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Abstract

Full Text

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INVESTIGATION OF THE REACTION OF CATALYTIC DEHYDROGENATION OF ISOPENTANE

The reaction of dehydrogenation of isopentane on oxide chromium–aluminum catalysts was investigated in the temperature range 500–600°. The principal feature of the work is the use of the fluidized-bed method for studying the kinetics of the process.

The scheme of the vacuum apparatus with a fluidized catalyst bed is shown in Fig. 1. The reactor (1) was a quartz tube 21 mm in diameter with an expansion in the upper part and with an electric spiral for heating. Catalyst of particle size 0.05–0.1 mm, in an amount of 10–20 ml, was placed on a quartz packing, which was located on a chamotte grate fastened to the pocket for the thermocouple. The catalyst was first dried in a stream of air, then activated for one hour with hydrogen. Isopentane, containing no chromatographically detectable impurities, was fed into the reactor from a thermostated cylinder (2). When isopentane passed through the catalyst, a fluidized bed was formed. Entrainment of the gas by the particles leads to equalization of the temperature and composition of the gas mixture along the length of the bed. Special experiments showed that a regime close to complete mixing of the gas is realized in the reactor ([1],[2]), when the gas composition throughout the bed is the same. The reaction products were withdrawn, through a valve (3) for maintaining the pressure (3) (which had proven itself well under analogous conditions (4)), into previously evacuated flasks (4) and then directed to the apparatus for chromatographic analysis. The total content of hydrocarbons C_2 and higher was found by measuring the pressure in the receivers (5) before and after removal of gases that do not condense over liquid nitrogen. Air and methane were separated on columns with activated carbon (6), using hydrogen as the displacing agent; the hydrogen content was found from the difference between the amount of noncondensing gases and the amount of air and methane. Hydrocarbons C_2–C_5 were

Fig. 1. Scheme of a vacuum apparatus with a fluidized catalyst bed

separated on columns with diisoamyl phthalate (7) and aceto-

nilacetone (8) according to the procedure described in (5). The analysis method made it possible to determine the individual composition of the mixture of C_5 hydrocarbons with a relative accuracy of 3-4%. During rectification of the products on a column with 30 theoretical plates, no hydrocarbons boiling above 40° were found; however, on the chromatogram a peak of an unidentified C_6 hydrocarbon appeared. In the balance, only hydrocarbons appearing on the chromatogram were taken into account. Along with experiments in a fluidized bed, a series of experiments was carried out with a fixed bed of catalyst, of particle size 0.25–0.50 mm, under conditions usually used for studying similar reactions (6–9) (see Table 1). Catalyst No. 1

Table 1

Dehydrogenation of isopentane in fixed and fluidized beds

	Fixed bed ($p =$ 760 mm)	Fixed bed ($p =$ 760 mm)	Fixed bed ($p =$ 760 mm)	Fixed bed ($p =$ 760 mm)	Fixed bed ($p =$ 760 mm)	Fixed bed ($p =$ 760 mm)	Fixed bed ($p =$ 760 mm)	Fluidized bed ($p =$ 100 mm)	Fluidized bed ($p =$ 100 mm)	Fluidized bed ($p =$ 100 mm)	Fluidized bed ($p =$ 100 mm)
	catalyst No. 1 520°	catalyst No. 1 550°	catalyst No. 1 580°	catalyst No. 2 520°	catalyst No. 2 550°	catalyst No. 2 580°	catalyst No. 3 550°	catalyst No. 2 580°	catalyst No. 2 580°	catalyst No. 2 600°	catalyst No. 2 600°
space velocity, vol/vol·h	1.04	1.12	2.74	1.15	0.96	2.30	0.95	0.50	1.01	0.35	0.79
Conversion of isopentane, %	28.1	47.0	60.7	27.6	45.5	54.3	46.5	50.3	39.1	62.2	50.4
Selectivity, %	79.3	65.6	61.7	81.9	66.3	69.0	65.9	63.2	65.9	57.0	59.4

	Fixed bed ($p =$ 760 mm)	Fixed bed ($p =$ 760 mm)	Fixed bed ($p =$ 760 mm)	Fixed bed ($p =$ 760 mm)	Fixed bed ($p =$ 760 mm)	Fixed bed ($p =$ 760 mm)	Fixed bed ($p =$ 760 mm)	Fluidized bed ($p =$ 100 mm)	Fluidized bed ($p =$ 100 mm)	Fluidized bed ($p =$ 100 mm)	Fluidized bed ($p =$ 100 mm)
Consumption of isopentane for formation of reaction products, mol.%:	21.2	28.5	33.0	21.2	27.6	32.8	29.2	21.0	16.0	20.2	17.7
isoamylenes:											
3-methylbutene-1	3.1	2.9	4.2	2.9	2.5	5.0	2.4	1.9	1.7	1.5	1.4
2-methylbutene-1	5.7	8.5	10.4	6.6	9.3	9.8	8.9	7.7	5.2	6.8	5.9
2-methylbutene-2	12.4	17.1	18.4	10.7	15.8	18.0	17.9	12.4	9.1	11.9	10.4
isoprene	1.1	2.3	4.5	1.3	2.5	4.6	1.4	10.8	9.8	15.3	12.2
n-C_5 + C_6	2.6	5.2	8.3	1.5	5.3	5.2	3.0	3.9	1.9	3.4	2.9
Coke	0.7	1.6	2.8	0.4	1.1	2.5	2.7	6.8	3.5	7.0	6.2
Hydrocarbons C_1 – C_4	2.5	9.4	12.1	3.2	9.0	9.2	10.2	7.8	7.9	16.3	10.4

contained 10.2 mol.% Cr_2O_3, 88.1 mol.% Al_2O_3, 1.7 mol.% K_2O. Catalyst No. 2 contained 7.0 wt.% Cr_2O_3, 92.5 wt.% Al_2O_3, 0.5 wt.% K_2O. The properties of catalyst No. 3 are described in (6).

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

As follows from Table 1, the catalysts of different composition studied had similar activity. At 550° and a space velocity of about 1, the yield of isoamylenes based on the isopentane passed was 27.6–29%, the yield of isoprene was 1.5–2.5%, the degree of conversion of isopentane was 46–47%, and the selectivity, calculated as the ratio of the yield of isoamylenes and isoprene to the reacted isopentane, was 65–67%. With an increase in temperature to 580°, the yield of isoamylenes increased to 31–33%, the yield of isoprene rose to 3.5–4.6%, and the maximum selectivity was 65–70%. At 520° and a space velocity of ~1 h^{-1}, the conversion of isopentane was 28%, and the yield of isoamylenes and isoprene was 23%.

Experiments in the fluidized bed at reduced pressures and comparative kinetic experiments in the fixed bed at atmospheric pressure were carried out on catalyst No. 2. Experimental conditions: temperatures 500 and 550°, pressure 100–500 mm Hg in the fluidized bed and 760 mm Hg in the fixed bed. The conversion of isopentane did not exceed 30%.

Figures 2 and 3 show typical product-distribution curves. Along the abscissa is plotted the degree of conversion of isopentane, (y); the difference of ordinates between two neighboring curves, Δy, is equal to the relative number of moles of isopentane consumed for formation of the product. At $y < 0.3$ the composition of the products changes little with conversion depth. The molar ratios $C_1 : C_4$ and $C_2 : C_3$ in the gases are close to unity; evidently, these hydrocarbo-

were formed during the cracking of isopentane. In the cracking reaction, at 500° 2–4%, at 520° 3–10%, and at 550° 6–12% of the total amount of reacted isopentane was consumed, with the decrease in selectivity as the temperature increased approximately coinciding with the increase in the consumption of isopentane for cracking.

Fig. 2. Distribution of reacted isopentane among the reaction products at 550° and a pressure of 300 mm Hg in a boiling bed

Fig. 3. Distribution of reacted isopentane among the reaction products at 520° and atmospheric pressure in a fixed bed

2-Methylbutene-2, 2-methylbutene-1, and 3-methylbutene-1 were present in the products in the ratio 100 : 50 : 16 at 500°, 100 : 54 : 18 at 520°, 100 : 55 : 16 at 550°, and 100 : 56 : 14 at 580°. This ratio depended little on the pressure and on the conversion of isopentane, and differed only slightly from the equilibrium ratio. The ratio of isoprene to the sum of isoamylenes, within the limits of experimental error, coincided with the equilibrium value. It follows from this that the isomerization and dehydrogenation reactions of isoamylenes on oxide catalysts proceed at a high rate.

In processing the experimental data in the region of conversions up to 30%, the equations used were

$$\frac{xy^2}{1-y} = K\frac{t}{p} \qquad \text{for the boiling bed,} \tag{1}$$

$$x\left(\ln\frac{1}{1-y} - y\right) = K\frac{t_0}{p} \qquad \text{for the fixed bed,} \tag{2}$$

where y is the degree of conversion of isopentane, x is the selectivity (the number of moles of isopentane consumed in the formation of isoamylenes and isoprene at $y = 1$), p is the pressure, t is the contact time (the ratio of the catalyst volume to the volume of the initial isopentane under the experimental conditions), and K is a constant.

It follows from Fig. 4 that the experimental points are grouped near straight lines 1 and 2, whose angle of inclination to the t/p axis is equal to the constant K independently of the pressure; the mean deviation of the experimental points from the straight lines is 5%.

In deriving equations (1) and (2), concepts (10,11) concerning the course of irreversible reactions on a homogeneous surface were used; in the region of conversions up to 30%, the rate of the reverse reaction did not exceed 4–6% of the rate of the forward reaction. These equations correspond to the case when isoamylenes and isoprene are strongly adsorbed on the surface with identical adsorption coefficients. Equation (1) characterizes

a regime of complete gas mixing. In deriving equation (2), it was assumed that there was no mixing and, moreover, the change in the stoichiometry of the process with the depth of conversion was not taken into account.

Systematic deviations of the points from the straight lines in Fig. 4, due to differences in the adsorption coefficients of the reaction products exceeding the experimental error, should have occurred when the ratio of the adsorption coefficients of isoprene and isoamylenes was greater than 2. Thus, from the experiment it follows that on the chromium catalyst this ratio did not exceed 2. In exactly the same way it could be concluded that the adsorption coefficient of isoamylenes is 2 orders of magnitude greater than the adsorption coefficient of isopentane. The value of K, found from the slope of the straight lines in Fig. 4, proved to be $3.87 \cdot 10^{-3}$, $6.72 \cdot 10^{-3}$, and $21 \cdot 10^{-3}$ sec/atm for temperatures of 500, 520, and 550° respectively. The observed activation energy, calculated from the Arrhenius equation, is 44000 cal/mol.

Fig. 4. Kinetic curves for the dehydrogenation of isopentane in the region of small conversions: a –100 mm Hg, fluidized bed; –300 mm Hg, fluidized bed; –500 mm Hg, fluidized bed; –atmospheric pressure, fixed bed

Figure 4: Fig. 4. Kinetic curves for the dehydrogenation of isopentane in the region of small conversions: a –100 mm Hg, fluidized bed; –300 mm Hg, fluidized bed; –500 mm Hg, fluidized bed; –atmospheric pressure, fixed bed

Fig. 4. Kinetic curves for the dehydrogenation of isopentane in the region of small conversions: *a* –100 mm Hg, fluidized bed; *b* –300 mm Hg, fluidized bed; *v* –500 mm Hg, fluidized bed; *g* –atmospheric pressure, fixed bed

Comparison of the results of experiments in fluidized and fixed beds shows that a) in the first case there existed a regime of complete gas mixing; b) in the second case the process proceeded in the kinetic region (particle size up to 0.5 mm, temperature 550°), since on large and small particles it is described by the same regularities.

Table 1 gives the results of experiments on the dehydrogenation of isopentane at elevated temperatures and reduced pressures. At 600°, 100 mm Hg, and a space velocity of 0.35, of the 62.2% of decomposed isopentane, 20.2% was converted into isoamylenes and 15.3% was converted into isoprene; in this case the isoprene content in the C_5 fraction was 21%.

Complete mixing of the gas in the reactor should have led to a decrease in the yield of isoprene owing to the increase in the share of secondary and side reactions. In the technical implementation of the process under conditions in which mixing can be reduced either by changing the hydrodynamic regime of the bed or by sectioning the reactor, it is possible to obtain a higher yield of isoprene.

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