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1962

SovietRxiv

Abstract

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PRODUCTION OF DIVINYL BY OXIDATIVE DEHYDROGENATION OF *n*-BUTYLENES

(Presented by Academician B. A. Kazanskii, March 13, 1962)

It is known that in the vapor-phase oxidation of butylenes with oxygen over oxide catalysts, for example vanadium or molybdenum-vanadium catalysts, the principal oxidation products, depending on the type of catalyst used, are maleic anhydride, carbonyl compounds, volatile fatty acids, and carbon dioxide ([1],[2]). We studied the oxidation of *n*-butylenes with air or oxygen over mixed catalysts consisting of oxides of metals of groups V and VI of the periodic system, deposited on various supports.

We established that at 460–550° the principal products of oxidation of *n*-butylenes with oxygen are not carbonyl compounds, but divinyl. The reaction was carried out in a flow system at atmospheric pressure. The butylenes were fed from a gas holder through a rotameter into a mixer, to which air was also supplied. The resulting mixture was saturated in a saturator with water vapor and entered a quartz reactor installed in an electric furnace. The contact gas was cooled, the water vapor was condensed, and the gas was collected in gas holders over a saturated sodium chloride solution. As feedstock we used an industrial butylene fraction of the following composition (vol. %): C_3H_6 0.3; C_4H_{10} 3.0; 1-C_4H_8 22.1; 2-C_4H_8 71.8; C_4H_6 2.4; C_5 and higher 0.4.

Table 1

Composition of the gas in the oxidative dehydrogenation of *n*-butylenes over an oxide catalyst
(mol. %) calculated on an air-free gas basis

Experiment No.	T-ra, °C	Space velocity of butylene, h^{-1}	Dilution with water vapor C_4H_8/H_2O (mol.)	Air/C_4H_8 (mol.)	CO_2	H_2	CH_4	CO	C_2	C_3	C_4H_{10}	C_4H_8	C_4H_6	Catalyst productivity with respect to C_4H_6, g/l·h
35	480	600	1 : 4.2	2.28	12.3	0.0	2.4	0.7	1.1	1.6	3.2	40.0	38.6	628
48	495	600	1 : 4.0	2.17	11.5	0.5	1.8	0.5	0.8	0.8	2.6	40.2	41.3	655
88	530	600	1 : 4.2	2.32	11.6	0.0	1.9	0.5	0.6	1.0	3.5	36.0	44.9	710
90	530	560	1 : 4.9	2.21	9.7	2.6	2.0	0.5	0.5	0.8	2.1	37.6	44.2	671
160	550	600	1 : 4.3	2.27	12.9	1.5	0.7	0.7	0.5	1.2	3.2	35.5	43.7	667
165	530	860	1 : 4.6	2.06	9.2	0.5	1.4	0.5	0.5	0.7	3.4	45.5	38.2	690
177	530	470	1 : 4.8	2.42	12.3	1.3	2.6	1.1	0.6	0.6	3.6	35.5	42.4	541
180	530	260	1 : 4.2	2.18	14.5	1.8	3.9	1.6	2.2	1.7	3.1	31.0	40.1	243

The contact gas was analyzed by the chromatographic method and on an Orsat apparatus. To determine the optimum reaction conditions, experiments were carried out at different temperatures, space velocities, and C_4H_8 : O_2 ratios. The effect of temperature (460-550°) was studied at a butylene feed rate of 600 h^{-1} (NTP), an air : butylene ratio = (2-2.3) : 1, and a fourfold dilution of butylene with water vapor (mol.). The results obtained are presented in Fig. 1, and the gas composition in Table 1*.

* In addition to the substances indicated in Table 1, a small amount of carbonyl compounds is formed.

As can be seen, the reaction proceeds with a sufficiently high selectivity. The reaction products consist mainly of divinyl (38-44%), unreacted butylene, carbon dioxide (10-13%), and a small amount of hydrocarbons C_2—C_3 (0.5-1.2%), with practically complete absence of hydrogen; the oxygen conversion in this case is 97-99%. The greatest yield of divinyl, amounting to 50% at a selectivity

[Figure 1 and Figure 2 graphs]

Fig. 1. Dependence of the yields of reaction products on temperature. 1 −selectivity; 2 −conversion of C_4H_8; 3 −yield of C_4H_6 per pass; 4 −yield of CO_2

Fig. 2. Effect of space velocity at 530°. 1 −selectivity; 2 −conversion of C_4H_8; 3 −yield of C_4H_6 per pass

of 82-85%, is achieved, as is evident from the curves in Fig. 1, at 530°. Changing the space velocities from 600 to 860 h^{-1} leads to a significant change in the yields of divinyl; at 530°, with an increase in the feed rate from 600 to 860 h^{-1}, the yield of divinyl per pass changes from 50 to 45%, while the selectivity increases from 85 to 93% (Fig. 2).

[Figure 3 graph]

Fig. 3. Effect of the $C_4H_8 : O_2$ ratio (mol.) on the yield of reaction products (460°; butylene space velocity 600 h^{-1}). 1 −reaction selectivity; 2 −conversion of C_4H_8; 3 −yield of C_4H_6 per pass; 4 −yield of CO_2

To determine the effect on the oxidative dehydrogenation process of the oxygen concentration in the butylene-oxygen mixture, a series of experiments was carried out at 460°, a space velocity of 600 h^{-1}, and dilution of butylene with water vapor in a ratio of 1:4 (mol.). Technical-grade oxygen was used as the oxidizing agent. The volumetric ratio $C_4H_8 : O_2$ was varied from 1:1 to 10:1.

As can be seen from Fig. 3, increasing the oxygen concentration in the mixture leads to a significant increase in butylene conversion. At the same time, the yield of deep oxidation products (CO and CO_2) also increases, as a result of which the selectivity of the reaction decreases. When the dilution of butylene with water vapor is increased from 1:4 to 1:12 (mol.), the conversion and selectivity practically do not change; decreasing the dilution to 1:1 leads to an increase in the rate of formation of deep oxidation products and to a decrease in the yields of divinyl.

Thus, the best conditions for the oxidative dehydrogenation of *n*-butylenes in our experiments are: temperature 530°, space velocity 600 h^{-1}, ratio $C_4H_8 : O_2 = 2 : 1$, and dilution of butylene with water vapor 1:3-1:4 (mol.).

Thus, it follows from the experimental data that, when *n*-butylenes are contacted in a mixture with an oxygen-containing gas over the catalyst developed by us

the reaction of divinyl formation proceeds predominantly over the catalyst,

$$\mathrm{C_4H_8} + \tfrac{1}{2}\mathrm{O} \rightarrow \mathrm{C_4H_6} + \mathrm{H_2O},$$

and not the formation of oxygen-containing compounds. This reaction, in contrast to the dehydrogenation reaction

$$C_4H_8 \to C_4H_6 + H_2,$$

proceeds with the release of heat. The yield of divinyl in oxidative dehydrogenation, owing to the binding of hydrogen, is not limited by reaction equilibrium. These features of oxidative dehydrogenation open up new possibilities for producing divinyl, as well as isoprene.

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Received
13 III 1962

REFERENCES

1. R. U. Brettow, Shen-Wu Wan, B. F. Dodge, *Ind. and Eng. Chem.*, **44**, 594 (1952).

2. B. A. Moldavskii, Yu. D. Kernos, *Kinetics and Catalysis*, **1**, no. 2, 267 (1960).

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