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Abstract

Full Text

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KINETICS OF THE CATALYTIC DEHYDROGENATION OF BUTANE TO BUTYLENES

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The kinetics of the catalytic dehydrogenation of butane to butylenes was investigated in the works of Lyubarskii (⁀1), Dodd and Watson (⁀2) by a flow method which, as shown by Temkin, Kiperman, Luk' yanova (⁀3) and Shendrik and Boreskov with co-workers (⁀4), is insufficiently accurate in the study of catalysts with variable activity. In the present work the kinetics of this reaction was studied by the flow-circulation method in a moving bed of catalyst. At the same time, in contrast to (⁀1, ⁀2, ⁀5), it was established that the dehydrogenation of butane is not inhibited by the butylenes formed.

The apparatus used by us differed from that described in the literature (⁀6) in the design of the reactor. The reactor scheme is shown in Fig. 1. The alumochromium-potassium catalyst (⁀7) (grains 0.5-1.0 mm), loaded into a hopper (1), entered at a constant rate, set by means of a dispenser (⁀8) (2), into a stream of argon in the catalyst preheater (3), flowed into the reactor (4), and then, through a receiver switch, entered one of four sample receivers (10). The reaction products, as well as argon, were removed from the apparatus through a tube sealed between the reactor and the catalyst preheater. Before the experiments the catalyst was regenerated with hydrogen in a flow system at 600° for 4 hr. Analysis of the contact gas was carried out by the chromatographic method (⁀9). The experiments were performed by a procedure excluding the influence on the kinetics of butane dehydrogenation of the coking reaction on the catalyst and of the divinyl formed.

Fig. 1. Reactor for studying the reaction of butane dehydrogenation by the flow-circulation method in a moving catalyst bed.
1 —hopper with catalyst, 2 —dispenser, 3 —catalyst preheater, 4 —reactor, 5, 6

—catalytic furnace, 7 —valve box, 8 —circulation pump, 9 —receiver switch, 10 —catalyst receiver.

Table 1 gives the results of experiments on the effect of space velocity on butane dehydrogenation at 550° and catalyst residence time (τ) in the reactor of 15 and 30 min. The data of Table 2 were obtained at a space velocity of 1500–1800 hr^{-1}, but at different temperatures and partial pressures of hydrogen, butane, and butylenes.

In deriving the kinetic equation we assumed, on the basis of (10), that the dependence of the rates of the forward and reverse reactions can be expressed by means of power functions of the partial pressures of butane, butylenes, and hydrogen. In this case the rate of the forward reaction (W_{deg}) can be determined from the expression:

$$W_{\text{deg}} = K P_{C_4H_{10}}^{n_1} P_{C_4H_8}^{n_2} P_{H_2}^{n_3} = \frac{W}{1 - \dfrac{P_{C_4H_8} P_{H_2}}{P_{C_4H_{10}} K_{\text{H}}}}, \tag{1}$$

where K is the rate constant of the forward reaction; n_1, n_2, n_3 are exponents determining the dependence of the reaction rate on the partial pressures of the reacting substances.

Table 1

Effect of space velocity and degree of conversion on the rate of dehydrogenation of butane to butylenes at 550° C

τ	Space velocity, h^{-1}	P_{H_2}, atm	$P_{C_4H_{10}}$, atm	$P_{C_4H_8}$, atm	Degree of conversion	W_{deg}, l(C_4H_8)/(l(cat.)· h)	K
$\tau =$ 15 min	475	0.268	0.451	0.231	0.32	320	700
$\tau =$ 15 min	1500	0.202	0.602	0.151	0.19	360	600
$\tau =$ 30 min	500	0.268	0.448	0.216	0.30	300	660
$\tau =$ 30 min	750	0.262	0.496	0.191	0.26	320	660
$\tau =$ 30 min	1500	0.202	0.600	0.169	0.21	400	660

τ	Space velocity, h^{-1}	P_{H_2}, atm	$P_{C_4H_{10}}$, atm	$P_{C_4H_8}$, atm	Degree of conversion	W_{deg}, l(C_4H_8)/(l(cat.)· h)	K
$\tau =$ 30 min	3000	0.163	0.714	0.115	0.14	460	640

From our data it follows that W_{deg} does not depend on the partial pressure of hydrogen, but is directly proportional to the partial pressure of butane (Table 2):

$$W_{deg} = KP_{C_4H_{10}} \tag{2}$$

or

$$W = KP_{C_4H_{10}} \left(1 - \frac{P_{C_4H_8}P_{H_2}}{P_{C_4H_{10}}K_p}\right). \tag{3}$$

In all calculations it was assumed that the equilibrium constant can be calculated most accurately from the equation:

$$\lg K_p = -\frac{5924.3}{T} + 2.9064 \lg T - 0.611 \cdot 10^{-3}T - 0.2445 \cdot 10^{-6}T^2 +$$

$$+0.1117 \cdot 10^{-9}T^3 - 1.2077 \pm 0.03. \tag{4}$$

Equation (4) was derived by us from the data of Rossini and Pitzer (11) and is valid in the temperature range 600–1000° K.

Table 2

Dependence of the rate of dehydrogenation of butane to butylenes on the partial pressure of the components of the reaction mixture at a space velocity of 1500–1800 h^{-1}

Conditions	P_{H_2}, atm	$P_{C_4H_{10}}$, atm	$P_{C_4H_8}$, atm	Degree of conversion	W_{deg}, l(C_4H_8)/(l(cat.)· h)	K
525°, $\tau = 45$ min	0.064	0.331	0.028	0.073	54	160

Conditions	P_{H_2}, atm	$P_{C_4H_{10}}$, atm	$P_{C_4H_8}$, atm	Degree of conversion	W_{deg}, $l(C_4H_8)/(l(cat.)\cdot h)$	K
525°, $\tau = 45$ min	0.085	0.827	0.072	0.077	130	160
540°, $\tau = 45$ min	0.088	0.221	0.051	0.18	170	480
540°, $\tau = 45$ min	0.167	0.248	0.054	0.17	122	490
550°, $\tau = 15$ min	0.089	0.186	0.048	0.18	110	580
550°, $\tau = 15$ min	0.202	0.602	0.155	0.19	360	600
550°, $\tau = 30$ min	0.083	0.094	0.035	0.29	80	900
550°, $\tau = 30$ min	0.136	0.193	0.073	0.25	185	950
550°, $\tau = 45$ min	0.070	0.114	0.030	0.19	64	560
550°, $\tau = 45$ min	0.125	0.120	0.032	0.18	68	570
550°, $\tau = 45$ min	0.239	0.104	0.024	0.18	56	540
550°, $\tau = 45$ min	0.170	0.648	0.153	0.18	350	530

The reaction-rate constants calculated from equation (3) are given in the last columns of Tables 1 and 2. The constancy of the constants in each series of experiments shows that our equation is valid over a broad range of variation in the degree of conversion (7–32%), the partial pressure of butane (0.1–0.8 atm), and at 525–550°.

The influence of temperature on the dehydrogenation of butane was studied in the temperature range 500–570°. The data obtained satisfactorily obey the

Fig. 2. Dependence of lg K on 1/T (sample 2)

Figure 2: Fig. 2. Dependence of lg K on 1/T (sample 2)

Arrhenius equation (Fig. 2). From the graph presented, the activation energy for the dehydrogenation of butane to butylenes was calculated and was found to be 46 ± 3 kcal/mole. It should be noted that the activation energy for the dehydrogenation of isopentane to isoamylenes, according to Lavrovskii and coworkers (12), is 44 ± 2 kcal/mole.

Fig. 2. Dependence of $\lg K$ on $1/T$ (sample 2)

The composition of the butylenes in all experiments did not depend on the conditions under which they were carried out and was close to the equilibrium composition (13), owing to the occurrence of isomerization reactions with migration of the double bond.

Taking into account adsorption measurements (14) of hydrocarbons on the given alumina-chromia-potassium catalyst, the mechanism of the reaction under study may be represented by the following scheme:

$$\text{butane} \rightleftarrows (\text{butane})_{\text{ads}} \tag{5}$$

$$\begin{aligned} (\text{butane})_{\text{ads}} &\longrightarrow \text{butene-1} + \mathrm{H_2} && (6)\\ &\longrightarrow \text{trans-butene-2} + \mathrm{H_2} && (7)\\ &\longrightarrow \text{cis-butene-2} + \mathrm{H_2} && (8) \end{aligned}$$

$$\begin{aligned} \text{butene-1} &\rightleftarrows \text{trans-butene-2}\\ &\rightleftarrows \text{cis-butene-2} \end{aligned} \tag{9}$$

This scheme does not exclude adsorption of the butylenes, if the latter does not prevent adsorption of butane.

The kinetic equation (3) obtained can be derived on the basis of work (15) and scheme (5)-(8), if it is assumed that the reaction proceeds in the region of low surface coverages and that the rate of dehydrogenation of butane is limited by the decomposition of adsorbed butane. In this case the rate constant (K) of equation (3) is the sum of the rate constants of reactions (6)-(8).

$$K = K_6 + K_7 + K_8. \tag{10}$$

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