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Abstract

Full Text

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ALKYLATION OF ISOPENTANE WITH PROPYLENE AND ISOBUTYLENE IN THE PRESENCE OF A SERIES OF PHOSPHORIC ACIDS CONTAINING FLUORINE AND BORON FLUORIDE

Catalytic alkylation of isoparaffins with olefins has now found broad industrial application for the synthesis of isoparaffins—high-octane components of motor fuel.

As catalysts for this reaction, sulfuric acid, hydrogen fluoride, aluminum chloride, and a number of compounds of boron fluoride with inorganic acids are usually used.

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

The authors of this article studied the alkylation reaction of isopentane with propylene and isobutylene in the presence of monofluorophosphoric and difluorophosphoric acids saturated with boron fluoride. For comparison, experiments were carried out using orthophosphoric acid saturated with boron fluoride as the catalyst.

The experiments were conducted in the apparatus shown in Fig. 1. Olefin from gasometer A was fed at a rate of 2 l/hour through a chlorocalcium column into reactor . The rate of passage of the olefin was measured by rheometer . The gas that did not enter into the reaction passed through condenser , safety bottle E, and was collected in gasometer A_1. Mixing of the isopentane and catalyst with the olefin being passed through was effected by a rapidly rotating frame stirrer with a mercury seal.

For the experiments, isopentane was used with a boiling point of 27-28°, specific gravity d_4^{20} 0.6196, and refractive index n_D^{20} 1.3562.

In order to obtain an idea of the activity of a series of catalysts in the alkylation reaction of isopentane with propylene, a number of experiments were carried

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

out to determine the duration of operation of these catalysts.

In each experiment, 15 ml of catalyst, 54 g of isopentane, and 9 l of propylene were taken for the reaction, which corresponded to a molar ratio of isopentane to propylene approximately equal to 2 : 1. The experiments were conducted at room temperature.

At the end of the experiment, the alkylation products were drained from the catalyst, and the catalyst was used in the subsequent experiment.

Fig. 2 shows the stability of operation of a number of catalysts for the alkylation of isopentane with propylene. The most active catalyst for the alkylation of isopentane with propylene among the acids studied is monofluorophosphoric acid saturated with boron fluoride, and the least active is orthophosphoric acid saturated with boron fluoride. Indeed, in the alkylation of isopentane with propylene, in the case of monofluorophosphoric acid saturated with boron fluoride, 35 volumes of alkylate are formed per one volume of catalyst, whereas in the case of difluorophosphoric and orthophosphoric acids saturated with boron fluoride, respectively, 15.8 and 9.2 volumes of alkylate are formed per one volume of catalyst.

Fig. 2. Duration of operation of a number of catalysts in the alkylation of isopentane with propylene.
I –$H_2PO_2 \cdot BF_3$, II –$HPO \cdot F_2 \cdot ½BF_3$, III –$H_2PO_3F \cdot BF_3$

The alkylates obtained were distilled on a rectification column with a separation efficiency equivalent to 40 theoretical plates. The distillation curves of the alkylates from isopentane with propylene are shown in Fig. 3. As is seen from the curves, as the catalytic activity of the catalysts decreases, the alkylates obtained contained noticeably smaller amounts of fractions boiling below 170°. For example, in the case of alkylation of isopentane with propylene in the presence of orthophosphoric acid saturated with boron fluoride, 65.4% of fractions boiling below 170° are formed, whereas when monofluorophosphoric and difluorophosphoric acids saturated with boron fluoride are used as alkylation catalysts, these fractions are formed in amounts of 77.9 and 70.8%, respectively.

Fig. 3. Fractional composition of alkylates of isopentane with propylene using various catalysts. For designations, see Fig. 2.

The alkylate fractions boiling below 170° contained no unsaturated compounds. The latter were detected in small amounts only in the residues from the distillation of the alkylates. The content of unsaturated compounds in the residues from the distillation of the alkylates increased as the activity of the catalyst decreased. For example, the residue from distillation of the alkylate obtained in the presence of monofluorophosphoric acid saturated with boron fluoride had a bromine number of 0.8, whereas the bromine number of the residue from distillation of the alkylate obtained in the presence of orthophosphoric acid saturated with boron fluoride was equal to 8.

As is seen from Fig. 3, in the alkylation of isopentane with propylene a larger amount of fractions boiling below the boiling point of the isooctane fraction is formed, and with increasing catalyst activity the amount of these fractions increases somewhat. For example, in experiments on the alkylation of isopentane with propylene in the presence of the most active of the catalysts studied—the molecular compound of monofluorophosphoric acid with boron fluoride—16% of these fractions were formed.

In experiments carried out under the same conditions in the presence of difluorophosphoric and orthophosphoric acids saturated with boron fluoride, fractions boiling below the boiling point of isooctanes were formed in amounts of 15.6 and 12.5%, respectively.

In addition, in the alkylation of isopentane with propylene, isoparaffins are also formed with a larger number of carbon atoms than in isooctanes, but with a smaller number than in the isoparaffins that may be obtained as a result of polyalkylation.

The formation of side isoparaffin fractions, along with the principal hydrocarbons, is explained by the fact that the catalytic alkylation reaction is reversible to a certain extent. This is confirmed by the observations of Birch and Dunstan (1), who established that 2,3-dimethylbutane, 2,2,4-, 2,2,3- and 2,3,3-trimethylpentanes, and 2,2,5-trimethylhexane decompose when stirred with sulfuric acid at 15–20°, as a result of which a mixture of isoparaffins of higher and lower molecular weight is obtained.

According to Yu. G. Mamedaliev and M. I. Nagiev (2), 2,2,4- and 2,2,3-trimethylpentanes at room temperature undergo cleavage upon prolonged stirring with 97% sulfuric acid, forming, along with liquid hydrocarbons, a mixture of iso- and normal butane. After distillation of isooctane treated with sulfuric acid, about 20% of the product distilled off up to 99° and about 30% above 120°, i.e., outside the boiling range of the isooctane fraction.

Thus, the formation of fractions containing hydrocarbons with a smaller number of carbon atoms than the expected product is explained by the fact that isoparaffins with a branched chain of carbon atoms are insufficiently stable under the conditions of catalytic alkylation. As a result, dealkylation of the isoparaffin formed occurs, with the formation of isoparaffins and olefins of a structure different from those taken into the reaction, if the bond between the carbon atoms is broken at a different place than in the formation. Upon secondary alkylation of this new isoparaffin, hydrocarbons are obtained with a higher molecular weight than the main product, but lower than that of a polyalkylate.

The octane fractions of the alkylates of isopentane with propylene (fractions 95-110° and 110-120°), obtained in the presence of a number of catalysts, were subjected to spectral analysis by the method of combination scattering of light. It was established that the octane fractions of the alkylates of isopentane with propylene, regardless of the catalyst used, consist of a mixture of three isomers: 2,3-, 2,4- and 2,5-dimethylhexanes.

In the alkylation of isopentane with isobutylene, the same regularities were observed as in the alkylation of isopentane with propylene. Both in the alkylation of isopentane with propylene and in the alkylation of isopentane with isobutylene, as the activity of the catalyst decreased, the yield of alkylate decreased, while its bromine number, refractive index, and specific gravity increased, and the content in the alkylate of light fractions boiling up to 170° decreased.

For example, in the alkylation of isopentane with isobutylene in the presence of monofluorophosphoric acid saturated with boron fluoride, at a molar ratio of isopentane to isobutylene equal to 2 : 1, 71.0% of fractions distilling up to 170° was obtained. When difluorophosphoric and orthophosphoric acids saturated with boron fluoride were used as catalysts, 68.2% and 65.2% of these fractions, respectively, were obtained.

The specific gravity and refractive index for the same fractions of the alkylates of isopentane with isobutylene, obtained with different catalysts, differ little from one another. At the same time, these constants are very close to the constants of isoparaffinic hydrocarbons boiling within the same limits. Consequently, as in the case of the alkylation of isopentane with propylene, the alkylate fractions we obtained consisted of isoparaffinic hydrocarbons. In the distillation residue, along with isoparaffinic hydrocarbons, unsaturated compounds were present, the amount of -

which increased as the activity of the catalysts decreased. In general, the content of unsaturated compounds in the alkylates of isopentane with isobutylene was greater than in the alkylates of isopentane with propylene. This is explained by the fact that isobutylene polymerizes much more readily than propylene.

In the alkylation of isopentane with isobutylene, the formation of isononanes may be expected. At the same time, a large number of fractions were obtained that boiled below the boiling point of the isononanes and above the boiling point of the isononanes, but below the boiling point of possible polyalkylation products. Consequently, as in the case of alkylation of isopentane with propylene, the reaction proceeds considerably more complexly than can be imagined on the basis of the direct addition of isobutylene to isopentane.

The investigations of the authors of this article showed that monofluorophosphoric and difluorophosphoric acids saturated with boron fluoride are the most active of the acidic catalysts studied for the alkylation of isoparaffinic and aromatic hydrocarbons with olefins.

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