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Abstract

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POLYMERIZATION OF ISOBUTYLENE IN THE PRESENCE OF BORON FLUORIDE ON ACTIVATED CARBON

The authors of the first work on the catalytic action of boron fluoride in the polymerization of olefins, A. M. Butlerov and V. Goryainov (^{1}), reported that, under the influence of boron fluoride, propylene forms a polymer.

In the present work we studied the influence of temperature, space velocity, support, and duration of catalyst operation on the fractional composition of the polymer and on the conversion of isobutylene in the polymerization of isobutylene in the presence of boron fluoride on activated carbon. The polymerization of isobutylene was carried out in the gas phase and at atmospheric pressure.

In addition, the conditions of use and the reason for the catalytic action of the new molecular compounds $K_2SO_4 \cdot BF_3$ and $Na_2SO_4 \cdot BF_3$ (^{2}) in the polymerization reaction of isobutylene (^{3}) were studied; this had not previously been investigated.

Isobutylene was obtained by catalytic dehydration of isobutyl alcohol (b.p. 107°) at 400° over alumina and contained 97-98% unsaturated compounds. Boron fluoride was obtained by heating 1 part by weight B_2O_3, 2 parts by weight CaF_2, and 10 parts by weight 5% oleum. To purify the boron fluoride from admixtures of water vapor and hydrogen fluoride, it was passed through a wash bottle with sulfuric acid containing boric anhydride.

Activated carbon was dehydrated under vacuum at 300°. Then 100 cm^3, or 20 g, of dry activated carbon was placed in a glass tube located in an electrically heated furnace. At 150°, dry boron fluoride was passed through the tube, and its amount adsorbed by the activated carbon was determined by weight. The samples were brought to constant weight, showing that adsorption of boron fluoride by the carbon had ended. Under the indicated conditions, 20 g of activated carbon bound 4-5 g of boron fluoride.

The prepared catalyst—boron fluoride on activated carbon—was loaded into a reactor whose length was 40 cm and diameter 2.6 cm. The reactor had a pocket for a thermocouple and electric heating. The lower part of the reactor was connected to a tube 12 cm long and 2 cm in diameter, filled with pieces of solid $NaOH$ on glass wool for trapping boron fluoride. At the end of the system there was a calcium chloride column.

The polymerization of isobutylene was carried out at 20, 70, 100, and 150°, with rates of 6, 12, 18, and 30 l/hr, or, respectively, at space velocities of 60, 120, 180, and 300 hr^{-1}. For each experiment, 50 l of isobutylene was used. In the experiments at 20°, the reactor jacket was cooled with water.

As is seen from Fig. 1, I, at a space velocity of 60 hr^{-1}, with increasing temperature the content in the polymer of the 99-126° fraction increases to 33%, and the amount of the $> 185°$ fraction decreases to 12%. The conversion of isobutylene, however, changes scarcely at all, fluctuating within the range 99-98%. From Fig. 1, II it is seen that, at a space velocity of 300 hr^{-1}, with increasing temperature the conversion of isobutylene decreases to 50%; the content of the residue $> 185°$ falls to 7.5%, while the amount of the 98-126° fraction increases to 48%.

Figure 2 presents the change in d_4^{20} and n_D^{20} of the polymer as a function of temperature at space velocities of 60 and 300 h^{-1}. In both cases, a decrease in the specific gravity and refractive index of the polymer is observed with increasing temperature. At the same temperatures, the indicated values are lower for a space velocity of 300 h^{-1}. Thus, the experiments have shown that an increase in temperature, as well as an increase in space velocity or a decrease —in contact time reduce the degree of polymerization of isobutylene. The physicochemical properties of polymers obtained at 150°, and of some of their fractions, are given in Table 1.

[Figure 1]

Fig. 1. Effect of temperature on the conversion of isobutylene (1) and on the yield of polymer fractions at a space velocity of 60 h^{-1} (I) and 300 h^{-1} (II) with a BF_3 catalyst on activated carbon.
2 —fr. 99-126° (I) and 98-126° (II), 3 —fr. 170-185°, 4 —fr. $> 185°$

[Figure 2]

Fig. 2. Dependence of d_4^{20} (a) and n_D^{20} (b) of polyisobutylene on temperature at space velocities of 60 h^{-1} (1) and 300 h^{-1} (2) with a BF_3 catalyst on activated carbon

To obtain the molecular compounds $K_2SO_4 \cdot BF_3$ and $Na_2SO_4 \cdot BF_3$, the corresponding salts K_2SO_4 and Na_2SO_4 were first calcined. Then, in the same apparatus that was used for adsorption of boron fluoride by carbon, but at 235° for K_2SO_4 and 330° for Na_2SO_4, the reaction of addition of boron fluoride was carried out, with the formation of molecular compounds, which were solid crystalline substances. The samples were brought to constant weight, which indicated completion of the addition reaction.

After it had been established by numerous experiments that the catalytic action of the molecular compounds $K_2SO_4 \cdot BF_2$ and $Na_2SO_4 \cdot BF_3$ is caused by boron fluoride, they were used for experiments on the polymerization of isobutylene with the introduction of boron fluoride, carried out at 150°.

For each experiment, 20 g, or 100 cm^3, of dry activated carbon was taken and placed in the reactor. Then isobutylene in an amount of 50 or 100 l, at a space velocity of 60 hr^{-1}, and boron fluoride from a molecular compound located in an electrically heated furnace were fed simultaneously into the reactor. Decomposition of the molecular compounds was carried out with a gradual rise in temperature from 360 to 390°. The amounts of molecular compounds used for an experiment were: 17.8 g of $K_2SO_4 \cdot BF_3$ or 15.4 g of $Na_2SO_4 \cdot BF_3$, each containing 5 g of boron fluoride.

The polymer obtained was washed, dried, and distilled on a column. The results are given in Table 1. These experiments demonstrated for the first time the possibility of using the new molecular compounds $K_2SO_4 \cdot BF_3$ and $Na_2SO_4 \cdot BF_3$ in the polymerization reaction of isobutylene and clarified the nature of their catalytic action (^{3}). At elevated temperature the molecular compound decomposes:

$$K_2SO_4 \cdot BF_3 \rightleftarrows K_2SO_4 + BF_3.$$

The boron fluoride evolved is the catalyst of the reaction.

Table 1

Physicochemical properties of the polymers and of some of their fractions

Fraction, °C	Fraction yield, vol. %	Isobutylene conversion, %	d_4^{20}	n_D^{20}	Bromine number	Unsaturated hydrocarbons, %	Molecular weight	Space velocity, hr^{-1}	Octane number	Fraction, °C	Fraction yield, vol. %	Isobutylene conversion, %	d_4^{20}	n_D^{20}	Bromine number	Unsaturated hydrocarbons, %	Molecular weight	Space velocity, hr^{-1}	Octane number
Without BF_3 feed	**Without BF_3 feed**	**Without BF_3 feed**	**Without BF_3 feed**	**Without BF_3 feed**	**Without BF_3 feed**	**Without BF_3 feed**	**Without BF_3 feed**	**Without BF_3 feed**	**Without BF_3 feed**	**With BF_3 feed**	**With BF_3 feed**	**With BF_3 feed**	**With BF_3 feed**	**With BF_3 feed**	**With BF_3 feed**	**With BF_3 feed**	**With BF_3 feed**	**With BF_3 feed**	**With BF_3 feed**
98–106°	27		0.7195	1.4118	141	99.0	112.4	60		98–106°	34		0.7168	1.4101	140	99.5	113.8	60	
170–185°	46		0.7613	1.4323	93	98.7	169.9	60		170–185°	41.2		0.7602	1.4327	94	99.2	168.9	60	
Polymer		98	0.7432	1.4222	106	98.8	149.2	60		Polymer		81	0.7357	1.4210	120	99.0	132.0	60	
Polymer		50	0.7309	1.4180			131.5	300	91	Polymer		70	0.7277	1.4180				60	

A method was also developed for carrying out the experiment using the molecular compound $K_2SO_4 \cdot BF_3$ for experiments with feeding of boron fluoride, and the possibility was demonstrated of obtaining, in this case, a lighter polymer than in experiments without feeding, as is evident from Table 1.

The duration of operation of the catalyst, consisting of 5 g of boron fluoride on 20 g of activated carbon, was also studied at 20°. For the experiment, 250 l of isobutylene was used, which was fed at a space velocity of 60 hr^{-1}. The results, presented in Fig. 3, show a high degree of conversion of isobutylene throughout the entire experiment and, consequently, the possibility of very prolonged operation of this catalyst after 41.5 hr of operation.

Fig. 3. Conversion of isobutylene (**1**) and yield of polymer fractions as a function of the duration of operation of the BF_3 catalyst on activated carbon at 20° and a space velocity of 60 hr^{-1}. **2** –fr. 100-126°, **3** –fr. 170-185°, **4** –fr. 185°.

At an average conversion of 96%, 540 g of polymer was obtained from 250 l of isobutylene. The physical constants of the polymer were: d_4^{20} 0.7715, n_D^{20} 1.4402, molecular weight 177.4, and octane number 87. The molecular weight was determined by the cryoscopic method, and the octane number by the motor method on a Waukesha apparatus.

Some polymer fractions were subjected to optical analysis by the method of combinational scattering. The results are given in Table 2.

The presence in the 108-120° fraction of the hydrocarbons 3,4,4-trimethylpentene-2, 2,3,4-trimethylpentene-2, and 2,3,4-trimethylpentene-1 indicates that the polymerization and butylation reaction is accompanied by isomerization, which is especially noticeable for the polymer obtained at 150° (7-9%).

Table 2

Spectral analysis of several polymer fractions (catalyst—BF_3 on activated carbon)

Experiment temperature, °C	Volumetric rate, hr^{-1}	Fraction, °C	Chemical composition	Boiling point, according to literature data (1), °C
20	60	98-106	2,4,4-trimethylpentene-1	101.36
20	60	98-106	2,4,4-trimethylpentene-2	104.85
150	60	98-106	2,4,4-trimethylpentene-1	101.36
150	60	98-106	2,4,4-trimethylpentene-2	104.85

Experiment temperature, °C	Volumetric rate, hr^{-1}	Fraction, °C	Chemical composition	Boiling point, according to literature data (1), °C
150	60	108–120	3,4,4-trimethylpentene-2	112.3
150	60	108–120	2,3,4-trimethylpentene-2	116.26
150	60	108–120	2,3,4-trimethylpentene-1	117.15

In studying the influence of the support on the polymerization of isobutylene in the presence of boron fluoride, experiments were carried out in parallel with the support and without the support. In the latter case, activated carbon was not charged into the reactor; only isobutylene was fed at a rate of 6 l/hr and boron fluoride from 17.8 g of $K_2SO_4 \cdot BF_3$. The experimental temperature was 150°, and the amount of isobutylene was 50 l.

The study showed that the conversion of isobutylene in the experiment without a support decreased with time and at the end of the experiment was only 18.7%. In the experiment with a support, however, the conversion gradually increased to 96%. The average conversion in the first case was 43%, and in the second 81%. These data indicate the expediency of using activated carbon as a support in the polymerization of isobutylene with boron fluoride.

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