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POLYMERIZATION OF ISOBUTYLENE UNDER THE ACTION OF BORON FLUORIDE ADSORBED ON SILICA GEL

This communication presents the results of an investigation of the polymerization of isobutylene in the presence of boron fluoride on silica gel; it was carried out by us for the first time ([1]), with the production of low-molecular-weight polymers of isobutylene, i.e., diisobutylenes and triisobutylenes.

The work investigated the dependence of isobutylene conversion and the fractional composition of the polymer on the space velocity, temperature, duration of catalyst operation, and the amount of boron fluoride adsorbed on silica gel.

The polymerization of isobutylene was studied at temperatures of 20, 70, 100, and 150° at isobutylene feed rates of 6 and 30 l/hr, or at a space velocity of 60 and 300 hr^{-1}. The experiments were carried out at atmospheric pressure.

Boron fluoride was obtained at elevated temperature by the interaction of 1 part by weight B_2O_3, 2 parts by weight CaF_2, and 10 parts by weight of 5% oleum. To remove traces of water and hydrogen fluoride, the boron fluoride was passed through a wash bottle containing sulfuric acid and boric anhydride. In the catalytic dehydration of isobutyl alcohol (b.p. 107°) over aluminum oxide at 400°, isobutylene containing 98% unsaturated compounds was obtained.

The polymerization of isobutylene was carried out in a reactor 40 cm long and 2.6 cm in diameter with electric heating. At the outlet of the reactor a tube 12 cm long, filled with pieces of NaOH, was attached for trapping boron fluoride and preventing polymerization outside the reactor.

For each experiment, 100 cm^3 (or 45 g) of dry silica gel of the ShSK grade was taken; at 150°, 3.5–4 g of boron fluoride and 50 l of isobutylene were adsorbed on it. The catalyst—boron fluoride on silica gel—was placed in the reactor, into which isobutylene from a gasometer was then passed. During adsorption of boron fluoride by the silica gel, the samples were brought to constant weight. In the experiments at 20°, the reactor was cooled with water. The collected polymer was washed, dried, and distilled on a column.

Table 1

Figure 1

Figure 1: Figure 1

Experimental characteristic	Amount of isobutylene, l	Space velocity, hr^{-1}	Conversion, %	Temp., °C	Amount of BF$_3$, g	d_4^{20}	n_D^{20}	Octane number
Without BF$_3$ feed	50	60	97	20	13	0.7940	1.4471	84
Without BF$_3$ feed	50	60	97	20	3.5	0.7790	1.4405	
Without BF$_3$ feed	50	60	95.5	70	4	0.7581	1.4309	
Without BF$_3$ feed	50	60	86	100	3.5	0.7412	1.4233	
Without BF$_3$ feed	50	300	32	100	3.5	0.7331	1.4190	
Without BF$_3$ feed	50	60	65	150	4	0.7376	1.4195	85
With BF$_3$ feed	50	60	30	150	5	0.7165	1.4120	

Fig. 1 shows that at a space velocity of 60 hr^{-1}, as the temperature rises the conversion of isobutylene decreases from 97 to 65%. Evidently, the surface of silica gel at 150° retains boron fluoride less strongly than at 20, 70, and 100°. The amount of the fraction $>$ 185° also falls with increasing temperature, from 52 to 8%, while the 98-126° fraction increases and reaches 37%.

Fig. 1. Effect of temperature on the conversion of isobutylene (1) and on the yield of polymer fractions at a space velocity of 60 hr^{-1} with the catalyst BF$_3$ on silica gel.
Fractions: 2—98-126°; 3—170-185°; 4—> 185°

Thus, at a higher temperature the polymer obtained is lighter, which is also confirmed by Table 1, where the physical constants of the polymers obtained are given.

Figure 2

Figure 2: Figure 2

Fig. 3. Dependence of the fractional composition of isobutylene polymer on the space velocity with the catalyst BF_3 on silica gel at 100°: 1—60 h^{-1}; 2—300 h^{-1}

Figure 3: Fig. 3. Dependence of the fractional composition of isobutylene polymer on the space velocity with the catalyst BF_3 on silica gel at 100°: 1—60 h^{-1}; 2—300 h^{-1}

In Fig. 2 are shown the fractional-distillation curves of two polymers. The first, obtained with a catalyst containing 13 g of BF_3 (adsorption at 20°), is considerably heavier than the second polymer, obtained with 3.5 g of BF_3 on silica gel (see Table 1). Consequently, with an increase in the amount of boron fluoride on the silica gel, the polymerization process proceeds more deeply.

In Fig. 3 it is seen that the polymer formed at a space velocity of 300 hr^{-1} contains 11% more of the 98-126° fraction, 9% less of the 170-185° fraction, and 5% less of the $> 185°$ fraction in comparison with the polymer obtained at a space velocity of 60 hr^{-1}.

Fig. 2. Fractional composition of isobutylene polymer obtained at 20° and a space velocity of 60 hr^{-1}, as a function of the amount of BF_3 on silica gel: 1—13 g; 2—3.5 g

From the material presented it follows that, with an increase in space velocity or with a decrease in the contact time with boron fluoride, the degree of polymerization of isobutylene will decrease.

The polymerization of isobutylene was also studied at 150° with the supply of boron fluoride from the molecular compound $K_2SO_4 \cdot BF_3$, first (2) used by us for this reaction. This compound was obtained (3) by the action of boron fluoride on calcined K_2SO_4 salt at 235°. The samples were brought to constant weight.

In each experiment, 45 g of silica gel, 50 l of isobutylene, and 17.8 g of $K_2SO_4 \cdot BF_3$, containing 5 g of boron fluoride, were used. Silica gel was placed in the reactor, and then isobutylene was passed from the gasometer at a space velocity of 60 hr^{-1}, while boron fluoride was supplied from $K_2SO_4 \cdot BF_3$, which underwent decomposition to K_2SO_4 and BF_3 at 360-390° in an electrically heated furnace.

The physicochemical constants of the polymer obtained were: d_4^{20} 0.7165, n_D^{20} 1.4120, bromine number 132, molecular weight 119.7, unsaturated 98.7% (the molecular weight was determined by the cryoscopic method). From Table 1 it is evident that the polymer obtained with the feeding of boron fluoride is lighter than the polymer obtained without feeding boron fluoride.

Fig. 3. Dependence of the fractional composition of isobutylene polymer on the space velocity with the catalyst BF_3 on silica gel at 100°: 1—60 h^{-1}; 2—300 h^{-1}

Table 2 gives the results of spectral analysis of some polymer fractions that were studied by the method of combinational light scattering.

Table 2

Catalyst	Temp., °C	Space velocity, h^{-1}	Fraction, °C	Chemical composition	B.p. according to literature data (4), °C
BF_3 on silica gel	20	60	98—106	2,4,4-trimethylpentene-12,4,4-trimethylpentene-2	101.36104.85
BF_3 on silica gel	20	60	108—120	3,4,4-trimethylpentene-22,3,4-trimethylpentene-22,3,4-trimethylpentene-1	112.3116.26117.15
BF_3 on silica gel	150	60	98—106	2,4,4-trimethylpentene-12,4,4-trimethylpentene-2	101.36104.85

The data of Table 2 show that the process of polymerization of isobutylene is accompanied by isomerization, as a result of which 3,4,4-trimethylpentene-2 appears, followed by 2,3,4-trimethylpentene-2 and 2,3,4-trimethylpentene-1.

The duration of catalyst operation was investigated at 20 and 100° with a space velocity of 60 h^{-1}. In the first case the adsorption of boron fluoride on silica gel was carried out at 20°. The catalyst obtained consisted of 14 g BF_3 on 45 g silica gel. For the experiment, which lasted 158.3 h, 1038 l of isobutylene were taken.

Figure 4 shows a very high conversion of isobutylene, from 98 to 90% at the end of the experiment. During 158.3 h of operation, 2217 g of polymer were obtained at an average conversion of 94.7%. The physicochemical constants of the polymer (average sample) were: d_4^{20} 0.7682, n_D^{20} 1.4335, octane number 85.

Figure 4

Figure 4: Figure 4

The octane number was determined by the motor method on a "Waukesha" unit.

The duration of catalyst operation was also studied at 100°. The catalyst consisted of 7.5 g of boron fluoride on 45 g of silica gel (adsorption at 100°). For this study, which lasted 33.3 h, 200 l of isobutylene were taken. At an average conversion of 74.3%, there was obtained

335 g of polymer. The physical constants of the polymer obtained at the end of the experiment were: d_4^{20} 0.7422, n_D^{20} 1.4238.

It follows from the above that the boron fluoride catalyst on silica gel remains active for a prolonged time and operates effectively at

Fig. 4. Conversion of isobutylene (1) and yield of polymer fractions as a function of the operating time of the BF_3 catalyst on silica gel at 20° and a space velocity of 60^{-1}. Fractions: 2—100-126°; 3—170-185°; 4—>185°

100°. The high conversion of isobutylene at the end of the study at 20° demonstrates the possibility of very prolonged and effective operation of the investigated catalyst after 158.3 hours of service without its regeneration.

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