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Abstract

Full Text

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ON THE QUESTION OF THE DEHYDROGENATION OF BUTANE-BUTYLENE MIXTURES ON AN ALUMINA-CHROMIA CATALYST*

In work (^1), the dehydrogenation of butane–butylene mixtures was investigated on two catalyst samples: an alumina–chromia catalyst and a mixed oxide catalyst for the dehydrogenation of butylene. On the mixed oxide catalyst the experiments were carried out with dilution by steam; on the alumina–chromia catalyst, in the absence of a diluent, since steam, as was found, inhibits the dehydrogenation of butane to butylene and promotes cracking of these hydrocarbons with the formation of decomposition products and carbon on the catalyst. In the dehydrogenation of butane–butylene mixtures on the alumina–chromia catalyst at atmospheric pressure and short contact time, the yields of butadiene obtained are lower than on the oxide catalyst. Thus, at temperatures of 600–635°, the yields of butadiene are 10–11.6% based on the feed passed and 44–49.5% based on the reacted mixture; on the oxide catalyst, with dilution by steam, butadiene is obtained in a yield of 19.8% based on the feed passed and 75–80% based on the reacted butane–butylene mixture.

The present work was undertaken with the aim of obtaining data concerning the kinetics and mechanism of the dehydrogenation of butane–butylene mixtures on an alumina–chromia catalyst. Under conditions optimal for the study, measurements were carried out of the rates of dehydrogenation of butane and of binary mixtures of the starting material with reaction products: butane–butylene, butane–butadiene, and butane–hydrogen. Since butylene and butadiene undergo decomposition on the catalyst, in order to determine the extent of decomposition, the reaction rates in binary mixtures of these hydrocarbons with ethane were measured, taking into account that ethane occupies the same portion of the active surface as butane, but does not dehydrogenate and does not decompose.

Experimental Part

The experiments were carried out by the flow method in a quartz tube 16 mm in diameter, with 4 ml of catalyst (^2). To prevent moisture from entering, the hydrocarbons supplied from the gasometer were dried by passage through a col-

umn with $CaCl_2$. The contact gas was collected in a gasometer over a saturated solution of common salt. Gas analysis was performed on a Podbilniak apparatus and on Bushmarin apparatus and a modified Orsat–Eger apparatus. Gas volumes were reduced to normal conditions (NTP). Experiments with butane and with its mixtures with butylene, butadiene, and hydrogen were carried out in the temperature range 600–635° at a space velocity of 1200 l/l · h.

In the dehydrogenation of butane at 600°, about 47% butylene and 5.4% butadiene are formed, based on the butane passed. With increasing temperature, the degree of hydrocarbon decomposition increases and the yields of butylene decrease to 38.0% at 620° and 32.2% at 635°. The amount of butadiene formed remains unchanged (Table 1).

Mixtures of butane and hydrogen. The experiments were carried out at temperatures of 600 and 620° under the same conditions as with pure butane. The mixtures contained 21.8 mol % hydrogen. These experiments showed that the amount of butylene formed during passage of the mixture decreases by 1% in comparison with the dehydrogenation of pure butane. In all probability, this is expla–

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* The work was carried out in 1950; the alumina–chromia catalyst was supplied by M. N. Maryushkin (⁀6).

Table 1

Dehydrogenation of butane and butane–hydrogen mixtures. Feed rate $v = 1200$ l/l · h.

T, °C	Feed substance	Analysis, vol. %: C_2H_4	Analysis, vol. %: C_3H_6	Analysis, vol. %: C_4H_6	Analysis, vol. %: C_4H_2	Analysis, vol. %: H_2	Analysis, vol. %: C H_2 $_2$	Obtained, %: C_4H_8	Obtained, %: C_4H_6
600	C_4H_{10}	1.0	1.5	2.7	23.5	36.0	35.3	46.8	5.4
620	Same	2.2	2.1	2.6	19.0	36.9	36.4	38.0	5.2
635	Same	3.8	2.8	2.8	15.6	34.4	40.0	32.2	5.6
600	C_4H_{10} 78.2% + H_2 21.8%	1.0	1.3	2.4	20.4		74.9	36.0	4.2
620	Same	2.0	2.0	2.4	16.4		7.27	29.7	4.3

is due to the occurrence of the reverse reaction of hydrogenation of butylene (Table 1).

Mixtures of butane and butylene. The mixtures contained 48.2 mol % butylene. The results obtained are given in Table 2. In these experiments up

to 8% butadiene is formed, and decomposition of butylene is observed (from 6 to 14.6% at 600-635°), with formation of light hydrocarbons. In order to take into account the decomposition of butylene, experiments were carried out with mixtures of butylene with ethane.

Table 2

Dehydrogenation of butane–butylene mixtures, $v = 1200$ l/l · h

T, °C	Mixture composition, mol %: C_4H_{10}	Mixture composition, mol %: C_4H_8	Analysis, vol. %: C_2H_4	Analysis, vol. %: C_3H_6	Analysis, vol. %: C_4H_6	Analysis, vol. %: C_4H_8	Degree of decomposition of C_4H_8, %	Obtained per feed mixture C_4H_6, %
600	51.8	48.2	1.7	3.1	4.8	20.4	14.0	8.0
620	51.8	48.2	3.0	4.3	4.6	17.4	17.3	8.2
635	51.8	48.2	3.7	6.0	4.0	13.7	22.2	7.6

Mixtures of butylene and ethane. Experiments with mixtures containing 50.4 mol % butylene were carried out under the same conditions. It was found that the degree of decomposition of butylene is 50.0% at 600°, 54.5% at 620°, and 59.0% at 635°, and about 7% butadiene is formed, calculated on the fed butylene. Decomposition of butylene is accompanied by formation of light hydrocarbons (methane, ethane, ethylene, propylene) and deposition

Table 3

Dehydrogenation of mixtures: butylene–ethane and butadiene–ethane, $v = 1200$ l/l · h

T, °C	Mixture composition, mol. %	Analysis, vol. %: C_2H_4	Analysis, vol. %: C_3H_6	Analysis, vol. %: C_4H_6	Analysis, vol. %: C_4H_8	Analysis, vol. %: H_2	Analysis, vol. %: C H_2 $_2$	Degree of decomposition, %	Formation, %: C_4H_6	Formation, %: carbon
600	C_4H_8 50.4% + C_2H_6 49.6%	3.6	2.0	2.4	16.8	29.6	45.6	50.1	7.2	20.0

T, °C	Mixture composition, mol. %	Analysis, vol. %: C_2H_4	Analysis, vol. %: C_3H_6	Analysis, vol. %: C_4H_6	Analysis, vol. %: C_4H_8	Analysis, vol. %: H_2	Analysis, vol. %: C H_2 $_2$	Degree of decomposition, %	Formation, %: C_4H_6	Formation, %: carbon
620	C_4H_8 50.4% + C_2H_6 49.6%	4.2	2.8	2.4	14.6	31.7	44.3	54.5	7.4	21.4
635	C_4H_8 50.4% + C_2H_6 49.6%	5.2	3.2	2.0	12.2	29.4	48.0	59.0	6.7	28.9
600	C_4H_6 18.0% + C_2H_6 82.0%	2.2	3.3	0.8	–	22.0	71.7	96.0	–	42.0
620	C_4H_6 18.0% + C_2H_6 82.0%	3.2	3.9	0.3	–	25.2	67.1	98.0	–	44.0
635	C_4H_6 18.0% + C_2H_6 82.0%	3.3	4.1	–	–	30.2	62.4	100.0	–	46.0

of carbon on the catalyst, reaching 20% at 600° and 28.9% at 635° (Table 3 and Fig. 1).

Mixtures of butane and butadiene. The mixtures contained 18 mol % butadiene. The data obtained are given in Table 4. The degree of decomposition

butadiene increases with increasing temperature, and when calculated for the butadiene contained in the initial mixture amounts to 67% at 600° and 74.2% at 635°, without taking into account its formation from butane (see Table 1). In addition,

[Figure 1 and Figure 2]

Fig. 1. Decomposition of butylene as a function of temperature:
1 –C_4H_8 (decomp.); formation: 2 –carbon; 3 –light hydrocarbons; 4 –C_4H_6

Fig. 2. Decomposition of butadiene as a function of temperature:
1 –C_4H_6 (decomp.); formation: 2 –light hydrocarbons; 3 –carbon

the butadiene contained in the mixture inhibits the dehydrogenation of butane to butylene. The amount of butylene formed per butane passed at 600° is only 26.4% instead of 46.8%, obtained in the dehydrogenation of pure butane (Table 1).

Table 4

Butane–butadiene mixtures, $v = 1200$ l/l · h

Temp., °C	Mixture composition, mol % C_4H_{10}	Mixture composition, mol % C_4H_6	C_4H_8 obtained, % per butane passed	Formation of C_3H_6, % per mixture passed	Formation of C_2H_4, % per mixture passed	Degree of C_4H_6 decomposition, %
600	82.0	18.0	26.4	5.7	6.2	67.0
620	82.0	18.0	24.9	9.8	9.0	70.3
635	82.0	18.0	23.2	13.7	12.8	74.2

Mixtures of butadiene and ethane. In order to take into account the decomposition of butadiene, experiments were carried out with mixtures under the same conditions. It was found that in the temperature range studied, 600–635°, butadiene decomposes by 96–100%. The products of butadiene decomposition are light hydrocarbons, resinous substances, and carbon on the catalyst; the latter amounts to 42–46% of the decomposed butadiene (Table 3 and Fig. 2).

Discussion of results

Experiments carried out with mixtures of butylene and butadiene with ethane confirm the suggestion made by us earlier that, in the dehydrogenation of butane-butylene mixtures on an alumina-chromium catalyst, the formation of carbon and resinous substances occurs as a result of decomposition of butylene and, to a greater extent, butadiene (see Table 3). At 600°, 50% of the butylene decomposes; from this are formed 7.2% butadiene, 20% carbon, and about 23% light hydrocarbons. With an increase in temperature to 635°, the degree of decomposition of butylene rises to 59%, which is accompanied by an increase in carbon deposition on the catalyst to 28.9% and a decrease in butadiene formation to 6.7% (see Fig. 1). Experiments with mixtures of butadiene and ethane showed that butadiene cracks more strongly on the alumina-chromium catalyst than butylene (Table 3). From Fig. 2 it is seen that at 600°, 96% of the

butadiene decomposes, with formation of 42% carbon and about 54% light hydrocarbons. At 635°, butadiene decomposes completely, by 100%. Experiments carried out with pure butane showed that the maximum yield

46.7% butylene is obtained at 600°. With an increase in temperature to 635°, the yield of butylene decreases to 32.2 mol %, which is due to further decomposition of butylene.

To determine the relative adsorption coefficients of the reaction products—butylene, butadiene, and hydrogen—the rates of dehydrogenation of binary mixtures were measured: butane—butylene, butane—butadiene, and butane—hydrogen. The relative adsorption coefficients were calculated by formula (2), taking into account the decomposition of butylene and butadiene on the catalyst, which was determined from experiments with binary mixtures with ethane.

The relative adsorption coefficients of butane, butylene, butadiene, and hydrogen at 600° are in the ratio 1 : 2.6 : 9.0 : 0.95.

The numerical values of the rate constants for the reactions of butane to butylene and butadiene, as well as of butylene to butadiene, on the alumina-chromia catalyst were found using the equation for monomolecular catalytic reactions in a flow system (3). Since at 600° the dehydrogenation reaction of butane is not very far from equilibrium, it should be noted that the results obtained are approximate in character (4). The data obtained are given below:

		K_c, ml · min · ml
Dehydrogenation	1. $C_4H_{10} \rightarrow C_4H_8$	10.9
Same	2. $C_4H_{10} \rightarrow C_4H_6$	0.76
Same	3. $C_4H_8 \rightarrow C_4H_6$	1.9

The ratio of the rate constants of reactions 1 : 2 : 3 is 100 : 7 : 17.4.

From the values found for the relative adsorption coefficients, by the known formula (5), the changes in the free energy of displacement of butane by butylene and butadiene from the active surface of the catalyst at 600° were calculated: $\Delta F_{C_4H_8} = -1662$ cal/mol; $\Delta F_{C_4H_6} = -3815$ cal/mol. The results obtained show that the free energy of adsorption displacement of butane by butadiene is more than twice as large as the free energy of adsorption displacement of butane by butylene.

Thus, in the process under consideration—the dehydrogenation of butane-butylene mixtures on an alumina-chromia catalyst—the following reactions occur: 1) dehydrogenation of butane to butylene, the rate of which is inhibited by the presence of butylene in the initial mixture; 2) dehydrogenation of butane and butylene to butadiene; 3) decomposition of butane; 4) decomposition of butylene into light hydrocarbons and carbon; 5) decomposition of butadiene into light hydrocarbons, carbon, and condensation products. In the dehydrogenation of

butane–butylene mixtures on an alumina–chromia catalyst at atmospheric pressure, as a result of the reactions taking place, butadiene is obtained in low yields both per passed and per reacted butane–butylene mixture. The catalyst rapidly becomes coked and requires frequent regeneration. The dehydrogenation of butane to butylene on this catalyst, as was shown earlier (6,1), proceeds more selectively at a lower temperature, with less formation of decomposition products (light hydrocarbons and carbon). This indicates that the alumina–chromia catalyst is specific for the dehydrogenation of saturated hydrocarbons (butane).

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REFERENCES

1. O. K. Bogdanova, A. A. Balandin, A. P. Shcheglova, ZhOKh, 2, No. 7, 2204 (1959).

2. A. A. Balandin, O. K. Bogdanova, A. P. Shcheglova. Izv. AN SSSR, OKhN, (1946), No. 5, 498.

3. A. A. Balandin, ZhOKh, 12, 156 (1942).

4. A. A. Balandin, Vestn. Moskovsk. univer., No. 4, 137 (1957).

5. A. A. Balandin, O. K. Bogdanova, A. P. Shcheglova, Izv. AN SSSR, OKhN, (1955), No. 4, 723.

6. A. A. Balandin, N. D. Zelinsky et al., DAN, 32, No. 2, 136 (1941).

Note: Figure translations are in progress. See original paper for figures.