

Synthesis and Study of Zeolites Modified with Cation Metals as Catalysts for the Reaction of Oxidative Dehydrogenation of Naphthenic Hydrocarbons

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Received April 14, 2016

Abstract—A study of the catalytic activity of modified zeolites in the reaction of selective oxidative dehydrogenation of cyclohexane and methyl cyclohexane demonstrated that catalysts prepared on the basis of natural clinoptilolite modified with Cu^{2+} , Zn^{2+} , Co^{2+} , and Cr^{3+} cations exhibit the highest activity in the reactions under consideration. Principles to be used when selecting high-efficiency catalytic systems for the reaction of oxidative dehydrogenation of alicyclic hydrocarbons to the corresponding dienes are formulated.

DOI: 10.1134/S107042721705010X

Zeolites modified with metal cations are widely used in practice as catalysts and are intensively studied in the basic catalysis. An important task is to develop approaches to optimization of the catalytic activity and selectivity of zeolite catalysts in the oxidative dehydrogenation of naphthenic hydrocarbons. Previously, studies have been carried out in order to synthesize modified ultradispersed metal-zeolite catalysts for oxidation of lower olefin hydrocarbons into carbonyl compounds, partial oxidation of paraffin hydrocarbons, oxidative conversion of aliphatic alcohols, oxidative coupling of methane, and oxidative dehydrogenation of naphthenic hydrocarbons [1–4]. It has been found that the natural clinoptilolite modified with Cu^{2+} , Zn^{2+} , Co^{2+} , and Cr^{3+} cations via ion exchange is an active catalyst for the reaction of oxidative dehydrogenation of cyclohexane into cyclohexadiene-1,3, and certain specific features of the reaction mechanism have been revealed [4].

The goal of our study was to optimize the structure of ultradispersed metal-zeolite catalysts for the reaction of oxidative dehydrogenation of naphthenic hydrocarbons, including the oxidative dehydrogenation of methyl cyclohexane, and determine the part played by components of the catalytic system in raising the activity and selectivity of the catalyst.

EXPERIMENTAL

The reaction was performed in a flow-through laboratory installation with a quartz reactor on a fixed bed of a catalyst under atmospheric pressure in the temperature range 280–390°C at a volumetric flow rate of the gas mixture of 1000–3000 h⁻¹ and cyclohexane : O₂ : N₂ molar ratio of 1 : (0.24–1) : 5.3.

We used synthetic zeolites NaY ($\text{SiO}_2/\text{Al}_2\text{O}_3 = \lambda = 4.2$), NaX ($\lambda = 2.9$), and NaA ($\lambda = 2.0$) and natural zeolites clinoptilolite ($\lambda = 8.68$) and mordenite ($\lambda = 9.6$) from an Azerbaijani deposit, modified with various cations of transition and nontransition elements (Zn, Cu, Co, Cr, Mn, Fe, Mg, Mo, etc.).

The catalysts were synthesized by the ion-exchange method [2]. Prior to being subjected to ion exchange, natural zeolites were treated with 0.5 n HCl. The amount of elements introduced into a zeolite was determined by ion-spectral analysis on Agilent ICP-MS. We used catalysts with particle sizes of 0.25–0.63 mm, cyclohexane of 99.5% purity (MerckCAS-N 110-82-7), and methyl cyclohexane of 99% purity (Merck, CAS-N 108-87-2).

The raw materials and reaction products were analyzed on a gas chromatograph directly connected to

the reaction unit. The reaction products were separated in a 3-m-long column packed with Porapak-T under the conditions linearly programmed rise in the temperature of the thermostat of the chromatograph from 50 to 200°C. The reaction products were also analyzed with an Agilent 7890 gas chromatograph with Agilent-5975 mass detector and 30-m-long HP-5 MS column.

RESULTS AND DISCUSSION

The results obtained in testing the catalytic activity of the metal-zeolites synthesized in the study in the reaction of cyclohexane dehydrogenation into cyclohexadiene-1,3 are listed in Table 1. It can be seen that natural clinoptilolite and its form modified with Zn cations exhibit a low catalytic activity in the reaction of oxidative dehydrogenation of cyclohexane (run nos. 1 and 2). The catalytic activity of natural clinoptilolite samples modified with Cr^{3+} , Cu^{2+} , and Co^{2+} cations is high, compared with the above zinc-containing catalytic systems, especially as regards the aromatization of cyclohexane (run nos. 3–5). The yields of benzene are 15.5, 12.5, and 9.8%, respectively. In this case, cyclohexadiene-1,3 is formed in low yield. Introduction of two cations (Cu^{2+} , Cr^{3+} and Co^{2+} , Cr^{3+}) into natural clinoptilolite leads to an insignificant increase in the yield of cyclohexadiene-1,3. However, the reaction of cyclohexane aromatization (run nos. 7 and 8) also dominates in this case. Introduction of a third cation (Zn^{2+}) into these catalytic systems leads to an increase in the yield of cyclohexadiene-1,3. In this case, the yield of benzene substantially decreases (run nos. 12 and 13).

The comparatively high yield of cyclohexadiene-1,3 is reached in catalytic systems containing Cu^{2+} , Cr^{3+} , Co^{2+} , and Zn^{2+} cations (run nos. 19 and 20). It follows from the data in Table 1 that natural clinoptilolite containing (wt %): Cu^{2+} 0.5, Zn^{2+} 0.2, Co^{2+} 0.1, and Cr^{3+} 0.1 (run no. 19) is an active catalyst for the reaction of oxidative dehydrogenation of cyclohexane into cyclohexadiene-1,3.

Natural clinoptilolite modified with Fe, Mn, Sn, Mo, Ni exhibits a comparatively high catalytic activity in the reaction of oxidative dehydrogenation of cyclohexane (run nos. 9–18) into cyclohexadiene-1,3.

Table 2 lists the results of experimental studies aimed to select an active catalyst for the reaction of dehydrogenation of methyl cyclohexane into cyclohexadiene-1,3. It can be seen that natural clinoptilolite modified with Zn, Cu, Cr, Co, Fe, and Ni cations exhibits a comparatively low activity in the reaction of dehydrogenation of methyl

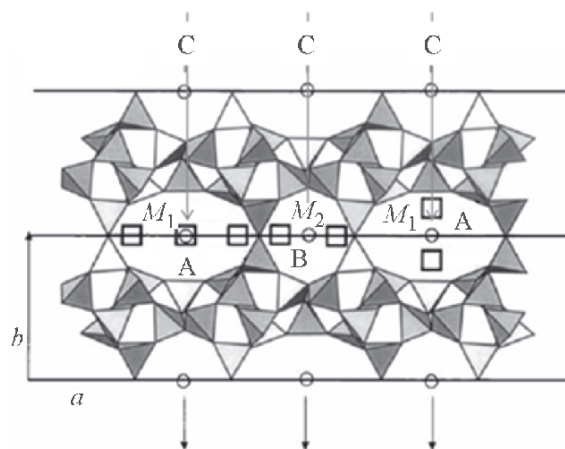


Fig. 1. Polyhedral model of clinoptilolite, which reflects a fragment of the structure with exchange cations [5].

cyclohexane into cyclohexadiene-1,3 (run nos. 1–6). The highest catalytic activity in this reaction is observed for natural clinoptilolite modified with Co^{2+} and Cr^{3+} cations (run nos. 11–15). Introduction of the Zn^{2+} cation into these catalytic systems makes lower their catalytic activity in this reaction (run nos. 16, 17). Clinoptilolite containing Cu, Zn, Co, and Cr cations has a relatively low catalytic activity in this reaction, compared with clinoptilolite containing Co and Cr^{3+} cations (run nos. 14 and 18).

Analysis of the data in Table 2 shows that clinoptilolite containing Co^{2+} (0.5 wt %) and Cr^{3+} (0.25 wt %) is an active catalyst for the reaction of oxidative dehydrogenation of methyl cyclohexane into cyclohexadiene-1,3.

It is known that the activity of zeolite catalysts in different reactions depends on the zeolite structure, nature of cations, preparation method, and distribution of cations over the zeolite surface. It has been found previously [4] that the optimal structure for preparing catalysts for the oxidative dehydrogenation of naphthenic hydrocarbons is that of clinoptilolite whose crystal lattice contains three open channels: A, B, and C. Figure 1 shows a polyhedral model that reflects a fragment of the clinoptilolite structure with exchange cations.

The first two parallel axes *c* are constituted by ten- and eight-membered rings. These are intersected by an eight-membered channel parallel to axis *a*. The hexagonal planes in the structure of clinoptilolite are surrounded by channels A, B, and C in which exchange cations are localized. The planar molecule of cyclohexane, which is a six-membered ring, is firmly adsorbed on the hexagonal planes in the structure of clinoptilolite, which are surrounded by exchange cations.

Table 1. Oxidative dehydrogenation of cyclohexane on modified natural clinoptilolite ($T = 380^{\circ}\text{C}$, $V_0 = 2000 \text{ h}^{-1}$, $\text{C}_6\text{H}_{12} : \text{O}_2 : \text{N}_2 = 1 : 1 : 5.3$). The figures in parentheses show the content of exchange cations in weight percent.

Run no.	Cations in the zeolite	Cyclohexane conversion, wt %	Selectivity with respect to cyclohexadiene, wt %	Yield of indicated reaction products, wt %					
				C_6H_{10}	C_6H_8	C_6H_6	$\text{C}_6\text{H}_9\text{OH}$	$\text{C}_6\text{H}_{10}\text{O}$	CO_2
1	–	14.8	6.1	10.8	0.9	1.7	0.3	0.8	0.3
2	Zn (0.2) ^a	14.3	2.8	0.7	0.4	0.3	12.1	–	0.8
3	Cr (0.1)	49.3	9.5	8.8	4.7	15.5	7.9	10.5	1.9
4	Cu (0.5)	49.7	5.8	3.6	2.9	12.5	10.5	17.7	2.5
5	Co (0.1)	41.6	9.4	6.9	3.9	9.8	6.5	10.6	3.9
6	ZnNi (0.2 : 0.1)	18.2	2.7	0.8	0.5	0.9	14.8	–	1.2
7	CuCr (0.5 : 0.1)	39.3	13.9	0.9	5.5	9.8	7.9	8.6	6.6
8	CoCr (0.1 : 0.1)	44.1	18.6	5.4	8.2	9.9	10.8	5.5	4.1
9	CuSn (0.5 : 0.1)	34.1	9.6	2.2	3.3	1.3	6.1	15.3	5.9
10	CuMn (0.5 : 0.1)	33.9	12.1	3.8	4.1	7.5	–	13.8	4.7
11	CuFe (0.5 : 0.25)	14.6	54.1	0.6	7.9	1.7	3.7	–	0.7
12	ZnCoCr (0.2 : 0.1 : 0.1)	39.2	30.3	4.8	12.5	4.9	8.5	2.2	6.3
13	ZnCuCr (0.2 : 0.5 : 0.1)	35.5	21.8	0.5	8.4	4.5	6.7	7.9	7.5
14	CuCoCr (0.5 : 0.1 : 0.1)	47.9	21.5	4.5	10.3	6.4	11.5	8.4	6.8
15	CuZnCo (0.5 : 0.2 : 0.1)	45.6	25.8	16.7	11.8	2.1	7.2	6.5	1.3
16	CoMnCu (0.1 : 0.5 : 0.5)	16.3	41.7	3.5	6.8	1.3	–	3.8	0.9
17	CoMnCr (0.1 : 0.5 : 0.5)	43.1	20.6	11.3	8.9	16.7	–	4.9	1.3
18	CoMoCr (0.1 : 0.5 : 0.1)	41.4	7.97	7.8	3.3	2.9	13.7	9.3	4.4
19	CuZnCoCr (0.5 : 0.2 : 0.1 : 0.1)	35.8	65.1	–	23.3	0.5	7.1	–	4.9
20	CuZnCoCr (2 : 2 : 1.0 : 0.5)	54.4	29.7	2.5	16.2	3.9	16.9	13.5	1.4

^a The figures in parentheses show the content of exchange cations in weight percent.

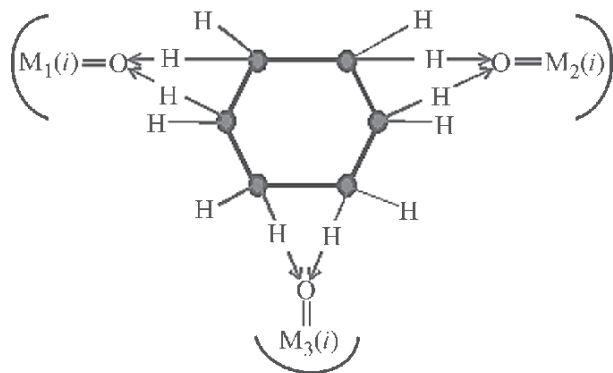


Fig. 2. General scheme of the oxidative dehydrogenation of cyclohexane on modified clinoptilolite. Cli–CuCrCoZn [i is an exchange cation, $i = 1-4$; (1) Cr^{3+} , (2) Cu^{2+} , (3) Zn^{2+} , (4) Co^{2+}] on the active center.

Clinoptilolite has four kinds of places for localization of exchange cations: M_1 in channel A, M_2 in channel B, M_3 in channel C situated along axis a near the center of the six-membered ring, M_4 is the site in channel A near the inversion center. Their number is small; M_3 is situated near M_1 [5].

The part played by components of a catalytic system in the reaction of dehydrogenation of cyclohexane can be understood by analyzing the environment of adsorbed cyclohexane molecules by exchange cations with dissociatively adsorbed oxygen, with consideration for their bonding energies, which can be found by the formula [6]

$$q_0 = 1/2(q_{\text{ads}} + 500), \quad (1)$$

where 500 kJ mol^{-1} is the energy of dissociation of molecular oxygen into atoms and q_{ads} is the heat of oxygen

adsorption on clean surfaces of polycrystalline samples of transition metals [9] (kJ mol^{-1}): $q_{\text{ads}}(\text{Cu})$ 478, $q_{\text{ads}}(\text{Zn})$ 240, $q_{\text{ads}}(\text{Co})$ 418, and $q_{\text{ads}}(\text{Cr})$ 753.

Using these data, we can calculate the bonding energies of the catalyst components with oxygen by formula (1) (kJ g at^{-1}): $q_0(\text{Cu})$ 489, $q_0(\text{Zn})$ 370, $q_0(\text{Co})$ 459, and $q_0(\text{Cr})$ 612. The force with which hydrogen atoms of cyclohexane are drawn off varies with the strength of these bonds. Oxygen atoms bound to the Cr^{3+} component of the catalyst show draw off hydrogen atoms in cyclohexane with the strongest force.

Based on the experimental data presented in Table 1 and taking into account the bonding energies of the catalyst components with atomic oxygen, we can group active centers in the components of the catalyst for the reaction of oxidative dehydrogenation of cyclohexane, which are responsible for the formation of cyclohexadiene-1,3, cyclohexene, and benzene. The general scheme of the oxidative dehydrogenation cyclohexane on these active centers is shown in Fig. 2.

For the reaction of oxidative dehydrogenation of cyclohexane into cyclohexadiene-1,3, there are two types of active centers: $\{M_1(1), M_2(2), M_3(3)\}$ and $\{M_1(1), M_2(4), M_3(3)\}$. Because the binding of the Cr^{3+} , Cu^{2+} , and Co^{2+} cations with atomic oxygen are strong, they draw off hydrogen atoms to a greater extent, with the resulting cyclohexadiene-1,3 molecules stabilized by zinc oxide, which has a relatively lower $\text{Zn}=\text{O}$ bonding energy. The formation of cyclohexadiene-1,3 is shown schematically in Fig. 3.

Analysis of the experimental data and bonding energies of the catalyst components with atomic oxygen

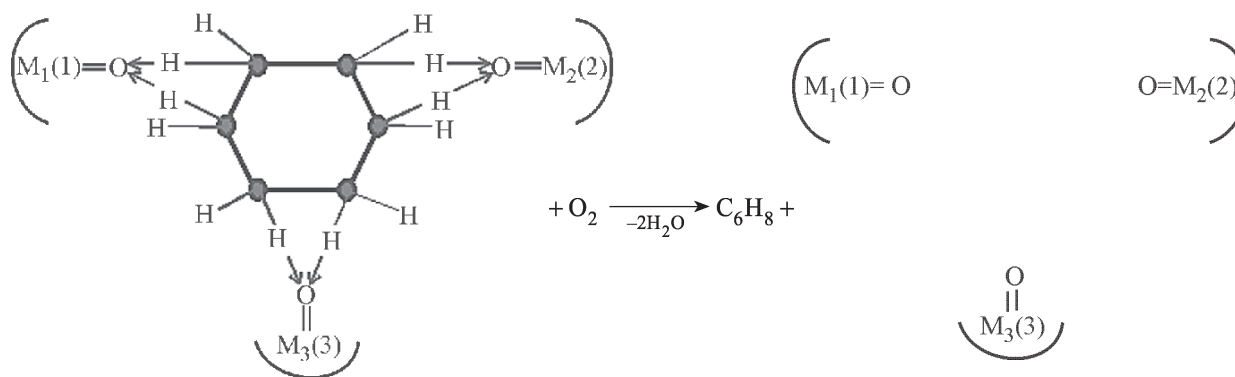


Fig. 3. Scheme of formation of cyclohexadiene-1,3 on modified clinoptilolite. Cli–CuCrCoZn [(1) Cr^{3+} , (2) Cu^{2+} , (3) Zn^{2+}] on the active center.

Table 2. Oxidative dehydrogenation of methyl cyclohexane on modified natural clinoptilolite ($T = 380^{\circ}\text{C}$, $V_0 = 2000 \text{ h}^{-1}$, $\text{C}_6\text{H}_{11}\text{CH}_3 : \text{O}_2 : \text{N}_2 = 1 : 1 : 5.3$)

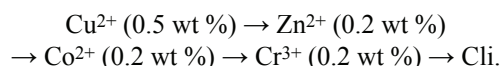
Run no.	Cations in the zeolite	Methyl cyclohexane conversion, wt %	Selectivity with respect to methyl cyclohexadiene, wt %	Yield of indicated reaction products, wt %			
				$\text{C}_6\text{H}_9\text{CH}_3$	$\text{C}_6\text{H}_7\text{CH}_3$	$\text{C}_6\text{H}_5\text{CH}_3$	CO_2
1	Zn (0.2) ^a	7.6	7.9	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	21.02	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

^a The figures in parentheses show the content of exchange cations in weight percent.

suggest that there are three kinds of active centers for the reaction of oxidative dehydrogenation of cyclohexane into benzene: $\{\text{M}_1(1), \text{M}_2(1), \text{M}_3(1)\}$, $\{\text{M}_1(2), \text{M}_2(2), \text{M}_3(2)\}$ and $\{\text{M}_1(4), \text{M}_2(4), \text{M}_3(4)\}$, and also three types of active centers for the reaction of oxidative dehydrogenation of cyclohexane into cyclohexane: $\{\text{M}_1(1), \text{M}_2(3), \text{M}_3(3)\}$, $\{\text{M}_1(2), \text{M}_2(3), \text{M}_3(3)\}$ и $\{\text{M}_1(4), \text{M}_2(3), \text{M}_3(3)\}$.

It should be noted that the predominant formation of a product in the reaction of oxidative dehydrogenation of cyclohexane depends on the number of active centers for the corresponding reactions, which, in turn, depends on the concentrations cations and the order of their introduction by ion exchange. In order to obtain

cyclohexadiene-1,3, the following order of introduction of cations into clinoptilolite is the optimal



The experimental data obtained in a study of the kinetic aspects of the reactions under consideration on active catalytic system indicate that these reactions do not occur by the successive mechanism. Figures 4 and 5 show how the conditional contact duration affects the course of the oxidative dehydrogenation reactions: cyclohexane on the CuCrCoZn–clinoptilolite catalyst and methyl cyclohexane on the CoCr–clinoptilolite catalyst, respectively.

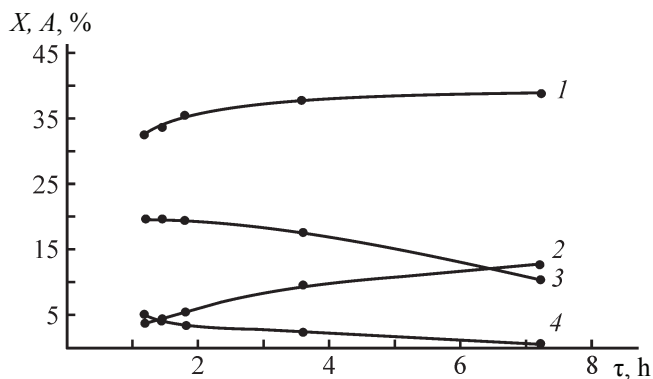


Fig. 4. (1) Conversion X of cyclohexane and the yield A of the reaction products (2) cyclohexane, (3) cyclohexadiene, and (4) benzene vs. the conditional contact duration τ at $C_6H_{12} : O_2 : N_2$ molar ratio of 1 : 1 : 5.3 and $T = 380^\circ C$.

If we assume that these reactions occur by the successive mechanism to give, respectively, benzene and toluene, then cyclohexane and cyclohexadiene-1,3 are intermediate products for the reaction of oxidative dehydrogenation of cyclohexane, and methyl cyclohexene and cyclohexadiene-1,3, for the reaction of oxidative dehydrogenation of methyl cyclohexane.

It can be seen in Figs. 4 and 5 that the runs of the curves describing the yield of intermediate and final products as a function of the conditional contact duration disagree with the successive reaction mechanism. Thus, it can be concluded on the basis of the experimental data obtained in the study that the surface of the catalysts has different active centers constituted by the components responsible for the formation of the reaction products, in agreement with the above active centers.

CONCLUSIONS

(1) The catalytic activity was studied of a number of ultradispersed multicomponent metal-zeolite catalysts synthesized on the basis of a natural zeolite, clinoptilolite, and metal cations (Ni^{2+} , Co^{2+} , Cr^{3+} , Zn^{2+} , Cu^{2+} , Mn^{2+} , and Mo^{2+}) in the reaction of vapor-phase oxidative dehydrogenation of cyclohexane and methyl cyclohexane with molecular oxygen into the corresponding dienes. It was found that the natural zeolite, clinoptilolite, containing 0.5 wt % Co^{2+} and 0.25 wt % Cr^{3+} is an active catalyst for the reaction of oxidative dehydrogenation of methyl cyclohexane into cyclohexadiene-1,3, and natural clinoptilolite containing (wt %): Cu^{2+} 0.5, Zn^{2+}

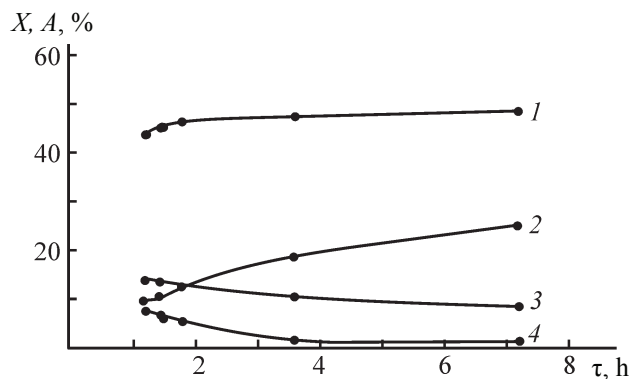


Fig. 5. (1) Conversion X of methyl cyclohexane and the yield A of the reaction products (2) methyl cyclohexane, (3) methyl cyclohexadiene, and (4) toluene vs. the conditional contact duration τ at $C_6H_{12} : O_2 : N_2$ molar ratio of 1 : 1 : 5.3 and $T = 380^\circ C$.

0.2, Co^{2+} 0.1, and Cr^{3+} 0.1 is the active catalyst for the reaction of oxidative dehydrogenation of cyclohexane into cyclohexadiene-1,3.

(2) The part played by the components of the catalytic system in the reaction of oxidative dehydrogenation of naphthenic hydrocarbons was determined. With the experimental data and the binding energies of the catalyst components with atomic oxygen taken into account, the active centers in the components of the catalyst for the reaction of oxidative dehydrogenation of cyclohexane, responsible for the formation of cyclohexadiene-1,3, cyclohexene, and benzene can be divided into groups. It was found that there are two kinds of active centers on the catalyst surface: $\{Cr^{3+}, Cu^{2+}, Zn^{2+}\}$ and $\{Co^{2+}, Cu^{2+}, Zn^{2+}\}$.

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