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Abstract

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ON THE POLYMERIZATION AND CYCLIZATION REACTION OF ISOBUTYLENE

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The polymerization of olefins with different numbers of carbon atoms proceeds at low temperatures, atmospheric and elevated pressures in the presence of various catalysts ([1],[2]) possessing acidic properties.

Thermodynamic data on the polymerization of isobutylene show that at 100—200° this reaction proceeds to a considerable extent.

Table 1

Value of K_p for the reaction $2\,i\text{-}C_4H_8 \rightleftarrows C_6H_4(CH_3)_2 + 3H_2$ at $P = 1$ atm

	At 400°K	At 500°K	At 600°K	At 700°K
o-Xylene	$1,23 \cdot 10^2$	$3,47 \cdot 10^3$	$3,32 \cdot 10^4$	$1,78 \cdot 10^5$
m-Xylene	$4,37 \cdot 10^2$	$9,1 \cdot 10^3$	$7,75 \cdot 10^4$	$3,8 \cdot 10^5$
n-Xylene	$1,8 \cdot 10^2$	$4,03 \cdot 10^2$	$3,47 \cdot 10^4$	$1,66 \cdot 10^5$
K_{cm}	$7,4 \cdot 10^2$	$16,1 \cdot 10^3$	$14,44 \cdot 10^4$	$7,24 \cdot 10^5$

An increase in temperature leads to a decrease in catalyst activity owing to its poisoning by resinous products.

H. Waterman and co-workers ([3]) studied the polymerization of isobutylene on aluminosilicate catalysts and showed that the polymerization products obtained on synthetic and natural aluminosilicates are identical in composition. B. A. Kazanskii and M. I. Rozengart ([4]) studied the polymerization of butylenes on an aluminosilicate catalyst and showed that the principal products are dimers and trimers. According to these authors, the rate of polymerization of isobutylene is considerably higher than that of butylene. At 200°, isobutylene is converted into polymers in a yield of about 60.0%. The polymerization of butylenes on aluminosilicate catalysts is accompanied by isomerization with the formation of various isomeric octenes. G. N. Maslyanskii and co-workers ([4a]) showed that over an aluminosilicate catalyst, butylene at 370° forms olefinic hydrocarbons, and at 450—500°—aromatic hydrocarbons. A. V. Topchiev and B. M. Tumerman ([5]) studied the polymerization of isobutylene over boron fluoride ethyl

etherate deposited on activated carbon at temperatures from 5 to 130°, with the formation mainly of trimers. According to Ya. M. Paushkin and co-workers ([6]), in the presence of boron fluoride isobutylene polymerizes with the formation of higher polymers. In the products of the catalytic polymerization of isobutylene over various catalysts, the presence of di-, tri-, tetra-, and pentamers has been established.

The brief literature review presented shows that the polymerization of isobutylene readily proceeds over various catalysts at 20—200°, with the formation of di-, tri-, tetra-, and pentamers.

Thermodynamic calculations show that for isobutylene not only the polymerization reaction is possible, but also the aromatization reaction (see Table 1).

The thermodynamic analysis we have carried out, both of the overall reaction and of its individual stages, leads to the following main conclusions:

1. The gross reaction $2C_4H_8 \rightleftarrows 3H_2 + C_6H_4(CH_3)_2$ (*o*-, *m*-, *p*-) (Table 1) is possible (at $P = 1$ atm), with practically complete conversion of isobutylene already at low temperatures (120-130°), with preferential formation of *m*-xylene.

The equilibrium of the cyclization stage of isooctene into isomeric (cis- and trans-, *o*-, *m*-, *p*-) dimethylcyclohexanes is practically shifted to the right irrespective of temperature.

2. The degree of dimerization of isobutylene decreases with increasing temperature. With increasing pressure, the reaction is shifted somewhat to the right.

3. The equilibrium yield of the mixture of xylenes upon dehydrogenation of isomeric (cis- and trans-, *o*-, *m*-, *p*-) dimethylcyclohexanes increases with increasing temperature. Practically complete conversion can be achieved at $T = 600$°K (at $P = 1$ atm).

The possibility of forming a mixture of xylenes from isobutylene will be determined by the conditions under which the last stage of the process is carried out —the dehydrogenation stage.

An increase in pressure necessitates an increase in the process temperature.

The ratio of *o*-, *m*-, *p*-xylenes is expressed, respectively, as follows: at 600°K, $1 : 1.25 : 0.80$; at 700°K, $1 : 1.1 : 0.88$.

When oxide catalysts are used, the process temperature (even at $P = 1$ atm) must be higher, which is connected with the conditions of hydrogen desorption.

It is highly desirable to carry out the process at elevated pressures, since in this case: a) the dimerization stage of isobutylene is facilitated; b) longer aromatization cycles are ensured.

On the basis of the literature material and the calculation data presented above, one should expect the possibility of carrying out the aromatization reaction proceeding over aromatization catalysts. It is known that the latter consist of chromium oxide or molybdenum oxide deposited on active alumina.

The present communication is devoted to the study of the polymerization and aromatization reaction over an MoO_3—Al_2O_3 catalyst.

Experimental Part

The isobutylene for the polymerization and aromatization process was obtained by passing isobutyl alcohol over active alumina at 350°. The isobutylene thus obtained contained 97-99% isobutylene proper.

The catalyst for the process was MoO_3 deposited on Al_2O_3. The experiments were carried out in a flow system.

As can be seen from the data presented in Table 2, with an increase in temperature from 120 to 385° the yields of liquid products decrease. At 300°, hydrogen already appears in the residual gas. The refractive index of the liquid products increases. A further increase in temperature to 450° practically does not change the yield of liquid products, but the refractive index of the latter increases; the hydrogen content in the residual gas increases.

The data presented in Table 3 on the analysis of the liquid products, in comparison with the data presented in Table 2, make it possible to suppose that up to 200° isobutylene over the mixed MoO_3/Al_2O_3 catalyst undergoes polymerization with the formation of di- and tri-isobutylene.

Already in experiments carried out at low temperatures, an increase in the refractive index is observed in the fraction boiling above 170°. With an increase in the experimental temperature, the refractive index rises. In experiments carried out at 300 and 400°, fractions boiling respectively above 170 and 132° have high refractive indices.

Spectral analysis of the fraction boiling at 132—148°, obtained in the experiment at 400°, showed the presence of about 10% olefins and 90% aromatic hydrocarbons, including approximately: 25% *p*-xylene, 35% *m*-xylene, and 30% *o*-xylene.

Table 2

Effect of temperature on the yield and composition of polymerization products (space velocity 100, P atm)

Temperature, °C	Isobutylene reacted, %	Yield of liquid products, ml/m^3	Refractive index, n_D^{20}	Condensation products on catalyst, g	Composition of off-gas, vol. %	Composition of off-gas, vol. %	Composition of off-gas, vol. %	Composition of off-gas, vol. %	Composition of off-gas, vol. %
					CO_2	CO	H_2	$C_{nH_{2n}}$	$C_{nH_{2n+2}}$
120	91.0	2740.0	1.4281	2.17	1.14	0.36	–	98.5	–
200	72.4	1950.0	1.4258	2.50	1.10	0.40	–	98.5	–
300	26.7	530.0	1.4348	1.23	1.20	0.30	1.1	97.4	–
350	18.6	197.0	1.4415	1.60	1.06	0.10	3.0	93.5	2.4
385	21.0	35.7	1.4880	2.10	1.20	0.20	8.0	89.0	1.6
400	22.2	37.7	1.4991	2.00	1.55	0.10	11.0	84.55	2.7
425	23.7	40.0	1.5120	–	1.55	0.10	14.4	81.75	2.2
450	21.5	36.0	1.5220	2.50	1.55	0.10	21.5	70.05	6.8

Table 3

Yields and characteristics of fractions obtained by passing isobutylene over the catalyst at different temperatures

Boiling limits of fractions, °C	Product obtained at 120°	Product obtained at 120°	Product obtained at 120°	Product obtained at 120°	Product obtained at 200°	Product obtained at 200°	Product obtained at 200°	Product obtained at 200°
	yield, wt. %	n_D^{20}	ρ_{20}^{20}	bromine number	yield, wt. %	n_D^{20}	ρ_{20}^{20}	bromine number
42–102	–	–	–	–	–	–	–	–
72–102	9.25	1.4128	–	–	12.1	1.4118	–	–
102–109	31.20	1.4158	0.7253	124.1	42.2	1.4181	0.7289	134.9
109–115	1.85	1.4182	–	–	12.0	1.4211	–	120.7
115–120	4.85	1.4198	–	–	6.6	1.4262	–	–
120–132	0.55	1.4330	–	–	>120 –22.8	1.4410	–	96.9

Boiling limits of fractions, °C	Product obtained at 120°	Product obtained at 120°	Product obtained at 120°	Product obtained at 120°	Product obtained at 200°	Product obtained at 200°	Product obtained at 200°	Product obtained at 200°
132–170	48.50	1.4343	0.7682	63.25	–	–	–	–
>170	3.00	–	–	–	–	–	–	–
Losses	0.80	–	–	–	2.3	–	–	–

Boiling limits of fractions, °C	Product obtained at 300°	Product obtained at 300°	Product obtained at 300°	Product obtained at 300°	Product obtained at 400°	Product obtained at 400°	Product obtained at 400°	Product obtained at 400°
	yield, wt. %	n_D^{20}	ρ_{20}^{20}	bromine number	yield, wt. %	n_D^{20}	ρ_{20}^{20}	bromine number
42–102	8.9	1.4080	–	162.0	69–132° 19.0	1.4325	–	–
72–102	–	–	–	–				
102–109	26.8	1.4168	0.7309	151.7	132–148° 17.3	1.4858	–	39.2
109–115	29.1	1.4208	0.7357	148.0		–	–	–
115–120	7.8	1.4241	–	155.5	148–170° 19.95	1.5040	–	–
120–132	3.4	1.4314	–	–	>170° –48.6	1.5461	–	–
132–170	5.9	–	–	108.2	–	–	–	–
>170	170–200° 8.2	1.4757	–	62.55	–	–	–	–
>170	above 200° 7.2	1.5350	–	–	–	–	–	–

Boiling limits of fractions, °C	Product obtained at 300°	Product obtained at 300°	Product obtained at 300°	Product obtained at 300°	Product obtained at 400°	Product obtained at 400°	Product obtained at 400°	Product obtained at 400°
Losses	2.7	—	—	—	1.5			

A decrease or increase in the space velocity within the range 50–200, in experiments carried out at 400°, affects the reduction in product yields; to a greater extent, an increase in space velocity affects the decrease in the refractive index. Thus, for example, the product,

obtained at 400° and a space velocity of 50 has $n_D^{20} = 1.4976$; at a space velocity of 100, $n_D^{20} = 1.4991$; and at 200, respectively, 1.4770.

In the course of the experiments with the MoO_3—Al_2O_3 catalyst, a decrease in catalyst activity with time was observed, especially at temperatures of 300 and 400°. Without a significant decrease in activity at these temperatures, the catalyst operates for 120–180 min, after which its activity begins to decline. Regeneration of the catalyst can be carried out, after removing it from the reaction tube, by calcination in a muffle at 450–500° for 120–180 min in an atmosphere of air or in a stream of inert gas with air added to the latter so that the oxygen content in the gas is about 5%, at the same temperatures.

Table 4

Influence of catalyst regeneration on its activity (amount of catalyst 60 ml, t— 400°, space velocity 100, duration of the working cycle 120 min)

Name of regeneration	Yield of liquid products, ml/m^3	Yield of liquid products, g/m^3	Refractive index	Product of condensation on the catalyst, g	CO_2, vol. %	CO, vol. %	H_2, vol. %	$C_{nH_{2n}}$, vol. %	$C_{nH_{2n+2}}$, vol. %
Fresh catalyst	37.7	—	1.4991	1.95	1.55	0.10	10.95	84.7	2.7

Name of regeneration	Yield of liquid products, ml/m^3	Yield of liquid products, g/m^3	Refractive index	Product of condensation on the catalyst, g	CO_2, vol. %	CO, vol. %	H_2, vol. %	$C_{nH_{2n}}$, vol. %	$C_{nH_{2n+2}}$, vol. %
After I regeneration	62.5	50.3	1.4920	1.80	1.10	0.40	12.00	83.8	2.7
After II regeneration	66.0	52.3	1.4921	1.90	1.20	0.50	16.30	79.20	2.8
After III regeneration	53.0	40.0	1.4976	1.70	–	–	–	–	–
After IV regeneration	66.0	–	1.4905	1.90	0.70	–	16.10	80.40	2.80
After V regeneration	–	–	1.4885	1.70	1.00	–	16.80	79.20	3.0

Name of regeneration	Yield of liquid products, ml/m^3	Yield of liquid products, g/m^3	Refractive index	Product of condensation on the catalyst, g	CO_2, vol. %	CO, vol. %	H_2, vol. %	$C_{nH_{2n}}$, vol. %	$C_{nH_{2n+2}}$, vol. %
After VI regeneration	57.5	43.3	1.4857	1.60	–	–	–	–	–
After VII regeneration	61.0	51.60	1.4860	1.80	0.90	0.10	15.70	80.70	2.6
After VIII regeneration	70.0	54.6	1.4848	1.60	–	–	–	–	–
After IX regeneration	72.7	55.6	1.4840	1.80	1.10	0.20	13.40	82.40	2.90

In order to confirm the unchanged activity of the catalyst upon regeneration, more than 10 cycles of aromatization of isobutylene and its subsequent regeneration were carried out on one and the same portion of catalyst.

As is evident from the data given in Table 4, the activity of the catalyst after regeneration does not change.

The process on the regenerated catalyst proceeds quite stably.

The results obtained allow the following conclusions to be drawn:

1. The possibility of polymerization with subsequent aromatization of isobutylene over a molybdenum-aluminum catalyst has been demonstrated for the first time.
2. At temperatures up to 200°, over a molybdenum-aluminum catalyst, a polymerization reaction proceeds with the formation of di-, tri-, and higher polymers. As the temperature is raised, the direction of the reaction changes, and aromatic hydrocarbons appear in the catalyzate.
3. In the fraction boiling at 132-148°, obtained by passing isobutylene over a molybdenum-aluminum catalyst at 400°, up to 60% of para- and meta-xylene was found, or about 6 g per 1 m^3 of gas.

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