Academician A. V. TOPCHIEV and L. A. ALYABINA

1958

SovietRxiv

Figure 1

Figure 1: Figure 1

Abstract

Full Text

CHEMISTRY

Academician A. V. TOPCHIEV and L. A. ALYABINA

POLYMERIZATION OF ISOBUTYLENE UNDER THE INFLUENCE OF BORON FLUORIDE ON ALUMINUM OXIDE

This article contains the results of an investigation of the process of polymerization of isobutylene under the action of boron fluoride adsorbed on aluminum oxide, as a function of temperature, space velocity, the support, and the duration of operation of the catalyst. The experiments were carried out at atmospheric pressure.

Isobutylene was obtained by dehydration of isobutyl alcohol (b.p. 107°) over aluminum oxide at 400°. Analysis showed that the resulting gas contained 97-98% isobutylene. Boron fluoride was obtained by the method described in papers ([1], [5]).

The experiments (without feeding BF_3) were carried out at space velocities of 60 and 300 hr^{-1} at temperatures of 20, 70, 100, and 150°. Aluminum oxide was dried for 3 hr at 250°, after which it was used for adsorption of boron fluoride, which was carried out at 150°. The samples were brought to constant weight.

Fig. 1. Effect of temperature on the conversion of isobutylene (1) and on the yield of fractions of the polymer at a space velocity of 60 hr^{-1} with BF_3 catalyst on aluminum oxide. 2 –fraction 98-126°, 3 –fraction 170-185°, 4 –fraction >185°.

In each experiment 50 l of isobutylene and 68 g, or 100 cm^3, of aluminum oxide with 20-21 g of adsorbed boron fluoride (29-31%) were used. The catalyst—boron fluoride on aluminum oxide—was placed in a reactor 40 cm long and 2.6 cm in diameter, through which isobutylene from a gasometer was then passed. At the outlet from the reactor a tube filled with pieces of NaOH was attached for trapping boron fluoride. The reactor was provided with electric heating. For experiments at 20°, cooling with water was used. The polymer obtained was washed, dried, and distilled on a column.

As can be seen from Fig. 1, at a space velocity of 60 hr^{-1} and at 20, 70, 100, and 150° the conversion of isobutylene is 94–98%. With increasing temperature the yield of the fraction >185° decreases from 51 to 40%, that of the fraction 170–185° from 40 to 27%, while the yield of the fraction 98–126° increases from 3.2 to 25.6%.

Thus, with increasing temperature the degree of polymerization of isobutylene decreases, which is also evident from Table 1, in which the physicochemical properties of the polymers and the experimental conditions are reported.

Table 1 presents the results of the investigation of two polymers obtained at 150° with space velocities of 300 and 60 hr^{-1} (without feeding BF_3). In the latter experiment the polymer is heavier. Consequently, with increasing time

contact with boron fluoride or with a decrease in the space velocity of isobutylene polymerization proceeds more deeply.

Polymerization of isobutylene was also studied at 150° with the introduction of boron fluoride from the molecular compound $K_2SO_4 \cdot BF_3$ as the source of boron fluoride. The compound $K_2SO_4 \cdot BF_3$, first used by us (^{2}) for

Table 1

Characteristics of the experiment	Amount of isobutylene, l	Space velocity, h^{-1}	Conversion, %	Temperature, °C	Amount of BF_3, g	d_4^{20}	n_D^{20}	Initial boiling point, °C	Fraction with initial boiling point — 106°, vol. %	Fraction 106 — 126°, vol. %
Without introduction of BF_3	50	60	98	20	20.5	0.7915	1.4479	105	0.8	2.4
Without introduction of BF_3	50	60	98	70	20	0.7745	1.4387	101	1.2	4

Characteristics of the experiment	Amount of isobutylene, l	Space velocity, h^{-1}	Conversion, %	Temperature, °C	Amount of BF$_3$, g	d_4^{20}	n_D^{20}	Initial boiling point, °C	Fraction with initial boiling point — 106°, vol. %	Fraction 106 — 126°, vol. %
Without introduction of BF$_3$	50	60	98	100	21	0.7638	1.4340	99	6.4	5.2
Without introduction of BF$_3$	50	60	94	150	21	0.7560	1.4294	75	14.4	11.2
Without introduction of BF$_3$	50	300	84	150	20	0.7339	1.4197	72	26	9.6
With introduction of BF$_3$	50	60	65	150	5	0.7190	1.4132	67	48.9	16
With introduction of BF$_3$	50	60	70	150	20	0.7216	1.4135	72	36	23.4

Characteristics of the experiment	Amount of isobutylene, l	Space velocity, h^{-1}	Conversion, %	Temperature, °C	Amount of BF_3, g	d_4^{20}	n_D^{20}	Initial boiling point, °C	Fraction with initial boiling point — 106°, vol. %	Fraction 106 — 126°, vol. %
With introduction of BF_3	250	60	67	150	5	0.7168	1.4126	67	49.2	14.8

the polymerization reaction of isobutylene was obtained ([3,4]) by interaction of dry boron fluoride with calcined K_2SO_4 salt at 235°. The samples were brought to constant weight.

Fig. 2 Fig. 3

Fig. 2. Fractional composition of isobutylene polymer obtained with the catalyst BF_3 on aluminum oxide at 150° and a space velocity of 60 h^{-1}, with introduction of BF_3 (1 –5 g, 2 –20 g) from $K_2SO_4 \cdot BF_3$ and without introduction (3–20 g)

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 aluminum oxide at 150° and a space velocity of 60 h^{-1}. 2 –fr. 67–126°, 3 –fr. 170–185°, 4 –fr. $> 185°$

For experiments with introduction of boron fluoride from $K_2SO_4 \cdot BF_3$, 68 g (100 cm^3) of dry aluminum oxide was placed in the reactor. Then boron fluoride in an amount of 5 or 20 g and 50 l of isobutylene from a gasometer were introduced simultaneously into the reactor at a space velocity of 60 h^{-1} (see Table 1). Boron fluoride was obtained by decomposition, respectively, of 17.8 and 71.2 g of $K_2SO_4 \cdot BF_3$ at 360–390°.

The physicochemical constants of the polymer obtained were as follows: d_4^{20} 0.7190, n_D^{20} 1.4132, M 119.7, bromine number 132, unsaturates 98.7%, octane number 87. The molecular weight was determined by the cryoscopic method; the octane number, by the motor method on a "Waukesha" apparatus.

Figure 2 presents the curves of fractional distillations of three polymers obtained at 150° with introduction of boron fluoride from $K_2SO_4 \cdot BF_3$ and without introduction. The polymers obtained with introduction of 5 and 20 g of boron fluoride are considerably lighter than the polymer obtained with 20 g of boron fluoride but without introduction (see Table 1).

From the material presented it follows that, in the polymerization of isobutylene with introduction of boron fluoride from the molecular compound $K_2SO_4 \cdot BF_3$, the degree of polymerization of isobutylene decreases.

All polymers obtained at 150° contained 6–13% of the 72–100° fraction, the presence of which is explained by the destructive effect of the alumina support.

The duration of operation of the boron fluoride catalyst on alumina was studied at 150° with the supply of boron fluoride from the molecular compound $K_2SO_4 \cdot BF_3$.

For the experiment, which lasted 41.5 hours, 68 g of alumina, 17.8 g of $K_2SO_4 \cdot BF_3$, containing 5 g of boron fluoride, and 250 l of isobutylene were taken (see Table 1).

It is seen from Fig. 3 that the polymer obtained is very light, since it contains 62.5–65.6% of the fraction with b.p. 67–126° and only 5% of the fraction $> 185°$. The average conversion of isobutylene was 67%. The octane numbers of the 98–106 and 170–185° fractions were, respectively, 100 and 90. The physicochemical constants of the polymer were as follows: d_4^{20} 0.7168, n_D^{20} 1.4126, bromine number 136, molecular weight 116, unsaturates 98.6%, octane number 87.

The investigation showed that the catalyst remains active for a long time and operates effectively at 150° without regeneration. The resulting polyisobutylene may be used as a component of motor fuel, as was noted in the work with silica gel (1).

Fig. 4. Effect of the support on the conversion of isobutylene during polymerization with a BF_3 catalyst at 150° and a space velocity of 60 h^{-1}. 1 –BF_3, 2 –alumina and BF_3, 3 –activated carbon and BF_3

Table 2 gives the chemical composition of certain polymer fractions, determined by optical analysis using the combinational light-scattering method.

Table 2

Catalyst	Experiment temperature, °C	Space velocity, h^{-1}	B.p. of fraction, °C	d_4^{20}	n_D^{20}	Chemical composition	B.p. according to (6), °C
BF_3 on alumina	150	60	98–106	0,7180	1,4117	2,4,4-Trimethylpentene-12,4,4-Trimethylpentene-2	101,36104,85

Catalyst	Experiment temperature, °C	Space velocity, h^{-1}	B.p. of fraction, °C	d_4^{20}	n_D^{20}	Chemical composition	B.p. according to (6), °C
Same	150	60	108–120	0,7350	1,4222	3,4,4-Trimethylpentene-2 2,3,4-Trimethylpentene-2 2,3,4-Trimethylpentene-1	112,3 116,26 117,15

As is seen from Table 2, the process of isobutylene polymerization is accompanied by an isomerization reaction, owing to which 3,4,4-trimethylpentene-2 is formed, then 2,3,4-trimethylpentene-2 and 2,3,4-trimethylpentene-1. In experiments at 150° the 108–126° fraction amounts to 16–23% (see Table 1).

For experiments on the effect of the support, 68 g of alumina dried at 250° or 20 g (100 cm^3) of activated charcoal dehydrated under vacuum at 300° were used. In each experiment at 150°, 5 g of boron fluoride, obtained by decomposition of 17.8 g of $K_2SO_4 \cdot BF_3$, was simultaneously fed into the reactor, and 50 l of isobutylene was passed through at a rate of 6 l/h.

As can be seen from Fig. 4, in the absence of a support the conversion of isobutylene decreases sharply with time and reaches 18.7%; in experiments with supports, however, the conversion either increases to 96% (with activated carbon) or remains within the range 61–71% (with aluminum oxide).

Thus, in the polymerization of isobutylene with boron fluoride, it is advisable to use such supports as activated carbon and aluminum oxide.

Received
2 VII 1957

REFERENCES

[1] A. V. Topchiev, L. A. Alyavdina, I. A. Strakhov, Inventor' s Certificate No. 96995 (15 VII 1952). [2] A. V. Topchiev, L. A. Alyavdina, B. M. Tumerman, Inventor' s Certificate No. 72392 (28 X 1947). [3] R. Baumgarten, E. Müller, Ber., 69, 2688 (1936). [4] P. Baumgarten, H. Hennig, Ber., 72, 1743 (1939). [5] A. V. Topchiev, L. A. Alyavdina, DAN, 119, No. 3 (1958). [6] R. D. Obolentsev, *Physical Constants of Hydrocarbons of Liquid Fuels and Oils*, Moscow-Leningrad, 1953.

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.