^{hes}}{A_{ji}^{eks}} \right)^2 \qquad (7)$$

A_{ji}^{eks}, A_{ji}^{hes} – experimental and theoretical values of outputs of i-component in j-experiment, m – number of experiments, n – number of components.

The numerical values of the parameters of the kinetic model are given in table 6.

It was determined that the kinetic model developed in the studied range of temperature, volume velocity and mole ratio of reagents adequately describes the experimental results, and the relative error of the experimental and calculated results does not exceed 8%.

Table 6

Numerical values of the constants of the kinetic model of the oxidative dehydrogenation of methylcyclohexane

$\ln k_i^0 \left(\ln K_i^0\right)$		$E_i (Q_i)$, kcal/mol	
$ln\, k_1^0$	40.93	E_1	34,86
$ln\, k_2^0$	7.06	E_2	46,20
$ln\, k_3^0$	11.44	E_3	46,16
$ln\, k_4^0$	26.20	E_4	28,27
$ln\, k_5^0$	11.70	E_5	18,73
$ln\, k_6^0$	27.97	E_6	25,45
$ln\, k_7^0$	8.63	E_7	32,21
$ln\, k_8^0$	24.41	E_8	16,8
$ln\, k_9^0$	5.81	E_9	16,76
$ln\, k_{10}^0$	9.43	E_{10}	35,24
$ln\, k_{11}^0$	5.70	E_{11}	16,8
$ln\, k_{12}^0$	16.16	E_{12}	30,95
$ln\, k_{13}^0$	22.0	E_{13}	147,63
$ln\, k_{14}^0$	–9.2	E_{14}	167,12
$ln\, k_{15}^0$	42.5	E_{15}	90,51
$ln\, K_1^0$	20.1	Q_1	10,46
$ln\, K_2^0$	0.99	Q_2	46,20
$ln\, K_3^0$	7.81	Q_3	35,99
$ln\, K_4^0$	7.04	Q_4	46,20
$ln\, K_5^0$	26.11	Q_5	13,39
$ln\, K_6^0$	3.24	Q_6	2.49

Technological design of the process of oxidative dehydrogenation of methylcyclohexane to methylcyclohexadiene on modified zeolites

Theoretical optimization of the process based on the kinetic model. As a result of studies conducted on the basis of kinetic models, it was determined that the optimal reactor for the oxidative dehydrogenation process of methylcyclohexane to methylcyclohexadiene is an ideal compression type reactor. Such a

hydrodynamic regime can be approached in fixed catalyst bed reactors.

In order to theoretically optimize the oxidative dehydrogenation process of methylcyclohexane to methylcyclohexadiene, the productivity of methylcyclohexadiene was determined based on the kinetic model:

$$q_{C_6H_7CH_3} = f\left(T, n^0_{C_6H_{11}CH_3}, \theta, \frac{G_{cat}}{n^0_{C_6H_7CH_3}}\right) \qquad (8)$$

Here $q_{C_6H_7CH_3}$ – yield of the catalyst relative to methylcyclohexadiene, g/(h g_{cat}); T– reactor temperature, ^oC; $\frac{G_{cat}}{n^0_{C_6H_{11}CH_3}}$ – contact period, (gr_{cat} h)/mol; θ – mole ratio of methylcyclohexane to oxygen, unitless measure; n_1^0 – initial cost of methylcyclohexane, mol/h.

Based on the created kinetic model, the objective function (optimization criterion) of determining the mode parameters that ensure the maximum productivity of the catalyst can be shown as follows:

$$\max(q_{C_6H_7CH_3}) = f\left(T, n^0_{C_6H_{11}CH_3}, \theta, \frac{G_{cat}}{n^0_{C_6H_{11}CH_3}}\right) \qquad (9)$$

The following limitations were taken into account during the determination of technological parameters:

$$320^0\,C \le T \le 400^0\,C$$

$$70 \le \frac{G_{cat}}{n^0_{C_6H_{11}CH_3}} \le 200$$

$$0.01 \le n^0_{C_6H_{11}CH_3} \le 0.05$$

$$0.5 \le \theta \le 2.0$$

The productivity of the catalyst was calculated for each option by the following formula:

$$g = \frac{Xn^0_{C_6H_7CH_3} M_{C_6H_7CH_3}}{G_{cat}}, \qquad (10)$$

here $M_{C_6H_{9CH_3}}$ – molecular weight of methylcyclohexadiene.

The given problem was solved on a personal computer using the software system "Poisk" and the following results were obtained: T=380^{o}C; $n^0_{C_6H_{11}CH_3} = 0.024$ mol/h; θ=0.9; $\frac{G_{cat}}{n^0_{C_6H_{11}CH_3}} = 150$ (gr_{cat} h/mol). As a result of these conditions, the productivity of the catalyst

was $q_{C_6H_7CH_3}$=0.250 gr/(gr$_{cat}$ h), the degree of conversion according to methylcyclohexane was X=50% and the yield of methylcyclohexadiene was 15%. The obtained results can be used in the optimal design of the industrial reactor.

Mathematical modeling of the reactor element of the process. Kinetic experimental studies carried out in a laboratory device play a leading role in putting forward a certain hypothesis about the mechanism of the reaction, and based on this, a kinetic model of the process is created. However, in a laboratory setup, the process is carried out in isothermal mode. However, the temperature and concentration gradients, mass and heat transfer accompanying the process on an industrial scale are not taken into account in the kinetic model. Therefore, the yields of products obtained by theoretical optimization based on kinetic models only are conditionally considered maximal. At this stage, in order to obtain a more accurate description of the flow distribution, a complete mathematical model of the process was developed by adding heat balance equations and pressure drop equations to the kinetic equations.

Based on the results of choosing the optimal type of reactor based on the kinetic equation, an ideal compression reactor of flow type was determined for conducting the researched process. The best approximation for an ideal compression reactor is to conduct the process in a reactor with a fixed bed catalyst, and its mathematical model can be summarized as follows:

$$D_E\left(\frac{\partial^2 C_i}{\partial R^2}+\frac{1}{R}\frac{\partial C_i}{\partial R}\right)-q\frac{\partial g_i}{\partial l}+\sum_{j=1}^{m}\nu_{ij}r_j(\bar{c}_i,\mathrm{T})=0 \qquad (11)$$

$$\alpha_E\left(\frac{\partial^2 T}{\partial R^2}+\frac{1}{R}\frac{\partial T}{\partial R}\right)-\mathrm{qC}_p\frac{\partial T}{\partial l}+\sum_{j=1}^{m}Q_j r_j(\bar{c}_i,\mathrm{T})=0 \qquad (12)$$

here D_E – effective diffusion coefficient; R – coordinate along the radial direction; g – mass density; ν_{ij} – stoichiometric coefficient of i-substance in j-reaction; q – mass velocity; r_j – speed of j-reaction; α_E – effective thermal conductivity of the layer; Q_j – thermal effect of j-reaction; T – reactor temperature;; l – reactor length; C_p – heat capacities of substances.

In order to achieve a mass rate of methylcyclohexadiene Q = 2000 kg/h at the outlet of the reactor, we determined the price of the volume of the catalyst based on the maximum productivity of the catalyst

$\left(q = 0.250 \frac{\text{gr}}{\text{gr}_{\text{cat}}\text{h}}\right)$ with the following formula:

$$V_{\text{cat}} = \frac{Q}{q \cdot \rho_{\text{cat}}} \approx 9.5 m^3 \qquad (13)$$

here ρ_{cat} – catalyst density, ρ_{cat}= 850 kq/m^3.

A fixed mass of catalyst can be placed in a fixed bed in a cylindrical reactor with height H = 4.4 m and diameter D = 1.7 m.

The heat balance equation includes the thermal effects of chemical reactions, as well as heat losses to the environment through the walls of the reactor. The equation that takes into account temperature changes can be shown as follows:

$$\frac{\text{dT}}{\text{dG}_{\text{kat}}} = -\frac{\sum_{j=1}^{m} r_j \Delta \text{H}_{\text{Rj}}}{\sum_{i=1}^{n} n_i C_{\text{pi}}} - \frac{\alpha(T - T_x)}{\sum_{i=1}^{n} n_i C_{\text{pi}}} \qquad (14)$$

here r_j – rates of formation of reaction products, mol/(kg_{cat}·hour); ΔH_{Rj} – j- thermal effect of j-reaction, kDj/mol; $C_{\text{pi}}\left(i = \overline{1,\text{k}}\right)$ – values of the heat capacities of the components of the process corresponding to the relevant indices, Dj/(mol·K); α – heat transfer coefficient, Dj/(K·kg_{cat}·hour); T_x – ambient temperature, K; T – gas mixture temperature, K; G_{cat} – amount of catalyst, kq; m – total number of reactions; n_i – i- molar rate of i-component, mol/h.

Below are the thermochemical equations for the oxidative dehydrogenation of methylcyclohexane to methylcyclohexadiene for standard conditions:

$$C_7H_{14} + 0.5\text{O}_2 \xrightarrow{k_{11}} C_7H_{12} + H_2O \ \Delta\text{H}_0 = \text{-}12.851\text{kcal/mol}$$
$$C_7H_{14} + 0.5\text{O}_2 \xrightarrow{k_3} C_7H_{10} + 2\text{H}_2O \ \Delta\text{H}_0 = \text{-}70.533\text{kcal/mol}$$
$$C_7H_{14} + 1.5\text{O}_2 \xrightarrow{k_8} C_7H_8 + 3\text{H}_2O \ \Delta\text{H}_0 = \text{-}124.421\text{kcal/mol} \qquad (15)$$
$$C_7H_{14} + 10.5\text{O}_2 \xrightarrow{k_{13}} 7\text{CO}_2 + 7\text{H}_2O \ \Delta\text{H}_0 = \text{-}1030.994\text{kcal/mol}$$
$$C_7H_{12} + 10\text{O}_2 \xrightarrow{k_{14}} 7\text{CO}_2 + 6\text{H}_2O \ \Delta\text{H}_0 = \text{-}1013.123\text{kcal/mol}$$
$$C_7H_{10} + 9.5\text{O}_2 \xrightarrow{k_{15}} 7\text{CO}_2 + 5\text{H}_2O \ \Delta\text{H}_0 = \text{-}955.442\text{kcal/mol}$$

To solve the heat balance equation, the values of the standard heats of formation ΔH_{0i} and the empirical coefficients of heat capacities for all reactions involved in the process according to their stoichiometric schemes of the heat effects ΔH_{Rj} from the temperature dependencies have been determined.

1) For isobaric heat capacity of components:

$$C_{\text{pi}} = a_i + b_i T + c_i T^2 + d_i T^3 \qquad (16)$$

2) For the change in isobaric heat capacity of the system:

$$\begin{aligned}&\Delta \text{C}_{\text{pj}} = \Delta \text{a}_j + \Delta \text{b}_j T + \Delta \text{c}_j T^2 + \Delta \text{d}_j T^3 = \\ &= \left(\sum_i \nu_i' a_i^{\text{meh}} - \sum_i \nu_i a_i^{\text{ilk}}\right) + \left(\sum_i \nu_i' b_i^{\text{meh}} - \sum_i \nu_i b_i^{\text{ilk}}\right) T + \\ &+ \left(\sum_i \nu_i' c_i^{\text{meh}} - \sum_i \nu_i c_i^{\text{ilk}}\right) T^2 + \left(\sum_i \nu_i' d_i^{\text{meh}} - \sum_i \nu_i d_i^{\text{ilk}}\right) T^3\end{aligned} \qquad (17)$$

3) *j*-standard heat of reaction:

$$\Delta \text{H}_{298\text{j}} = \left(\sum_i \nu_i' \Delta \text{H}_{298}^{\text{meh}} - \sum_i \nu_i \Delta \text{H}_{298}^{\text{ilk}}\right)_j \qquad (18)$$

4) *j*- reaction temperature change:

$$\begin{aligned}&\Delta \text{H}_{\text{Rj}} = \int_{298}^{T} \Delta \text{C}_{\text{pj}} \text{dT} + \Delta \text{H}_{298\text{j}} = \Delta \text{a}_j (T - 298) + \\ &+ \frac{\Delta \text{b}_j}{2}\left(T^2 - 298^2\right) + \frac{\Delta \text{c}_j}{3}\left(T^3 - 298^3\right) + \\ &+ \frac{\Delta \text{d}_j}{4}\left(T^4 - 298^4\right) + \Delta \text{H}_{298\text{j}}\end{aligned} \qquad (19)$$

Here ν_i and ν_i' – ' are the stoichiometric coefficients of the i-component of the initial substances and products of the reaction; $\Delta \text{H}_{0\text{i}}^{\text{ilk}}$, $\Delta \text{H}_{0\text{i}}^{\text{meh}}$ – standard heats of formation of the i-component of initial substances and products of the reaction; $\Delta \text{H}_{\text{Rj}}$ – *j*-thermal effect of j-reaction; $\Delta \text{H}_{0\text{j}}$ – *j*-standard heating effect of j-reaction.

We get the mass of the catalyst from its density, diameter and length of the reactor:

$$\frac{\text{dA}_i}{d\left(\frac{G_{\text{kat}}}{n_1^0}\right)} = \frac{n_1^0}{\rho_{\text{kat}} \cdot \frac{\pi \text{D}^2}{4}} \frac{\text{dA}_i}{\text{dl}} = r_j \qquad (20)$$

A_i – output of i-product, %; ρ_{cat} – catalyst density; l – reactor length; D – reactor diameter; r_j – j- rate of j-reaction.

Then the heat balance equation can be shown as follows:

$$\frac{N_1^0}{\rho_k \cdot \frac{\pi D^2}{4}} \frac{\mathrm{dT}}{\mathrm{dl}} = -\frac{\sum_{j=1}^{m} r_j \Delta \mathrm{H_{Rj}}}{\sum_{i=1}^{n} n_i C_{\mathrm{pi}}} - \frac{\alpha(T - T_x)}{\sum_{i=1}^{n} n_i C_{\mathrm{pi}}} \qquad (21)$$

The passage of reagents through flow-type reactors is accompanied by pressure losses. The considered process is carried out at atmospheric pressure. Although the pressure drop here is not very high, it is necessary to take into account the pressure drop in order to obtain a more correct and accurate distribution of the yield of the reaction products along the length of the reactor.

The pressure drop in the pipelines is due to the reduction of the resistances in the gas flow path. These resistances are of two types: 1) frictional resistances of the gas mixture against the pipe walls; 2) local resistances caused by the change in the direction of movement of the gas mixture. It should be noted that the listed resistances occur both in internal hydrodynamic problems and in other mixed problems, for example, when the gas flow passes through a fixed bed catalyst. In this case, the characteristics of the considered process should be taken into account in the corresponding pressure calculation formulas. Thus, for heterogeneous catalytic processes, the calculation equation proposed by Ergun is used, which well describes the experimental values of different authors about the resistance occurring in the catalyst layer and can be used to calculate the pressure loss along the length of the reactor of the studied process.

This is expressed by the following equation:

$$\frac{\mathrm{dP}}{\mathrm{dl}} = -\left(\frac{150}{\mathrm{Re}} + 1.75\right) \cdot \frac{\rho_{\text{газ}} u_0^2 (1-\varepsilon)}{d_p g \varepsilon^3}, \qquad (22)$$

here Re – Reynolds criterion, $\frac{d_p \rho_{\text{газ}} u_0}{\mu(1-\varepsilon)}$; D – reactor diameter, m; ρ_{gas} – qazın sıxlığı, kg/m^3; g – acceleration of release, m/sec^2; u_0 – linear speed, m/sec; d_p – equivalent diameter of particles, м; ε – porosity, unitless; μ – gas viscosity, kg/m ·sec); l – reactor length, m.

The kinetic equations of the oxidative dehydrogenation of methylcyclohexane to methylcyclohexadiene, the equations taking into account the heat balance and pressure drop form a complete mathematical model of the process:

$$\begin{cases} \dfrac{n_1^0}{\rho_{kat} \cdot \dfrac{\pi D^2}{4}} \dfrac{dA_1}{dl} = r^1_{C_7H_{12}} - r^2_{CO_2} \\ \dfrac{n_1^0}{\rho_{kat} \cdot \dfrac{\pi D^2}{4}} \dfrac{dA_2}{dl} = r^1_{C_7H_{10}} - r^3_{CO_2} \\ \dfrac{n_1^0}{\rho_{kat} \cdot \dfrac{\pi D^2}{4}} \dfrac{dA_3}{dl} = r^1_{C_7H_8} \\ \dfrac{n_1^0}{\rho_{kat} \cdot \dfrac{\pi D^2}{4}} \dfrac{dA_4}{dl} = r^1_{CO_2} + r^2_{CO_2} + r^3_{CO_2} \\ \dfrac{dP}{dl} = -\left(\dfrac{150}{Re} + 1.75\right) \cdot \dfrac{\rho_{газ} u_0^2 (1-\varepsilon)}{d_p g \varepsilon^3} \\ \dfrac{N_1^0}{\rho_k \cdot \dfrac{\pi D^2}{4}} \dfrac{dT}{dl} = -\dfrac{\sum_{j=1}^{m} r_j \Delta H_{Rj}}{\sum_{i=1}^{n} n_i C_{pi}} - \dfrac{\alpha (T - T_x)}{\sum_{i=1}^{n} n_i C_{pi}} \end{cases} \quad (23)$$

here $r^1_{CO_2}$, $r^2_{CO_2}$, $r^3_{CO_2}$– rates of formation carbon dioxide from methylcyclohexane (C_7H_{14}), methylcyclohexene (C_7H_{12}) and methylcyclohexadiene (C_7H_{10}); $r^1_{C_7H_{12}}$, $r^1_{C_7H_{10}}$, $r^1_{C_7H_8}$ –formation rates of methylcyclohexene, methylcyclohexadiene and toluene.

Based on the selected optimal reactor type and the set optimal technological mode, the following principle technological scheme can be proposed for the oxidative dehydrogenation process of methylcyclohexane to methylcyclohexadiene (Figure 1).

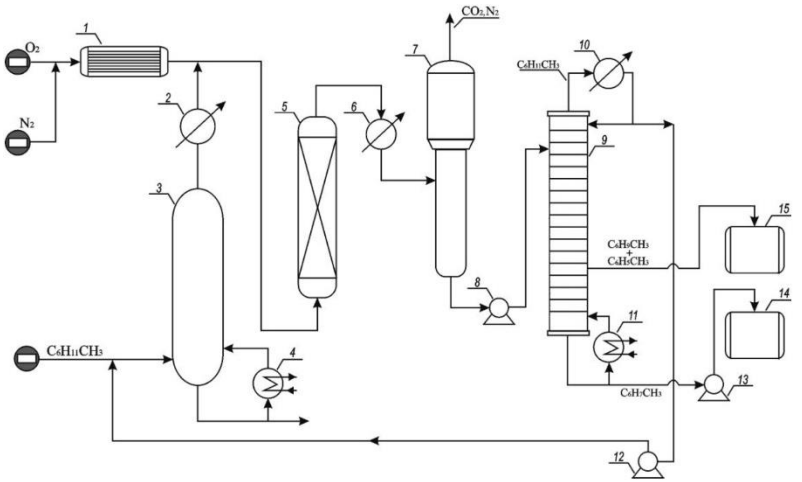


Figure 1. The principle technological scheme of the methylcyclohexadiene production process: (1 – heater; 2, 6, 10 – heat exchangers; 3 – evaporating boiler; 4, 11 – boilers (reboiler); 5 – reactor; 7 – separator; 8, 12, 13 - pumps; 9 - rectification tank; 14 - finished product tank; 15 - by-product tank)

As can be seen in the picture, the raw material - methylcyclohexane turns into vapor in the evaporator tank (3) and is sent to the heat exchanger located at the outlet (2), then it is mixed with heated oxygen and nitrogen in the heater (1) and enters the reactor (5) where the zeolite catalysts modified with CoCr metals are located, at the outlet of the reactor again passes through the heat exchanger (6) and enters the separator (7), the obtained carbon dioxide and carrier nitrogen leave the upper part of the separator, the product from the bottom of the separator is fed to the rectification column (9) by means of a pump to be separated into fractions. Methylcyclohexane from the top of the flask, which does not enter into the reaction and has a lower boiling point than other products, passes through the heat exchanger (10) and is returned to the beginning of the process, and part of the methylcyclohexane is returned to the rectification flask as cold water. Methylcyclohexene and toluene separated from the middle part of the flask are collected in the by-product tank (15). The methylcyclohexadiene coming from the bottom of the rectification tank is sent to the finished product tank (14).

CONCLUSIONS

1. Based on synthetic zeolites - A, X, Y, natural zeolites - clinoptilolite, mordenite and metal cations (Ni^{2+}, Co^{2+}, Cr^{3+}, Zn^{2+}, Cu^{2+}, Mn^{2+} və Mo^{2+}), a number of ultradisperse multicomponent metal zeolite catalysts were synthesized and molecular oxygen and methylcyclohexane 13 - their activity was determined in the oxidative dehydrogenation reaction of methylcyclohexadiene in the vapor phase [2-4, 6, 7, 11, 12].
2. It was determined that natural clinoptilolite with silicate modulus SiO_2/Al_2O_3=8.68, Co^{2+}-0.5% : Cr^{3+}-0.25% content exhibits relatively high catalytic activity and selectivity in the considered reaction. The yield of 1,3-methylcyclohexadiene at a temperature of 390°C, a volume rate of 2000 h^{-1} and a molar ratio of $C_6H_{11}CH_3:O_2:N_2$=1:1:5.3 is 14.4%, and the selectivity of the process according to the target product is 49.8% conversion of methylcyclohexane is 28,9% [5, 6, 7, 9, 12, 13, 14].
3. CoCr-Kl (Co^{2+}-0,5%:Cr^{3+}-0,25%) metal zeolite catalyst temperature 320-400°C, volume speed 500-3000 $hour^{-1}$ and partial pressure of reagents $P_{C6H11CH3}$=0.05-0.14 atm; P_{O2}=0.07-0.25 atm. kinetic regularities of the oxidative dehydrogenation reaction of methylcyclohexane were determined experimentally [7, 11, 15, 16].
4. The mechanism of the possible stepwise scheme of the oxidative dehydrogenation reaction of methylcyclohexane over the modified zeolite catalyst CoCr-clinoptilolite is proposed. According to the Langmur-Hinshelwood mechanism, 1,3-methylcyclohexadiene is formed by the interaction of the adsorbed methylcyclohexane molecule with the dissociatively adsorbed oxygen molecule. A kinetic model of the process was developed [7, 12, 15,16].
5. The developed kinetic model of the reaction was statistically analyzed based on experimental kinetic data. The numerical values of the constants of the kinetic model were calculated. It was determined that the kinetic model developed in the studied range of temperature, volume velocity and mole ratio of reagents adequately describes the experimental results, and the relative error of the

experimental and calculated results does not exceed 8% [17, 18].

6. Theoretical optimization of the selective oxidative dehydrogenation reaction of methylcyclohexane to methylcyclohexadiene was carried out, an optimal reactor was selected based on the kinetic model, and a basic technological scheme for the process was developed based on the technological mode [17, 18].

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