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Abstract

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STUDY OF SELECTIVE OXIDATIVE DEHYDROGENATION BY THE PULSE CHROMATOGRAPHIC METHOD

In earlier works of our laboratory ($^{1-3}$), the principal advantages of chromatographic methods for studying catalysts and catalytic reactions were considered, and new techniques were described for coupling chemical processes with chromatographic separation. It was shown that such coupling makes it possible to increase substantially the yields of reversible reactions, lower the process temperature, and increase the purity of the target product ($^{2-4}$).

New effects may also be expected for irreversible reactions, but in this case, in order to specify the conclusions of the theory, complete information is required on the stage mechanism, the adsorption properties of intermediate compounds, etc., or else direct experimental investigation of appropriately selected reactions under conditions of pulse chromatography is needed. For such an investigation, reactions of oxidation of organic substances by oxygen are of interest, since the reaction of complete oxidation to water and carbon dioxide and almost all reactions of mild oxidation in the temperature range usual for catalysis are irreversible.

This paper presents results obtained in the oxidation of butylenes on complex bismuth–molybdenum catalysts, which had already been studied previously for the oxidation of propylene to acrolein (^{8}). Recent works (^{6},^{7}) show that catalysts of this type are effective for the oxidative dehydrogenation of olefins to diolefins. Butylenes were chosen as the specific object, which provided additional possibilities for comparing oxidative dehydrogenation with the previously studied simple dehydrogenation in the pulse chromatographic regime (^{4}).

Method

The experimental setup did not differ in principle from those described previously for carrying out a reaction by the pulse method. For the oxidation of butylene, two variants are possible:

a) With continuous purging through the reactor of a mixture of inert carrier gas with oxygen, a definite amount of butylenes is periodically introduced.

b) A preliminarily prepared mixture of butylenes and oxygen in a specified ratio is introduced into the carrier-gas stream.

When working by method a, a small amount of air from a cylinder was added to the helium stream. The air content in the mixture was determined chromatographically, using silica gel as the adsorbent. When working by method b, the mixture was prepared in a medical syringe, by means of which pulsed injection into the carrier-gas stream was then carried out. The butylenes were obtained by dehydration of *n*-butyl alcohol over aluminum oxide at a temperature of 380°. The composition of the butylene fraction obtained in this way, deter-

separated chromatographically, was approximately as follows: α-C_4H_8 82.2%; β-trans-C_4H_8 7.6%, β-cis-C_4H_8 10.2%.

Results Obtained

Figure 1 presents a typical chromatogram obtained with pulsed introduction of a reaction mixture consisting of 1 cm^3 of butylene and 0.2 cm^3 of oxygen. The weight of the Bi—Mo catalyst* (without support) was 0.50 g. Reactor temperature 488°. Separation was carried out at room temperature on a composite column: 4 m of firebrick + 20% adiponitrile and 4 m of firebrick + 20% dibutyl phthalate. The carrier-gas flow rate was 80 cm^3/min.

From Fig. 1 it is evident that, under the specified conditions, almost 100% conversion is observed—the starting butylenes are practically absent from the chromatogram. The divinyl yield based on feed passed is 63.5%. It should be noted that this yield corresponds to the "stationary state," which is reached after 16-20 pulses (see Fig. 2). Apparently, with such "stabilization" of the catalyst by successive pulses of *n*-butenes, the active centers that lead to the deep-oxidation reaction are removed first of all. Comparison of the chromatogram obtained on a fresh catalyst with an analogous chromatogram on the stabilized catalyst reveals a sharp decrease in the CO_2 content in the second case. In a series of experiments, the stability of divinyl under the conditions of the dehydrogenation reaction was investigated. The experiments showed that, when a mixture of divinyl and oxygen was pulsed into the stream over the catalyst at a temperature of 488°, butylenes were not formed, since only CO_2 and divinyl were detected in the reaction products.

Fig. 1. Typical chromatogram in selective oxidative dehydrogenation of *n*-butenes on a Bi—Mo catalyst without support. 1—O_2; 2—C_2 fraction; 3—CO_2; 4—β-trans-C_4H_8; 5—β-cis-C_4H_8; 6—divinyl.

The catalyst we studied on a support made from a mixture of 50% corundum + 50% kaolin behaves quite differently. Its activity is considerably

Fig. 1. Typical chromatogram in selective oxidative dehydrogenation of n-butenes on a Bi—Mo catalyst without support. 1—O_2; 2—C_2 fraction; 3—CO_2; 4—β-trans-C_4H_8; 5—β-cis-C_4H_8; 6—divinyl.

Figure 1: Fig. 1. Typical chromatogram in selective oxidative dehydrogenation of n-butenes on a Bi—Mo catalyst without support. 1—O_2; 2—C_2 fraction; 3—CO_2; 4—β-trans-C_4H_8; 5—β-cis-C_4H_8; 6—divinyl.

Table 1

Composition of the products of divinyl oxidation on a Bi—Mo catalyst on a support
(in % of the amount of divinyl introduced).
Divinyl pulse volume—1 cm^3, temperature 488°

Oxygen volume, cm^3	α-Butylene	β-trans-butene-2	β-cis-butene-2	C_4H_6	CO_2 + by-products	Conversion of C_4H_6
0.2	6.7	6.6	5.1	65.0	16.6	35.0
0.4	8.5	8.8	6.5	69.0	7.2	31.0
0.6	7.2	8.0	6.5	65.5	12.8	34.5
0.8	9.2	11.0	8.5	60.4	10.9	39.6
1.0	8.5	9.90	6.8	59.0	15.8	41.0
2.0	5.4	6.0	4.5	46.1	38.0	53.9

lower than that of the preceding catalyst, but it does not change from pulse to pulse. When divinyl was introduced over this catalyst, the formation of substantial amounts of butylenes was noted, and the composition of the C_4 fraction of the catalyzate

* The atomic ratio of Bi to Mo is 1:1; bismuth was in the pentavalent state, and molybdenum in the hexavalent state.

practically does not depend on the concentration of oxygen introduced in pulses within the range from 0.2 : 1 to 2 : 1.

From the data of Table 1 it follows that the sum of CO_2 and by-products increases with increasing concentration of the introduced oxygen.

The isomerizing action of these catalysts was also studied. It turned out that the Bi—Mo catalyst without a support has a weak isomerizing action—appreciable isomerization of α-C_4H_8 to β-C_4H_8 begins only above 250°, when significant amounts of divinyl are already observed in the reaction products. On the Bi—P—Mo catalyst on a support, isomerization processes begin already at 80°, and by the time divinyl appears in the products (280°) they have proceeded quite far owing to oxidative dehydrogenation (Fig. 3). In most works published to date ([6], [7]), the yield of divinyl when the process is carried out under dynamic conditions does not exceed 50% based on the butylene passed. In our work, on the Bi—Mo catalyst with pulsed introduction of butylenes, divinyl yields were observed within the range of 70-80%. The reason for such selective oxidation of hydrogen without formation of carbonyl and carboxyl compounds may lie in the lower thermodynamic stability, and therefore in the lower probability of formation, of radicals with delocalization and conjugation of the allenic type (through which, apparently, acrolein and its analogs are formed ([9])) as compared with radicals with divinyl conjugation, typical for oxidative dehydrogenation.

Fig. 2. Dependence of the yield of divinyl on the number of pulses introduced on the Bi—Mo catalyst. Temperature 470°.

Fig. 3. Composition of the C_4 fraction as a function of the temperature of the selective oxidation reaction on the Bi—P—Mo catalyst. 1—α-butylene; 2—β-trans-C_4H_8; 3—β-cis-C_4H_8; 4—divinyl.

These questions will be examined in greater detail elsewhere.

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