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Kinetic and Mechanistic Study of the Oxidative Dehydrogenation of Isobutane over Cobalt and Nickel Molybdates

Yu. A. Agafonov, N. V. Nekrasov, and N. A. Gaidai

Zelinskii Institute of Organic Chemistry, Russian Academy of Sciences, Moscow, 119991 Russia

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Abstract—The kinetics and mechanism of the oxidative dehydrogenation of isobutane on nickel and cobalt molybdates are studied. Cobalt molybdate is found to be more active than nickel molybdate. The rate laws and mechanisms for the formation of isobutene, carbon oxides, and cracking products are the same for both catalysts. Isobutene is formed via the redox mechanism with the participation of lattice oxygen. The formation of carbon oxide occurs with the participation of chemisorbed oxygen. The steps of the mechanism are proposed.

INTRODUCTION

The oxidative dehydrogenation of light paraffins attracts considerable recent attention in connection with an increasing demand for light olefins. This especially concerns isobutene since it is used for the synthesis of various organic products: polybutylenes, alkylates, copolymers, methyl *tert*-butyl ether (high-octane additive to gasoline, which is used instead of other toxic antiknock agents), and others. The main pathway to olefins is their isolation from the products of catalytic or thermal cracking. However, these processes have low selectivity to olefins, and their separation and purification are related to substantial difficulties. An increasing demand for olefins can be met by their synthesis via the catalytic dehydrogenation of the corresponding paraffins. A drawback of these processes is that high yields are only possible at high temperatures. Because dehydrogenation is an endothermic reaction, substantial heat should be supplied to the reactor. High temperatures lead to side reactions (cracking and coking) that lead to catalyst deactivation and more frequent catalyst recovery. Oxidative dehydrogenation is a solution to the cited problems: oxidative reactions are exothermic and have less energy expenditures and coking is suppressed in the presence of oxidants. Review papers on the oxidative dehydrogenation of light paraffins show that a great variety of systems are usable as catalysts for these processes. These include simple and mixed oxides, oxychlorides, zeolites, borates, heteropoly acids, and other compounds [1–8]. Cobalt and nickel molybdates are also known as efficient catalysts for the oxidative dehydrogenation of light paraffins [9–14]. Available literature deals mostly with catalyst screening. Little attention has been given to the kinetics and dynamics of the process, which can provide useful information on the process mechanism [15–17]. The mechanism of the oxidative dehydrogenation of isobutane has not been studied. Non-steady-state methods were only used in the studies devoted to the oxidative dehydrogenation of propane [14, 18–20].

This work deals with to the kinetics and mechanism of the oxidative dehydrogenation of isobutane on nickel and cobalt molybdates by steady-state and non-steady-state methods.[1]

EXPERIMENTAL

Kinetic runs under stationary conditions were carried out in an all-soldered gradient-free flow-circulation setup at an atmospheric pressure. Helium was used to dilute the components. Chromatographic analysis of the reaction mixture was carried out using two columns. The first column was packed with Chromaton with 20% ester of triethyleneglycol and *n*-butyric acid to analyze isobutane, isobutene, cracking products (methane and propylene in the equimolar amount), and carbon dioxide. The second column with 5 Å molecular sieves was used to analyze oxygen, nitrogen, and carbon monoxide.

The reaction kinetics was studied at temperatures ranging from 470–550°C, initial partial pressures $P^0_{C_4H_{10}} = 0.08$–0.50, $P^0_{O_2} = 0.032$–0.180 atm, and space velocities of 1000–16000 h^{-1}. Under these conditions, the general conversion (X) and the selectivity (S) to olefins were 0.02–0.27 and 0.50–0.97%, respectively. The main products of the reaction were isobutene, cracking products, carbon oxides, and water. At a constant space velocity and constant initial concentrations of isobutane and oxygen, the rate of isobutene formation was independent of circulation. That is, the external diffusion did not retard the process. Comparison of the rates of isobutane dehydrogenation at different sizes of catalyst particles showed that the reaction occurred in the

[1] The catalysts were kindly provided by the Institute of Catalysis and Petrochemistry (Spain) and the Higher Technical University (Portugal).

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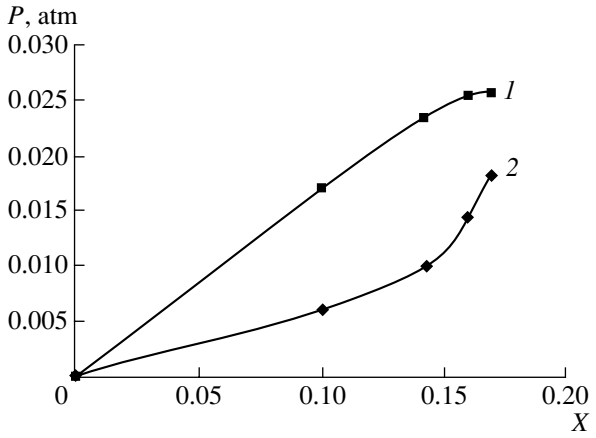

Fig. 1. Dependence of the partial pressures of (*1*) C_4H_8 and (*2*) CO_2 on the C_4H_{10} conversion on $CoMoO_4$ at 530°C.

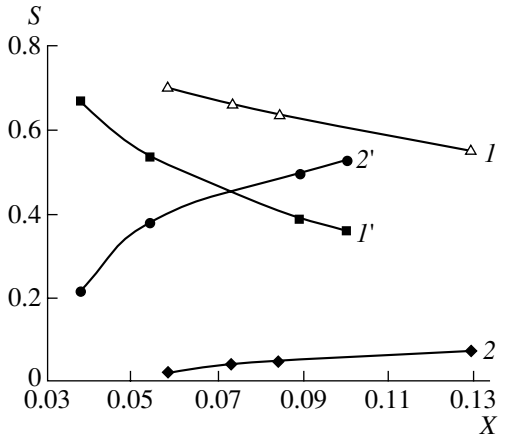

Fig. 2. Dependence of the selectivity to (*1*, *1*') C_4H_8 and (*2*, *2*') CO_2 on the C_4H_{10} conversion on (*1*, *2*) $CoMoO_4$ and (*1*', *2*') $NiMoO_4$.

kinetics-controlled regime at 550°C on granules smaller than 1 mm.

Experiments under non-steady-state conditions were carried out by the response method [16, 17] by monitoring a change in the system state in response to a drastic change in the concentration of one or both components. The small-volume setup was used coupled with a MSKh-6 time-of-flight mass spectrometer that enabled online analysis of relatively fast relaxation processes. The process conditions enabled the reaction regime analogous to the regime of a differential reactor. The contact time (i.e., the ratio of the mixture volume to the flow rate) was at most 4 s. In most runs, it was 2.5 s. This was taken into account when constructing relaxation curves. In all runs, the relaxation time was shorter than the turnover time. This is one of the main conditions that make it certain that relaxations are intrinsic [21, 22] and stipulated by the reaction mechanism rather than side processes.

The following mass numbers were measured (*m/e*): 15 (methane), 18 (water), 32 (oxygen), 43 (isobutane), 44 (carbon dioxide), and 56 (isobutene).

Cobalt and nickel molybdates were prepared according to the procedures described in [23]. Their specific surface areas were 13 and 15 m^2/g, respectively.

The reactor was charged with 0.2–0.4 g of the catalyst with particle sizes ranging from 0.25–0.50 mm. Before runs, the catalysts were heated at 550°C for 2 h by a flow of air.

RESULTS AND DISCUSSION

1. Steady-State Kinetic Study

Figure 1 shows the dependence of the partial pressure of the main reaction products (isobutene and carbon dioxide) on the overall isobutane conversion. As can be seen, the rate of isobutene formation decreases and the rate of CO_2 formation increases with an increase in the conversion (the curve is concave). This means that carbon dioxide is formed not only from isobutane, but also from the reaction products, and this latter process has a higher rate. This is confirmed by changes in the selectivity to isobutene and carbon dioxide on the overall conversion (Fig. 2). The experimental data show that the selectivity to isobutene decreases with a decrease in the space velocity and an increase in temperature. The selectivity to carbon dioxide increases with a decrease in the space velocity and an increase in temperature.

To derive adequate kinetic models, we used the method developed by Kiperman [24, 25]. For preliminary data processing, the plots of the reaction rate versus the degree of dilution and the selectivity versus reaction conditions were constructed [26]. The form of the dependence of the selectivity to cracking products on the overall conversion was used to determine that the formation of cracking products occurs via a parallel scheme. Also, we showed that the overall order in the numerator of the rate law of carbon dioxide formation is higher than the order of the denominator. At the same time, the overall order of the numerator of the rate law of cracking product formation is equal to the order of the denominator. Then, we performed final data processing using the corresponding programs on a PC.

The experimental and calculated data are shown in Table 1.

For the studied catalysts, we obtained the following rate laws that describe the formation of reaction products:

(1) isobutene:

$$w_I = k_I \frac{P_{C_4H_{10}} P_{O_2}}{P_{O_2} + k_1 P_{C_4H_{10}}}, \quad (1)$$

Table 1. The rates of the formation of products of isobutane oxidative dehydrogenation on $CoMoO_4$ and $NiMoO_4$

$P_{C_4H_{10}}$	P_{O_2}	$P_{C_4H_8}$	w_i, mol g^{-1} h^{-1}							
			C_4H_8		C_3H_6		CO_2		CO	
atm			experiment	calculation	experiment	calculation	experiment	calculation	experiment	calculation
$CoMoO_4$, 500°C										
0.286	0.088	0.0232	0.014	0.022	0.0096	0.011	0.0082	0.0098	0.0049	0.0050
0.296	0.105	0.0188	0.023	0.026	0.012	0.012	0.0090	0.0107	0.0054	0.0054
0.305	0.115	0.0166	0.031	0.027	0.013	0.013	0.0098	0.0113	0.0059	0.0057
0.312	0.121	0.0137	0.034	0.029	0.014	0.013	0.0098	0.0119	0.0059	0.0059
0.318	0.127	0.0095	0.035	0.030	0.015	0.014	0.0103	0.0126	0.0062	0.0063
530°C										
0.277	0.076	0.0256	0.016	0.0217	0.013	0.0181	0.011	0.0111	0.0080	0.0085
0.280	0.085	0.0254	0.021	0.0236	0.016	0.0177	0.010	0.0115	0.0086	0.0087
0.286	0.101	0.0227	0.028	0.0268	0.021	0.0178	0.012	0.0122	0.0088	0.0093
0.300	0.115	0.016	0.033	0.0300	0.025	0.0198	0.012	0.0133	0.0090	0.0101
550°C										
0.272	0.072	0.0296	0.018	0.030	0.018	0.030	0.011	0.012	0.0088	0.0086
0.276	0.092	0.0270	0.033	0.035	0.029	0.030	0.013	0.013	0.010	0.0092
0.287	0.100	0.0248	0.046	0.039	0.032	0.031	0.014	0.013	0.011	0.0097
0.299	0.116	0.0180	0.055	0.043	0.034	0.034	0.014	0.014	0.011	0.0088
$NiMoO_4$, 500°C										
0.152	0.084	0.0060	0.0074	0.0086	0.0022	0.0019	0.032	0.032	0.0085	0.0082
0.152	0.096	0.0055	0.0094	0.0098	0.0021	0.0019	0.034	0.034	0.0089	0.0086
0.155	0.108	0.0048	0.012	0.0110	0.0019	0.0020	0.038	0.036	0.0091	0.0092
0.158	0.118	0.0037	0.013	0.0120	0.0018	0.0021	0.039	0.039	0.0093	0.0099
530°C										
0.143	0.053	0.0094	0.012	0.012	0.0071	0.0062	0.051	0.053	0.012	0.012
0.144	0.062	0.0086	0.015	0.014	0.0065	0.0062	0.058	0.056	0.013	0.013
0.150	0.075	0.0076	0.019	0.018	0.0059	0.0063	0.062	0.060	0.014	0.014
0.151	0.093	0.0057	0.021	0.022	0.0057	0.0065	0.065	0.067	0.014	0.015
550°C										
0.135	0.0285	0.0089	0.011	0.0072	0.0088	0.0120	0.059	0.053	0.026	0.024
0.140	0.0520	0.0084	0.014	0.0150	0.010	0.0110	0.062	0.061	0.028	0.027
0.147	0.0740	0.0074	0.018	0.0210	0.011	0.0099	0.064	0.067	0.028	0.029
0.153	0.0935	0.0056	0.021	0.0270	0.012	0.0098	0.065	0.071	0.029	0.032

Table 2. Rate constants of Eqs. (1)–(5)

Constant	Catalyst	
	$NiMoO_4$	$CoMoO_4$
k_I, mol g^{-1} h^{-1} atm^{-1}	$4.71 \times 10^5 \exp(-10900/T)$	$57.7 \exp(-4240/T)$
k_1	$0.033 \exp(3260/T)$	$0.058 \exp(1870/T)$
k_{II}, mol g^{-1} h^{-1} atm^{-1}	$245 \exp(-6240/T)$	$0.33 \exp(-2630/T)$
k'_{II}, mol g^{-1} h^{-1} atm^{-1}	$781 \exp(-6080/T)$	$38.1 \exp(-5390/T)$
k_{III}, mol g^{-1} h^{-1} atm^{-1}	$2.5 \times 10^5 \exp(-12700/T)$	$32.8 \exp(-6730/T)$
k'_{III}, mol g^{-1} h^{-1} atm^{-1}	$1.09 \times 10^6 \exp(-12800/T)$	$973 \exp(-8250/T)$
k_{IV}, mol g^{-1} h^{-1} $atm^{-0.5}$	$5.32 \times 10^7 \exp(-17700/T)$	$2.54 \times 10^5 \exp(-12700/T)$
k_2, $atm^{-0.5}$	$1.06 \times 10^{-6} \exp(13300/T)$	$0.781 \exp(1780/T)$

(2) carbon dioxide:

$$w_{II} = \frac{(k_{II}P_{C_4H_{10}} + k'_{II}P_{C_4H_8})P_{O_2}^{0.5}}{P_{O_2}^{0.5} + k_2P_{C_4H_8}}, \quad (2)$$

(3) carbon monoxide:

$$w_{III} = \frac{(k_{III}P_{C_4H_{10}} + k'_{III}P_{C_4H_8})P_{O_2}^{0.5}}{P_{O_2}^{0.5} + k_2P_{C_4H_8}}, \quad (3)$$

(4) cracking products:

$$w_{IV} = k_{IV}\frac{P_{C_4H_{10}}}{P_{O_2}^{0.5} + k_2P_{C_4H_8}}. \quad (4)$$

The meaning of constants in Eq. (1) will be clear from the discussion below. The rate constants k_{II}, k_{III}, and k_{IV} in the numerators of Eqs. (2)–(4) involve the constants of slow steps, and k_2 is the ratio of the adsorption constants of isobutene and oxygen.

The apparent rate of isobutene formation (w'_I) is described by the following equation that takes into account its transformations into carbon oxides:

$$w'_I = w_I - \frac{(k'_{II} + k'_{III})P_{C_4H_8}P_{O_2}^{0.5}}{P_{O_2}^{0.5} + k_2P_{C_4H_8}}. \quad (5)$$

Other equations, such as Langmuir-Hinshelwood equations for isobutene formation or Eqs. (2)–(4) with other exponents of the partial pressures in the numirators and denominators, agreed more poorly with experimental data. Table 2 shows the values of the rate constants from Eqs. (1)–(5) for $CoMoO_4$ and $NiMoO_4$. The deviations of the rates of isobutene, carbon dioxide, carbon monoxide, and cracking product formation were 15.0, 20.0, 7.0, and 12.0% for $CoMoO_4$ and 12.0, 5.0, 5.0, and 9.0% for $NiMoO_4$, respectively. The data in Fig. 2 and Table 1 show that $CoMoO_4$ is less active than $NiMoO_4$. The stable operation of $NiMoO_4$ requires a higher concentration of oxygen. A decline in coke formation on $NiMoO_4$ takes place only at an oxygen/hydrocarbon ratio equal to unity. Cobalt molybdate can operate in a stable manner only at a ratio of 0.2.

2. Study of Transient Processes with a Response Method

In the experiments with the replacement of one component for another of the $(N_2 + O_2)/N_2/(N_2 + C_4H_{10})$ type when the $N_2 + O_2$ flow is first replaced by N_2 and then by $N_2 + C_4H_{10}$, the formation of isobutene was observed, whereas carbon dioxide was not formed. This means that different forms of oxygen participate in the formation of isobutene and carbon dioxide. After purging with nitrogen, the surface did not contain adsorbed oxygen. Therefore, only mobile lattice oxygen of the catalyst can participate in the formation of isobutene. The participation of lattice oxygen is also supported by a change in the concentration of isobutene when the reaction mixture is supplied onto the catalysts preliminarily treated with air (Figs. 3a and 4a); that is, the $(O_2 + N_2)/(O_2 + C_4H_{10})$ responses. For both catalysts the maximum is seen, which is related to the participation of mobile lattice oxygen whose concentration, as well as the concentration of surface oxygen, is maximal in the beginning of the run. To replace oxygen by butane on the surface, some time is required. Therefore, the formation of isobutene begins with a delay. With a decrease in the concentration of oxygen in the mixture, the maximum becomes less extended, and the period required for the system to achieve the steady state shortens. Likewise, the isobutene begins to yield more early in a given response. On $NiMoO_4$, where the concentration of surface oxygen is lower even at a higher concentration of oxygen in the gas phase, isobutene yields earlier than on $CoMoO_4$.

Nitrogen purging in the $O_2/N_2/(O_2 + C_4H_{10})$ response for 30 s for $NiMoO_4$ and 60 s for $CoMoO_4$ leads to a monotonic change in the concentration of isobutene in the response. This also supports the idea that the concentration of mobile oxygen in $CoMoO_4$ is much higher than in $NiMoO_4$.

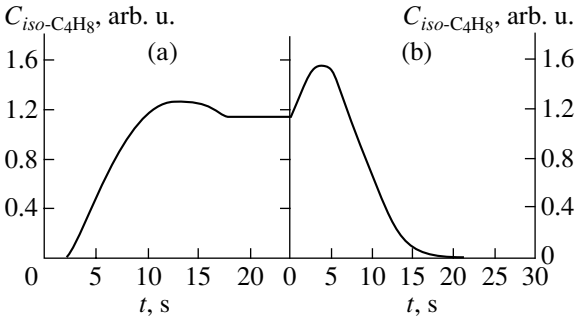

Fig. 3. Changes in the concentration of isobutene formed on $CoMoO_4$ in the responses (a) $(N_2 + O_2)/(O_2 + C_4H_{10})$ and (b) $(O_2 + C_4H_{10})/(N_2 + O_2)$. $T = 536°C$; $P^0_{O_2}/P^0_{C_4H_{10}} = 0.4$.

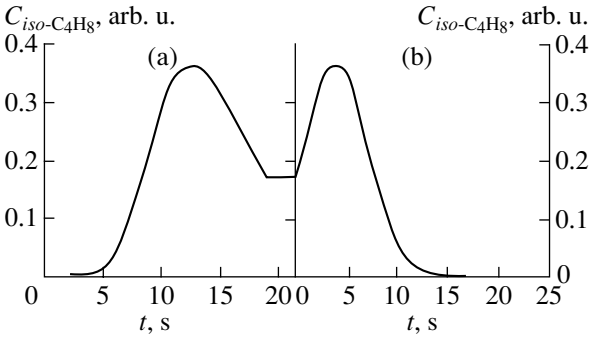

Fig. 4. Changes in the concentration of isobutene formed on $NiMoO_4$ with time in the responses (a) $(N_2 + O_2)/(O_2 + C_4H_{10})$ and (b) $(O_2 + C_4H_{10})/(N_2 + O_2)$. $T = 537°C$; $P^0_{O_2}/P^0_{C_4H_{10}} = 1.0$.

In the reverse response $(O_2 + C_4H_{10})/(N_2 + O_2)$ on $CoMoO_4$ at low temperatures (below 520°C), the concentration of isobutene changes monotonically. Above 520°C, on $CoMoO_4$ and $NiMoO_4$ (Figs. 3b and 4b), responses have maxima at all studied temperatures. A maximum corresponds to the optimal ratio of the surface concentrations of intermediate species.

In the forward and reverse responses $(N_2 + C_4H_{10})/(O_2 + C_4H_{10})$, the formation of isobutene begins immediately after the reaction mixture is supplied onto the catalyst. That is, no time is required for isobutane adsorption, but the forms of responses on the studied catalysts differ: responses are monotonic on $CoMoO_4$ at low temperatures (below 520°C) and with extrema at high temperatures; there is a maximum in the forward direction on $NiMoO_4$, and the reverse response is monotonic. The form of responses is related to a change in the strength of oxygen binding to the catalyst with temperature. At a high temperature, oxygen binding to $CoMoO_4$ weakens and this results in the appearance of a maximum.

In the forward and reverse responses $(N_2 + O_2)/(O_2 + C_4H_{10})$, on $CoMoO_4$, the time dependences of carbon dioxide concentration (Figs. 5a and 5b) have extrema. On $NiMoO_4$, the forward response is monotonic at 500°C and has a maximum at 549°C and at an oxygen/isobutane ratio equal to unity (Fig. 6a). The maximum can also be seen in the direct response at an oxygen/isobutane ratio equal to 0.2. In this case, the amount of oxygen on the surface is smaller than at a ratio equal to 1 and it is easier to remove it. In the reverse response, there is a broad maximum on nickel molybdate (Fig. 6b). The smaller the concentration of oxygen in the gas phase and the lower the temperature, the broader is the maximum. The formation of the maximum is related to coke burning, which is formed when the reaction mixture passes through the catalyst. Carbon dioxide in the $(O_2 + C_4H_{10})/N_2$ response at 520°C is removed for 20 s. The amount of CO_2 formed when coke is burning can be determined from the $(O_2 + C_4H_{10})/N_2/O_2$ response.

The above data suggest that adsorbed oxygen, which is easy to remove from the surface (this results in the appearance of the maximum on the relaxation curves), participates in the formation of carbon dioxide. These data also show that a much smaller amount of coke is formed on $CoMoO_4$ than on $NiMoO_4$ even in the substantial oxygen excess. That is, coke-forming isobutene binds more strongly to $NiMoO_4$ than to $CoMoO_4$. Kinetic data also confirm that the values of k_2 on $NiMoO_4$ are higher than on $CoMoO_4$ (Table 2).

In the $(N_2 + O_2)/(O_2 + C_4H_{10})$ response, where we measured the amount of oxygen, the time of reaching the steady state is longer for $CoMoO_4$ than for $NiMoO_4$. That is, more time is required for settling the equilibrium between oxygen in the gas phase and on the surface of $CoMoO_4$ than on $NiMoO_4$.

3. Kinetic Model of the Process

Based on the data obtained in this work, we propose the following scheme for the formation of isobutene (steps 1 and 2), carbon oxides (steps 3–9), and cracking products (steps 10 and 11):

$$1.\ C_4H_{10} + [O] = C_4H_8 + H_2O + [\ ],$$

$$2.\ O_2 + 2[\ ] = 2[O],$$

$$3.\ O_2 + 2Z = 2ZO,$$

$$4.\ C_4H_{10} + 2ZO = C_4H_9OZ + OHZ,$$

$$5.\ 2OHZ = H_2O + ZO + Z,$$

$$6.\ C_4H_9OZ + (8.5 + n)OZ = nCO_2 + (4 - n)CO + 4.5H_2O,$$

$$7.\ C_4H_8 + ZO = C_4H_8ZO,$$

$$8.\ C_4H_8OZ + ZO = C_4H_7OZ + OHZ,$$

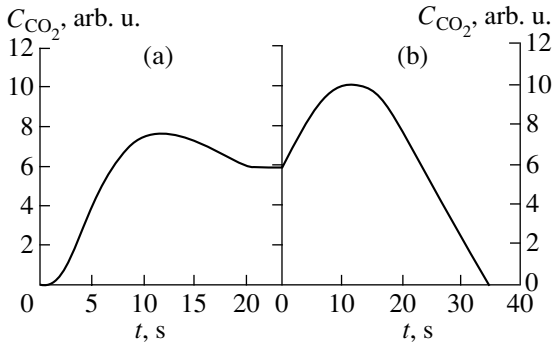

Fig. 5. Changes in the concentration of CO_2 formed on $CoMoO_4$ with time in the responses (a) $(N_2 + O_2)/(O_2 + C_4H_{10})$ and (b) $(O_2 + C_4H_{10})/(N_2 + O_2)$. T = 546°C; $P^0_{O_2}/P^0_{C_4H_{10}} = 0.4$.

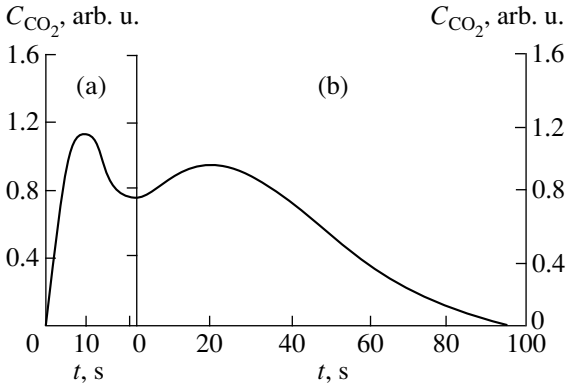

Fig. 6. Changes in the concentration of CO_2 formed on $NiMoO_4$ with time in the responses (a) $(N_2 + O_2)/(O_2 + C_4H_{10})$ and (b) $(O_2 + C_4H_{10})/(N_2 + O_2)$. T = 549°C; $P^0_{O_2}/P^0_{C_4H_{10}} = 1.0$.

$$9.\ C_4H_7OZ + (6.5 + n)OZ = nCO_2 + (4 - n)CO + 3.5H_2O,$$

$$10.\ C_4H_{10} + Z = C_3H_6Z + CH_4,$$

$$11.\ C_3H_6Z = C_3H_6 + Z.$$

Here, [ ] is an oxygen vacancy in the catalyst lattice, [O] is lattice oxygen, Z is a free site on the catalyst surface, and ZO is oxygen chemisorbed on the catalyst surface.

This scheme assumes the participation of different forms of oxygen in the formation of isobutene and oxidation products.

The formation of isobutene occurs via the redox reaction according to the model proposed by Mars and van Krevelen [27]. This model is assumed in most models for the oxidation of light paraffins [1–4, 11, 12, 16–20]. According to this model, the steady-state concentration of vacancies in the catalyst lattice is supported by the dynamic equilibrium of two processes: the removal of oxygen with reaction products in the reduction steps and the oxidation of vacancies by gaseous oxygen.

Chemisorbed oxygen participates in the reactions of complete oxidation (step 3). The formation and consumption of vacancies takes place in steps 1 and 2.

The rates of oxidation and reduction are expressed as follows:

$$w_{red} = k_{red}P_{C_4H_{10}}\theta, \quad (6)$$

$$w_{ox} = k_{ox}P_{O_2}(1 - \theta), \quad (7)$$

where θ is the concentration of oxygen vacancies.

In the equilibrium, these rates are equal. It follows from Eqs. (6) and (7) that θ is expressed as follows:

$$\theta = \frac{k_{ox}P_{O_2}}{k_{ox}P_{O_2} + k_{red}P_{C_4H_{10}}}. \quad (8)$$

Then, the expression for the rate of isobutene formation is

$$w = k_{red}\frac{P_{O_2}P_{C_4H_{10}}}{P_{O_2} + \frac{k_{red}}{k_{ox}}P_{C_4H_{10}}}. \quad (9)$$

It can be seen by comparing Eqs. (1) and (9) that $k_I = k_{red}$ and $k_1 = k_{red}/k_{ox}$. The values of k_I on the studied catalysts are very close; that is, the catalyst reduction by the hydrocarbon occurs at the same rate. The higher the k_{ox}, the lower the k_1 and the faster the process of vacancy filling. The catalyst works in a stable manner if its vacancies are filled by the reaction with gaseous oxygen. Therefore, the concentration of oxygen should not be low. Otherwise, the catalyst is reduced and it becomes susceptible to coking. Catalyst deactivation begins when oxygen vacancies cannot be filled. However, there should not be much oxygen because this would lead to a decrease in the process selectivity. The values of k_1 at 500°C on the studied catalysts are 0.65 ($CoMoO_4$) and 2.2 ($NiMoO_4$). The constant is higher in the case of $NiMoO_4$ and, therefore, at low oxygen concentrations, not only mobile oxygen interacts with the hydrocarbon but also oxygen from the catalyst lattice. This leads to catalyst reduction and coking. The stable work of the catalyst is possible only at a high concentration of oxygen in the gas phase. The conditions for the process are probably better on $CoMoO_4$ than on $NiMoO_4$.

In the reaction of complete oxidation, isobutane and isobutene are consecutively destructed during the interaction of oxygenate fragments with oxygen. It is known

that oxygenates are oxidized more readily and rapidly than hydrocarbons [28, 29]. Therefore, steps 4 and 8 are slow, and steps 3, 5–7, and 9 are fast and equilibrium.

The slow step in the formation of cracking products is also step 4, and fast equilibrium steps are 3, 10–12. Proceeding from the theory of stationary reactions, assuming that steps 4 and 8 are slow, and assuming that the catalyst surface coverages are moderate, we can obtain equations that are analogous to the experimental ones.

Thus, a comparative study of the process on two molybdate catalysts showed that on cobalt molybdate, the conditions for the process are optimal: oxygen vacancies are rapidly filled with gaseous oxygen, coke is formed in small amounts, and the catalyst can operate stably with a high selectivity for a long period of time. Catalyst operation does not require oxygen excess and, therefore, its productivity can be higher than in the case of nickel molybdate.

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