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RESEARCH INTO KINETIC REGULARITIES OF THE REACTION OF OXIDATIVE DEHYDROGENATION OF METHYLCYCLOHEXANE OVER MODIFIED ZEOLITES

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Abstract: *Kinetic regularities of the oxidative dehydrogenation reaction of methylcyclohexane on the* CoCr-*clinoptilolite catalyst were investigated. Absence of internal and external diffusion inhibition was established, the reaction proceeds in the kinetic area, in which all diffusion stages proceed much faster than all chemical stages that make up the mechanism of this reaction. The influence of partial pressures of reagents, the reaction temperature and the space velocity of the reaction mixture on the course of the reaction was studied and optimal conditions for obtaining the intentional reaction product determined.*

Keywords*: methylcyclohexane, methylcyclohexadiene, oxidative dehydrogenation, clinoptilolite, naphthenic hydrocarbons.*
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Introduction

The kinetic modeling of experimental data and the development of a model equation can be applied in the design of a chemical reactor. Knowledge of the reaction mechanism in describing what actually happens during a chemical reaction makes it possible to perform the safe extrapolation and optimization of reaction variables and thus assist in better development and design of a new catalyst and catalyst system [1].

The mechanism of formation of diene hydrocarbons in terms of heterogeneous oxidative dehydrogenation of naphthenic hydrocarbons has for long been a subject of discussion [2-5].

There are many schools of thought and disagreements in the literature regarding the kinetic mechanism of the oxidative dehydrogenation of naphthenic hydrocarbons to the corresponding diene hydrocarbons. Therefore, the detailed and rigorous kinetic analysis of extensive experimental datais necessitated.

The article depicts the outcomes of studying the kinetic regularities of the oxidative dehydrogenation of methyl-cyclohexane in order to clarify the possible mechanism of the reaction.

Experimental part

The results of the experimental investigation over selection of an active catalyst for the oxidative dehydrogenation of methyl cyclohexane showed that a metal zeolite catalyst synthesized on the basis of natural zeolite clinoptilolite by ion exchange and containing cations $(Co_2 + - 0.5\%;\ Cr_3 + - 0.25\%)$ exhibits the highest activity in reactions of oxidative dehydrogenation of methylcyclohexane to methylcyclohexadiene - 1,3. On this basis, the kinetic regularities of the course of the reaction were studied with the participation of this catalyst [6].

Table 1. Influence of catalyst particle sizes and linear velocity of the initial reaction mixture in the course of the reaction at a molar ratio of C_7H_{14}: O_2: N_2 = 1: 1: 5.3, V_h = 1.026 h^{-1}, T = 3800℃

№	Catalyst particle size, mm	Linear velocity of the reaction mixture, m/h	Methylcyclohexadiene-1,3 yield, %
1	0.23-0.40	73.56	15.7
2	0.23-0.40	35.72	15.8
3	0.23-0.40	24.46	16.1
4	0.23-0.40	18.34	15.7
5	0.40-0.63	73.56	15.9
6	0.40-0.63	35.72	15.7
7	0.40-0.63	24.46	15.8
8	0.40-0.63	18.34	16.1
9	0.63-1.25	73.56	15.8
10	0.63-1.25	35.72	15.7
11	0.63-1.25	24.46	15.6
12	0.63-1.25	18.34	15.9
13	1.25-1.75	73.56	15.8
14	1.25-1.75	35.72	16.1
15	1.25-1.75	24.46	15.8
16	1.25-1.75	18.34	15.9
17	1.75-2.00	73.56	15.7
18	1.75-2.00	35.72	15.6
19	1.75-2.00	24.46	15.8
20	1.75-2.00	18.34	15.9

Preceding to studying the kinetic laws of the reaction, the region of occurrence was determined. For this purpose, a series of experiments was carried out with various sizes of catalyst grains: 0.25-0.40 mm, 0.40-0.63 mm, 0.63-1.25 mm, 1.25-1.60 mm, 1.60-2.00 mm and various linear velocities of the initial reaction mixture. The linear velocity varied by changing the volume of the catalyst at equal volumetric velocities [Table 1]. As follows from data in Table 1, a change in the size and linear velocity of the initial reaction mixture does not have a significant effect on the main parameters of the process; therefore, there are no internal and external diffusion inhibitions, i.e. the reaction proceeds in the kinetic region, in which all diffusion stages proceed much faster than all the chemical stages constituting the mechanism of this reaction. Kinetic experiments were carried out on a flow-through laboratory setup in the temperature range 320–380 °C, volumetric velocities 500–3000 h-1, partial pressures of reagents P_{C7H14} = 0.04–0.14 atm; P_{O2} = 0.07–0.25 atm. The results of experimental studies of the kinetic laws in the process of oxidative conversion of methylcyclohexane are presented in Table 2-4. The reaction produces methylcyclohexene (A_1), methylcyclohexadiene (A_2), toluene (A_3), and carbon dioxide (A_4). As you can see from Table 2, an increase in P_{O2} from 0.04 to 0.14 atm leads to an increase in the yield of methicyclohexadiene-1,3 which is explained as being due to an increase in the concentration of surface oxygen, and with a further increase in P_{O2} to 0.2 atm. decreases slightly. In the entire studied range, the conversion of methylcyclohexane (X) is continuously increasing.

Table 2. Influence of oxygen partial pressure on oxidative dehydrogenation of methylcyclohexane on CoCr-clinoptilolite catalyst Vo = 2500 h^{-1}; V_{C7H14} = 0.69 l/h; = 0.02255mol / h; = 0.11 atm.; G_{cat} = 1.78 g

T,^{0}C	$n^0_{C_7H_{14}}$	$n^0_{O_2}$	$n^0_{N_2}$	$P_{C_6H_{11}CH_3}$	P_{O_2}	P_{N_2}	X,%	A_1	A_2	A_3	A_4
320	0.02255	0.00858	0.16768	0.11	0.04	0.84	4.25	1.5	0.6	2.1	0.05
	0.02255	0.01799	0.15828	0.11	0.09	0.79	9.2	1.9	2.8	4.2	0.3
	0.02255	0.02822	0.14805	0.11	0.14	0.75	10.7	2.2	3.1	4.6	0.8
	0.02255	0.03926	0.13701	0.11	0.20	0.69	13.9	2.0	2.9	6.8	2.2
340	0.02255	0.00858	0.16768	0.11	0.04	0.84	11.4	3.2	2.6	3.8	1.8
	0.02255	0.01799	0.15828	0.11	0.09	0.79	19.4	3.9	6.2	6.8	2.5
	0.02255	0.02822	0.14805	0.11	0.14	0.75	21.2	4.4	6.5	7.0	3.3
	0.02255	0.03926	0.13701	0.11	0.20	0.69	24.2	3.7	5.9	9.5	5.1
360	0.02255	0.00858	0.16768	0.11	0.04	0.84	23.7	5.8	6.6	6.4	4.9
	0.02255	0.01799	0.15828	0.11	0.09	0.79	31.1	6.2	10.5	8.6	5.8
	0.02255	0.02822	0.14805	0.11	0.14	0.75	33.8	6.7	11.1	9.3	6.7
	0.02255	0.03926	0.13701	0.11	0.20	0.69	38.3	6.4	10.7	12.3	8.9
380	0.02255	0.00858	0.16768	0.11	0.04	0.84	36.3	6.9	10.5	10.1	8.8
	0.02255	0.01799	0.15828	0.11	0.09	0.79	44.8	7.1	15.8	11.6	10.3
	0.02255	0.02822	0.14805	0.11	0.14	0.75	46.6	7.2	15.7	12.2	11.5
	0.02255	0.03926	0.13701	0.11	0.20	0.69	49.9	7.0	14.4	15.8	12.7
400	0.02255	0.00858	0.16768	0.11	0.04	0.84	38.7	6.3	9.2	13.0	10.2
	0.02255	0.01799	0.15828	0.11	0.09	0.79	47.2	6.5	13.5	14.9	12.3
	0.02255	0.02822	0.14805	0.11	0.14	0.75	49.9	7.2	14.4	15.6	12.7
	0.02255	0.03926	0.13701	0.11	0.20	0.69	55.1	6.5	14.0	18.8	15.8

Table 3 shows that in the studied temperature range at a volumetric velocity of 2000 h^{-1}, constant P_{O2} (0.14 atm.) And P_{C7H14} variation from 0.06 to 0.25 atm., the dependence of the yield of methylcyclohexadiene-1,3 has an extreme feature and passes through a maximum. The maximum output is achieved when P_{C6H12} = 0.11 atm. Further increase in P_{C7H14} to 0.25 atm. leads to a decrease in the yield of methylcyclohexadiene-1,3 and conversion of methylcyclohexane. The decrease in the conversion of methylcyclohexane is explained as being due to the fact that at a given partial pressure of oxygen, the relatively high partial pressures of methylcyclohexane prevent the coordination of oxygen with active sites of the metal zeolite catalyst.

Table 3. Effect of the partial pressure of methylcyclohexane on the oxidative dehydrogenation of methylcyclohexane on the CoCr-clinoptilolite catalyst Vo = 2000 h^{-1}; V_{O2} = 0.69 l / h; = 0.02822 mol / hour; = 0.14 atm ; G_{cat} = 1.78 g

T,^{0}C	$n^0_{C_7H_{14}}$	$n^0_{O_2}$	$n^0_{N_2}$	$P_{C_7H_{14}}$	P_{O_2}	P_{N_2}	X,%	A_1	A_2	A_3	A_4
320	0.01143	0.02822	0.16196	0.06	0.14	0.80	11.4	0.8	1.9	7.5	1.2
	0.02255	0.02822	0.14805	0.11	0.14	0.75	10.7	2.2	3.1	4.6	0.8
	0.03382	0.02822	0.13395	0.17	0.14	0.68	9.9	3.4	2.9	3.1	0.5
	0.04509	0.02822	0.11983	0.25	0.14	0.61	8.5	4.1	2.0	2.2	0.2
340	0.01143	0.02822	0.16196	0.06	0.14	0.80	22.6	3.6	5.2	9.3	4.5
	0.02255	0.02822	0.14805	0.11	0.14	0.75	21.2	4.4	6.5	7.0	3.3
	0.03382	0.02822	0.13395	0.17	0.14	0.68	18.4	5.2	6.0	5.4	1.8

	0.04509	0.02822	0.11983	0.25	0.14	0.61	15.4	6.0	3.9	4.5	1.0
360	0.01143	0.02822	0.16196	0.06	0.14	0.80	35.1	6.2	9.8	11.5	7.6
	0.02255	0.02822	0.14805	0.11	0.14	0.75	33.8	6.7	11.1	9.3	6.7
	0.03382	0.02822	0.13395	0.17	0.14	0.68	30.8	8.0	10.8	7.8	4.2
	0.04509	0.02822	0.11983	0.25	0.14	0.61	27.4	8.7	8.5	6.9	3.3
380	0.01143	0.02822	0.16196	0.06	0.14	0.80	48.4	7.4	13.9	15.0	13.1
	0.02255	0.02822	0.14805	0.11	0.14	0.75	46.6	7.2	15.7	12.2	11.5
	0.03382	0.02822	0.13395	0.17	0.14	0.68	43.2	9.1	15.5	10.3	8.2
	0.04509	0.02822	0.11983	0.25	0.14	0.61	39.1	9.9	12.8	10.2	6.2
400	0.01143	0.02822	0.16196	0.06	0.14	0.80	51.1	6.9	11.0	19.1	14.1
	0.02255	0.02822	0.14805	0.11	0.14	0.75	49.9	7.2	14.4	15.6	12.7
	0.03382	0.02822	0.13395	0.17	0.14	0.68	47.1	8.5	14.2	14.2	10.2
	0.04509	0.02822	0.11983	0.25	0.14	0.61	40.5	9.2	10.1	13.3	7.9

It follows from results above that optimal partial pressures of the reagents at which the highest yield of methylcyclohexadiene-1,3 is achieved are: P_{C7H14} = 0.11 atm. and P_{O2} = 0.14 atm. The effect of temperature and space velocity in the course of the reaction was studied at optimal P_{C7H14} and P_{O2}; the results of these studies are presented in Table 4. From Table 4 it follows that as temperature rises from 320^0C to 400^0C, the yield of methylcyclohexadiene-1,3 grows continuously.

Table 4. Influence of temperature and space velocity on the process of oxidative dehydrogenation of cyclohexane on a $CoCr$ - clinoptilolite catalyst at a molar ratio of C_6H_{12}: O_2: N_2 = 1.00: 1.00: 5.3; G_{cat} = 1.78 q; V_{cat} = 2 cm^3

№	$n^0_{C_6H_{11}CH_3}$	$n^0_{O_2}$	$n^0_{N_2}$	$V_{h,}$ h^{-1}	T,^{0}C	X,%	A_1	A_2	A_3	A_4
1	0.00902	0.01129	0.05922	1000	320	16.45	0.05	0.6	11.9	3.9
2					340	26.59	0.09	1.9	16.8	7.8
3					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	0.01804	0.022576	0.14806	2000	320	12.9	0.9	1.5	8.7	1.8
7					340	23.1	1.9	3.6	12.7	4.9
8					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	0.02255	0.028226	0.14806	2500	320	10.7	2.2	3.1	4.6	0.8
12					340	21.2	4.4	6.5	7.0	3.3
13					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	0.02706	0.03386	0.77661	3000	320	10.3	5.2	3.2	1.6	0.3
17					340	19.9	6.9	6.9	3.7	2.4
18					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

With an upsurge in the space velocity from 1000 to 3000 $^{h-1}$, the conversion of methylcyclohexane decreases due to a decrease in the contact time (Fig. 1). A decrease in the contact time prevents the preoxidative dehydrogenation of these products into toluene and deep oxidation to CO_2.

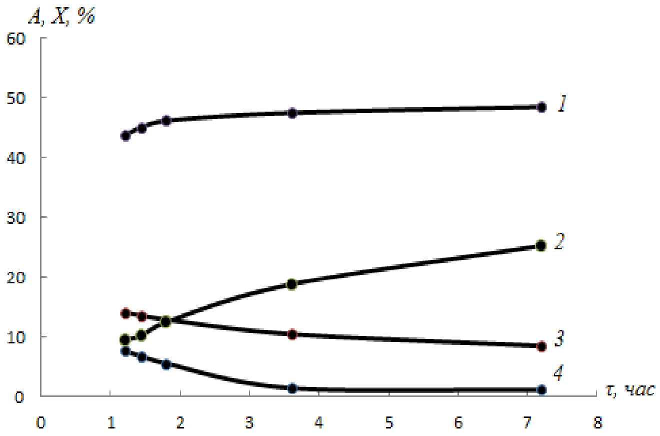

Fig. 1. Dependences of the conversion (X) of methylcyclohexane (1) and the yields (A) of the reaction products of methylcyclohexene (2), methylcyclohexadiene (3), and toluene (4) on the conditional contact time at a molar ratio of C_6H_{12}: O_2: N_2 = 1: 1: 5.3 and T = 380^0C

If we assume that this reaction proceeds according to a sequential mechanism with the formation of toluene, respectively, then for the reaction of oxidative dehydrogenation of methylcyclohexane - methylcyclohexene and methylcyclohexadiene-1,3 these are intermediate products Fig. 1. It can be seen that the nature of curves of the dependences of the yields of intermediate and final products on the conditional contact time does not correspond to the sequential mechanism of the reaction. Thus, on the basis of the experimental data obtained, it can be concluded that on the surface of the catalysts there are different active centers consisting of their components, which are responsible for the formation of reaction products, which is consistent with [7].

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MODİFİKASİYA OLUNMUŞ SEOLİTLƏR ÜZƏRİNDƏ METİLTSİKLOHEKSANIN OKSİDLƏŞDİRİCİ DEHİDROGENLƏŞMƏ REAKSİYASININ KİNETİK QANUNAUYĞUNLUQLARININ ÖYRƏNİLMƏSİ

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Metilsikloheksanın CoCr-klinoptilolit katalizatoru üzərində oksidləşdirici dehidrogenləşmə reaksiyasının kinetic qanunauyğunluqları araşdırılmışdır. Daxili və xarici diffuziya tormozlanmanın olmaması təsbit edildi, yəni reaksiya kinetic bölgədə davam edir, burada bütün diffuziya mərhələləri bu reaksiyanın mexanizmini təşkil edən bütün kimyəvi mərhələlərə nisbətən daha sürətli gedir. Reagentlərin parsial təzyiqlərinin, reaksiya temperaturu və reaksiya qarışığının həcmi sürətinin reaksiya gedişinə təsiri öyrənilmişdir. Məqsədli reaksiya məhsulunu almaq üçün optimal şərtlər müəyyən edilmişdir.

Açar sözlər: *metiltsikloheksan ,metiltsikloheksadien, oksidləşdirici dehidrogenləşmə, klinoptilolit, naften karbohidrogenləri.*

ИССЛЕДОВАНИЕ КИНЕТИЧЕСКИХ ЗАКОНОМЕРНОСТЕЙ ПРОТЕКАНИЯ РЕАКЦИИ ОКИСЛИТЕЛЬНОГО ДЕГИДРИРОВАНИЯ МЕТИЛЦИКЛОГЕКСАНА НА МОДИФИЦИРОВАННЫХ ЦЕОЛИТАХ

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Исследованы кинетические закономерности протекания реакции окислительного дегидрирования метилциклогексана на катализаторе CoCr-клиноптилолит. Установлено отсутствие внутренне- и внешне-диффузионного торможения, т.е. реакция протекает в кинетической области, в которой все диффузионные этапы протекают значительно быстрее всех химических стадий, составляющих механизм этой реакции. Изучено влияние парциальных давлений реагентов, температуры реакции и объёмной скорости реакционной смеси на протекание реакции. Определены оптимальные условия получения целевого продукта реакции.

Ключевые слова: *метилциклогексан, метилциклогексадиен, окислительное дегидрирование, клиноптилолит, нафтеновые углеводороды.*