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Abstract

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CATALYTIC DEHYDROGENATION OF ISOPROPYLBENZENE

Derivatives of aromatic hydrocarbons with unsaturated radicals in the side chains are widely used in the synthetic-rubber, plastics, and other sectors of the national economy. The most convenient and cheapest method for obtaining these monomers is the catalytic dehydrogenation of alkylbenzenes, which has proved to be of great practical importance. A. A. Balandin and G. M. Marukyan (1) studied the dehydrogenation of isopropylbenzene over a copper-chromium catalyst with dilution by carbon dioxide. At 625°, the yields of α-methylstyrene amounted to 50% based on the isopropylbenzene passed through. In the dehydrogenation of isopropylbenzene over alumina-chromium and iron-magnesium catalysts with dilution by water vapor (2), the yields of α-methylstyrene at 625° were about 71% based on the reacted isopropylbenzene, with an overall conversion of 44%.

The aim of the present work was to study the kinetics of the reaction and the influence of the structure of the hydrocarbon molecule on the reaction rate. The experiments were carried out by the flow method over a mixed oxide catalyst (3) with dilution by water vapor. The catalyst, in an amount of 10 ml, was placed in a quartz tube. The substance and water were fed from a syringe by means of an automatic device. Before entering the reaction tube, the water vapor was superheated to 300°. The degree of dilution with water vapor in all experiments was kept constant and was 1 : 2 (by weight). The liquid products were condensed in a receiver, and the gas was collected in a cylindrical gasometer. The volume

Table 1

Dehydrogenation of isopropylbenzene, feed rate 0.42 ml in 3 min
(800 ml/l · h), dilution with water vapor 1 : 2 (by weight)

Catalyst grain size, mm	Temp., °C	n_D^{20} of the catalyzate	α-Methylstyrene in the catalyzate, %	H_2 (N.T.P.) in 3 min	Degree of dehydrogenation by H_2, %	CO_2	C_nH_{2n}	H_2
1.5	516	1.4963	12.0	7.7	11.4	0.4	none	99.6
1.5	520	1.4981	15.5	9.8	15.1	2.0	»	98.0
1.5	544	1.5051	30.0	20.6	30.1	4.4	»	95.2
1.5	550	1.5096	39.5					
1.5	568	1.5196	59.0	42.9	67.5	4.2	0.6	95.0
1.5	582	1.5250	70.5	54.7	81.0	5.8	0.6	95.0
3.0	516	1.4958	13.0	6.5	10.1			
3.0	528	1.5000	19.5	12.0	18.2	1.6	none	98.0
3.0	544	1.5051	30.0	20.5	31.8	2.6	0.4	96.5
3.0	550	1.5069	34.0	20.8	31.6	2.4	0.4	97.0
3.0	562	1.5143	49.0	33.6	50.9	4.2	0.8	
3.0	607	1.5310	83.0	72.1		9.0	2.0	88.5
5.0	524	1.4991	17.5	11.8	17.2	0.8	–	99.0
5.0	538	1.5033	27.5	18.0	27.3	1.8	–	98.2
5.0	546	1.5061	32.0	23.4	34.7	5.6	0.2	94.0
5.0	554	1.5110	42.5	27.1	41.1	2.2	0.2	96.6
5.0	566	1.5157	52.0	38.8	57.4	5.2	–	94.8

the gas was measured after 3 min with an accuracy of up to 2 ml and reduced to normal conditions (N.T.P.). In the collected gas, the content of CO_2 was determined by absorption with KOH solution, unsaturated compounds by a solution of mercuric sulfate in sulfuric acid, and hydrogen and saturated hydrocarbons by combustion over copper oxide. The catalyst obtained was colorless. The content of α-methylstyrene in the catalyzate was determined from the refractive index and checked by the Rosenmund bromine-number method (ˆ4). Close agreement was observed between the amounts of hydrogen evolved and α-methylstyrene formed (Table 1). After each experiment the catalyst was purged with a steam-air mixture and with air for 30 min. The activity of the catalyst was checked after each series of experiments on the dehydrogenation of isopropylbenzene under constant conditions and remained constant throughout all the experiments. The initial isopropylbenzene boiled at 152.5-153°; d_4^{20} 0.8620, n_D^{20} 1.4947; literature data: b.p. 152.5°, d_4^{20} 0.8620, n_D^{20} 1.4947 (^{5},6).

Fig. 1. Logarithmic dependence between the reaction-rate constant and $1/T$

The kinetics of the dehydrogenation of isopropylbenzene was studied at temperatures of 500-550° and a feed rate of 0.42 ml in 3 min, which corresponds to a space velocity of 800 ml per 1 l of catalyst per hour. The reaction rate

Fig. 1. Logarithmic dependence between the reaction-rate constant and $1/T$

Figure 1: Fig. 1. Logarithmic dependence between the reaction-rate constant and $1/T$

was determined from the hydrogen evolved. The contact gas consists mainly of hydrogen with a small amount of CO_2 (from 0.5 to 2.0%) and unsaturated hydrocarbons (up to 0.4%). Saturated hydrocarbons were not found in the gas (Table 1). From the experimental data, as in (^7), the reaction-rate constants were calculated from the equation

$$\frac{dx}{dt} = k\frac{[A_1]}{[A_1] + z_2[A_2] + z_3[A_3]} \tag{1}$$

in a form suitable for use under flow-system conditions (^7), where z_2 and z_3 are the relative adsorption coefficients of the reaction products. To determine the relative adsorption coefficients under analogous conditions, experiments were carried out to study the rate of dehydrogenation of binary mixtures—of isopropylbenzene with α-methylstyrene and with hydrogen. The relative adsorption coefficients were calculated by formula (^8). The values found for the relative adsorption coefficients are presented in Table 2, from which it is seen that for α-methylstyrene z_2 changes from 3.8 at 520° to 0.95 at 550°. The value of z_3 for hydrogen, equal to 0.7, does not change with temperature.

Table 2

Rate constant for the dehydrogenation of isopropylbenzene k_c and thermodynamic functions of adsorption displacement of isopropylbenzene by α-methylstyrene

Temp., °C	z_2	k_c, ml/min	$-\Delta F$, cal/mol	ΔH, kcal/mol	ΔS, cal/g · mol
520	3.8	0.7759	2092	60.0	77
530	2.4	0.9790	1395	60.0	74.6
540	1.5	1.227	654	60.0	72.8
550	0.95	1.570	−83	60.0	71.0

In Fig. 1, constructed from the data of Table 1, the logarithmic dependence of the reaction-rate constant on the reciprocal absolute temperature is shown. The points fall on a straight line—the Arrhenius equation is obeyed. The activation energy calculated from the reaction-rate constants is 30.3 kcal/mol, and the pre-exponential factor is $\lg k_0 = 6.25$.

To determine the region in which the catalyst operates—kinetic or diffusion—experiments were carried out with different degrees of grinding

Fig. 2. Effect of catalyst grain size on the yields of α-methylstyrene at different temperatures. *a*—1.5 mm; *b*—3.0 mm; *v*—5.0 mm

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of the catalyst. The grain diameter was 1.5, 3, and 5 mm (Table 1). The experiments showed that the catalyst grain size has no effect on the process. Figure 2 shows the dependence of the yields of α-methylstyrene on temperature for different catalyst samples. The points fall on one and the same curve. Thus, it may be concluded that the experiments are carried out in the kinetic region. From the values found for the relative adsorption coefficients, the changes in the free energy ΔF, heat content ΔH, and entropy ΔS upon adsorption displacement from the active dehydrogenation centers were calculated.

Along with the study of the kinetics of the dehydrogenation reaction, experiments with isopropylbenzene were carried out at higher temperatures. As was found, the degree of dehydrogenation of isopropylbenzene increases with increasing temperature. At temperatures of 580 and 607°, and a space velocity of 800 ml/g · h, the yields of α-methylstyrene reach 70.5 and 83%, respectively, based on the hydrogen passed (Table 1). The results obtained may be of definite practical interest.

Fig. 2. Effect of catalyst grain size on the yields of α-methylstyrene at different temperatures.
a—1.5 mm; *b*—3.0 mm; *v*—5.0 mm

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