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Abstract

Full Text

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ALKYLATION OF BENZENE WITH ETHYLENE IN THE PRESENCE OF A SERIES OF PHOSPHORIC ACIDS CONTAINING FLUORINE AND BORON FLUORIDE

Catalytic alkylation of aromatic hydrocarbons with olefins is at present one of the most important processes in the processing of aromatic hydrocarbons. Of the aromatic hydrocarbons, in industry benzene is usually subjected to alkylation with ethylene and propylene.

Fig. 1. Apparatus for the alkylation of benzene with olefins

Recently, a large number of catalysts have been proposed for the alkylation of benzene with olefins. Among these catalysts, compounds of boron fluoride with various substances have acquired particular importance ([1]).

Phosphoric and sulfuric acids, which are commonly used in industry for the alkylation of benzene with propylene, do not bring about the alkylation of benzene with ethylene. Alkylation of benzene with ethylene is usually carried out in the presence of aluminum chloride ([2]). In addition, a series of catalysts based on boron fluoride has been proposed for this purpose ([3],[4]).

The authors of this article studied the reaction of alkylation of benzene with ethylene in the presence of molecular compounds of orthophosphoric, monofluorophosphoric, and difluorophosphoric acids with boron fluoride. The preparation of these catalysts has been described by the authors previously ([5]).

The alkylation reaction of benzene with ethylene was carried out in the apparatus shown in Fig. 1.

Ethylene from gasometer A was fed at a rate of 2 liters per hour through a column with calcium chloride into reactor . The rate of gas passage was measured with rheometer . Stirring of benzene with the catalyst was carried out in reactor by a mechanical stirrer rotating at a speed of about 1000 rpm. Gas that did not

enter into the reaction was passed through condenser and safety bottle and was collected in gasometer A_1.

For the alkylation reaction, benzene boiling within the range 79.5–80.5°, with specific gravity $d_4^{20} = 0.8721$ and refractive index $n_D^{20} = 1.4992$, was used. The benzene was dried over metallic sodium.

For each experiment, 40 ml of catalyst, 156 g of benzene, and 22 liters of ethylene were taken. Ethylene was fed into the reactor at a rate of 2 liters/hour. The experiments were carried out at room temperature.

The results of experiments on the alkylation of benzene with ethylene in the presence of molecular compounds of phosphoric, monofluorophosphoric, and difluorophosphoric acids with boron fluoride are given in Table 1.

Table 1

Alkylation of benzene with ethylene in the presence of a series of catalysts

Catalyst	Ethylene conversion, %	Alkylate obtained, g	90–134°	134–138°	138–178°	178–184°	Residue
$H_3PO_4 \cdot BF_3$	52.3	58	4.7	77.9	–	–	17.4
$HPO_2F_2 \cdot 0.5BF_3$	66.0	60	3.7	76.0	3.1	8.0	9.2
$H_2PO_3F \cdot BF_3$	95.5	87	3.0	75.6	1.9	11.3	8.2

Fractional composition of the alkylate, wt. %

At the beginning of the experiments with all the catalysts studied, ethylene entered completely into the reaction. As the catalysts operated, the conversion of ethylene gradually decreased. An especially sharp decrease in ethylene conversion was observed in experiments carried out in the presence of the molecular compound of orthophosphoric acid with boron fluoride.

It is seen from Table 1 that the principal product of the alkylation reaction of benzene with ethylene was ethylbenzene. The best yield of alkylate was obtained when monofluorophosphoric acid saturated with boron fluoride was used as the catalyst. In the presence of the molecular compound of difluorophosphoric acid with boron fluoride, the yield of alkylate was lower, apparently because this acid adds a smaller amount of boron fluoride than does monofluorophosphoric acid.

With an increase in the yield of alkylate, and consequently also in the activity of the catalyst, the amount of the monoalkylate fraction decreased somewhat.

This decrease in the amount of monoalkylate is explained by the increase in ethylene conversion, which ultimately led to a decrease in the molar ratio of benzene to ethylene.

The main properties of the ethylbenzene fractions obtained by us, together with the constants of pure ethylbenzene, are given in Table 2.

Table 2

Main properties of ethylbenzene fractions

Property	Ethylbenzene fraction	Pure ethylbenzene
Boiling temperature, °C	134–138	136.10
Specific gravity (d_4^{20})	0.8671	0.8670
Refractive index (n_D^{20})	1.4961	1.4959
Molecular weight	105.5	106.16
Bromine number	0	–

It is seen from Table 2 that, in the alkylation of benzene with ethylene in the presence of a series of phosphoric acids containing fluorine and boron fluoride, fairly pure ethylbenzene is obtained, containing no impurities of unsaturated compounds.

The authors of this article constructed an apparatus for evaluating the catalytic activity of a series of phosphoric acids containing fluorine and boron fluoride in the reaction of alkylation of benzene with ethylene. The activity of the catalysts was determined from the change in the rate of interaction of benzene with ethylene as the composition of the catalyst changed. The apparatus resembles an instrument for determining the hydrogen number.

A diagram of the apparatus is shown in Fig. 2. Into an ordinary "duck" for determining the hydrogen number (A), 10 ml of benzene and 5 ml of catalyst were charged. Then a burette of 100 ml capacity was filled with ethylene from gasometer B,

For this purpose, the burette was connected by one three-way stopcock to gasometer B, and by the other to a rubber tube carrying the displaced water to the sewer (stopcocks 1 and 2 in position I). The three-way stopcocks 1 and 2 were then switched to position II, whereby pressure was created in the burette by means of a bottle of water mounted at a height of 1.5 m above the lower level of the burette. To displace air from the apparatus, several burettes of ethylene were passed through the "duck" ; the ethylene had first been dried over calcium chloride in tube B. After the air had been displaced from the apparatus, the burette was again filled with ethylene and, with the "duck" stopcock closed, was connected by the three-way stopcocks to the "duck" and to the bottle of water, by means of which a pressure of approximately 100 mm Hg was maintained in

Fig. 2. Apparatus for determining the conversion of ethylene in the alkylation of benzene with ethylene

Figure 2: Fig. 2. Apparatus for determining the conversion of ethylene in the alkylation of benzene with ethylene

Fig. 3. Conversion of ethylene in the alkylation of benzene with ethylene in the presence of catalysts: 1–$H_2PO_3F \cdot BF_3$, 2–$HPO_2F_2 \cdot 0.5BF_3$, 3–$H_3PO_4 \cdot BF_3$

Figure 3: Fig. 3. Conversion of ethylene in the alkylation of benzene with ethylene in the presence of catalysts: 1–$H_2PO_3F \cdot BF_3$, 2–$HPO_2F_2 \cdot 0.5BF_3$, 3 –$H_3PO_4 \cdot BF_3$

the burette. The motor of the shaker was then switched on, and the absorption of ethylene by benzene was recorded every 2 min.

Fig. 2. Apparatus for determining the conversion of ethylene in the alkylation of benzene with ethylene

The results of experiments on determining the conversion of ethylene in the alkylation of benzene with ethylene in the presence of molecular compounds of orthophosphoric, monofluorophosphoric, and difluorophosphoric acids with boron fluoride are shown in Fig. 3.

It can be seen from Fig. 3 that, in the experiment carried out in the presence of orthophosphoric acid activated with boron fluoride, 21 ml of ethylene entered into reaction within 10 min, whereas in the presence of monofluorophosphoric and difluorophosphoric acids saturated with boron fluoride, 56 and 50 ml of ethylene, respectively, reacted during the same period of time.

Fig. 3. Conversion of ethylene in the alkylation of benzene with ethylene in the presence of catalysts: 1–$H_2PO_3F \cdot BF_3$, 2–$HPO_2F_2 \cdot 0.5BF_3$, 3–$H_3PO_4 \cdot BF_3$

The results of experiments on the alkylation of benzene with ethylene and on determining the rate of interaction of benzene with ethylene in the presence of a series of phosphorus acids containing fluorine and boron fluoride indicate that, of the acids studied, the most active catalyst in the alkylation of benzene with ethylene is monofluorophosphoric acid saturated with boron fluoride. The catalysts for the alkylation of benzene with ethylene that we studied may be arranged in the following order of decreasing catalytic activity:

$$H_2PO_3F \cdot BF_3 > HPO_2F_2 \cdot 0.5BF_3 > H_3PO_4 \cdot BF_3.$$

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