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Abstract

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Catalytic Dehydrogenation of Isopentane

The use of isopentane, as a petroleum hydrocarbon, for expanding the raw-material base of the synthetic-rubber industry is of great importance for the national economy. One of the routes for obtaining isoprene, the monomer of SK, may be the catalytic dehydrogenation of isopentane to isoamylenes, and of the latter to isoprene:

$$C_5H_{12} \rightarrow C_5H_{10} \rightarrow C_5H_8.$$

The literature data on the conversion of isopentane to isoamylenes are very scant: only the works of Shuikin and co-workers on the catalytic dehydrogenation of isopentane (1) and of Mamedaliev and co-workers on the formation of isoamylenes during the contact dehydrogenation of gasoline fractions with b.p. 27-29° and 27-32° (2) have been published. In the foreign patent literature, the description of the reaction of catalytic dehydrogenation of isopentane is limited to general indications, and alumina-chromia catalysts with activating additives or without them are most often recommended as contacts, for example in (3).

Thus, the study of the reaction of catalytic dehydrogenation of isopentane to isoamylenes is still at an initial stage.

At the Institute of Organic Chemistry of the Academy of Sciences of the USSR, as a result of many years of investigations by M. N. Marushkin, by the end of 1953 an active alumina-chromia catalyst for the dehydrogenation of *n*-butane and propane had been developed; it was used in 1954 to study the reaction of dehydrogenation of isopentane to isoamylenes. The composition of the catalyst in mole percent was: Al_2O_3 88, Cr_2O_3 9, K_2O 3; bulk density 1.14 g/cm^3. The catalyst had high mechanical crushing strength: its beads, 5-6 mm in diameter, were destroyed only under a load of 40-60 kg.

The dehydrogenation reaction of isopentane was carried out in a quartz tube in a laboratory flow-type apparatus. A fresh or regenerated portion of catalyst (20 cm^3) was heated to the experimental temperature in a stream of air; the latter was then displaced with nitrogen, and isopentane was introduced into the tube. The catalyst was regenerated with a stream of air at the experimental temperature for about an hour. The feedstock for the experiments was petroleum

Fig. 3

Figure 1: Fig. 3

isopentane, which, after distillation on a 35-plate column, had b.p. 27.8°/760 mm, n_D^{20} 1.3538; d_4^{20} 0.6194.

The liquid reaction products were condensed by cooling with solid CO_2, and the off-gases were collected in a gasometer over brine. Sampling of the reaction products was carried out after stabilization of the catalyst had been achieved, i.e., 5-10 min after the start of feeding isopentane into the tube.

In the condensate, the total unsaturation was determined by the bromometric method according to Rosenmund (4), and the isoprene content gravimetrically by reaction with maleic anhydride. The gaseous reaction products were analyzed on an Orsat apparatus. The activity and selectivity of the catalyst were characterized by the yield (in weight percent) of unsaturated hydrocarbons, respectively, based on the isopentane passed and on the isopentane decomposed.

The study of catalyst operation in short operating cycles* (30-90 min.) in the temperature range 500-575° and at space velocities from 0.3 to 4.2 h^{-1} showed that its activity increases with an increase in the process temperature, reaching its highest value at 550° (Fig. 1). With increasing reaction temperature, the maximum activity of the catalyst shifts toward a decrease in the contact time from 8 to 3 sec (Fig. 2), and the sharpest change in activity with contact time is observed at 550°. When the space velocity is changed, the activity of the catalyst remains practically at its maximum value in the range of velocities from 0.7 to 2.6 h^{-1} (Fig. 1). Under these conditions, the catalyzates obtained at 550° contained up to 58 wt.% unsaturated hydrocarbons, while the yields of the latter, based on the isopentane passed through, varied within 45-49 wt.%, and based on the decomposed isopentane—within 70-90 wt.%; the yields of catalyzates varied from 80 to 95 wt.%. The selectivity of the catalyst (see above) increases with decreasing contact time; at 525 and 550° the selectivity is practically the same, while at 575° it decreases as a result of the intensification of cracking at this reaction temperature (Table 1).

Fig. 1 Fig. 2

Fig. 1. Effect of space velocity on the activity of the catalyst

Fig. 2. Effect of contact time on the activity of the catalyst

Fig. 3. Productivity of the catalyst

The productivity of the catalyst increases sharply with increasing reaction temperature and feed rate of the raw material. The highest productivity of the

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* An operating cycle is understood as the duration of catalyst operation between two regenerations.

catalyst—about 700 g of unsaturated hydrocarbons per 1 l of catalyst per hour —is attained at 550° and a space velocity of 2.6 h^{-1}. At 575° the productivity of the catalyst decreases (Fig. 3).

Thus, the optimum reaction temperature is 550°. At this temperature all further investigations of the working properties of the catalyst were carried out: its stability and the degree of poisoning under different conditions were established, and the most advantageous duration of the operating cycle was selected. In order to obtain comparable results, all experiments were carried out at a constant space velocity equal to 1.2 h^{-1}.

It was shown that the average activity (productivity) of the catalyst over a cycle decreases linearly with increasing cycle duration (Fig. 4). The catalyst has the greatest activity during a one-hour cycle. It also follows from Fig. 4 that the selectivity of the catalyst does not depend on the degree of its poisoning.

During continuous operation of the catalyst without regeneration (550°, space velocity 1.2 h^{-1}) for more than 8 hours, the degree of dehydrogenation of isopentane decreases almost threefold (from 46 to 17 wt.%) during the first 4 hours, and thereafter practically does not change. After regeneration the catalyst completely restores its initial activity. This poisoning is evidently associated with coking of the catalyst during the dehydrogenation process. Deposition of "coke" on the catalyst occurs to a greater extent in

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in the first hour of its operation than in the subsequent hours. Under the conditions studied, during the first hour 3.9 wt.% of "coke" was formed on the catalyst, whereas during three hours of catalyst operation without regeneration only 6.3 wt.% was formed.

In the case of periodic regeneration, the activity of the catalyst over 45 one-hour operating cycles (550°, space velocity 1.2 hr^{-1}) does not change. Under these conditions the yield of catalyzate per hour is on average 90 wt.%, and the total content of unsaturated compounds in it is 52 wt.%; the yield based on isopentane passed through is 47-49 wt.% for isoamylenes and about 2 wt.% for isoprene; the selectivity of isopentane dehydrogenation in the reaction of isoamylene formation is on average 78 wt.%. The data presented indicate good stability of the catalyst, which is also consistent with the results of dehydrogenation of *n*-butane to butylenes over the same contact—the activity of the latter changed hardly at all after 220 one-hour operating cycles.

Fig. 4. Influence of the duration of the operating cycle on catalyst performance (550°, space velocity 1.2 hr^{-1});
a—catalyst activity, *b*—productivity, *v*—selectivity.

In the process of the dehydrogenation reaction of isopentane, gaseous products are formed, the composition of which is determined by the reaction temperature and the space velocity. The reaction gas consists mainly of hydrogen (70–90 vol.%); the content of saturated hydrocarbons varies from 9 to 26 vol.% when the reaction temperature is raised from 500 to 550° and the feed rate of isopentane is lowered from 1.2 to 0.5 hr^{-1}. The concentration of unsaturated hydrocarbons in the reaction gas proved to be insignificant and was about 1 vol.% over the entire temperature and space-velocity range studied. The results of gas analysis show that cracking reactions during the dehydrogenation of isopentane, as was to be expected, are intensified with an increase in the temperature of the process or with a decrease in the space velocity.

Table 1

Space velocity, hr^{-1}	Contact time, sec	Catalyst selectivity, wt.% at 525°	Catalyst selectivity, wt.% at 550°	Catalyst selectivity, wt.% at 575°
0.45	11-12	56	53	–
0.64	8	70	60	–
0.76	7	74	78	–
0.96	5-6	78	72	–
1.20	4	78	80	71
1.80	3	–	85	72
2.66	2	–	89	73
4.17	1	–	80	–

To investigate the composition of the catalyzates obtained at different space velocities in the range 500-550°, they were first freed from the gaseous portion (up to b.p. 20°) and from products boiling above 38°. All the catalyzates investigated boiled within the range 20-170°, with up to 90 wt.% of the total amount consisting of the 20-38° fraction and up to 9% of the 38-170° fraction. The 20-38° fraction was treated with maleic anhydride to remove dienes, distilled again, and examined by means of combination light-scattering spectra. Table 2 gives the results of determining the unsaturated components of the catalyzates in the 20-38° C fraction.

When the reaction temperature is raised from 500 to 550°, the total content of unsaturated compounds in the catalyzate increases almost threefold; at the same time the concentration of isoprene increases tenfold, that of 2-methylbutene-2 twofold, and that of 2-methylbutene-1 threefold, while the content of 3-methylbutene-1 changes hardly at all. The predominant products of the catalytic dehydrogenation of isopentane in the temperature range 500-550° are 2-methylbutene-2 and 2-methylbutene-1; 3-methylbutene-1 and isoprene are present in the catalyzate only in small amounts.

The data presented in Table 2 show that the use of combination light-scattering spectra for the analysis of the products of catalytic dehydrogenation of isopentane must be approached with caution. In the case of the presence in the reaction products of isoprene, its brightest lines and those of 3-methylbutene-1, which are very close in frequency, overlap one another.

Table 2

Fraction 20–38°	Undefined catalyst components, wt. % at 500°	Undefined catalyst components, wt. % at 525°	Undefined catalyst components, wt. % at 550°
Total uncertainty*	18.6	41.6	52.2
Isoprene**	0.4	1.5	4.2
2-Methylbutene-2	10	15	20/25***
2-Methylbutene-1	5	15	15/30***
3-Methylbutene-1	3	3	5/35***

* Determined by Rozemund.
** Determined from the maleic anhydride addition product.
*** The second figure was obtained in the analysis of the 20–38° fraction not treated with maleic anhydride.

In this case the 1640 cm^{-1} line of isoprene is about 12 times more intense than the 1642 cm^{-1} line of 3-methylbutene-1, and therefore even with a small isoprene content (4%) the 1640 cm^{-1} line masks not only the 1642 cm^{-1} line of 3-methylbutene-1, but also the 1651 cm^{-1} line of 2-methylbutene-1, which in analysis leads to sharply elevated results for the latter.

The combination light-scattering spectra of the fractions from the isopentane dehydrogenation catalyst were studied at the Spectroscopy Commission of the Academy of Sciences of the USSR by V. T. Aleksanyan and Kh. E. Sterin, to whom we express our gratitude for their assistance in the study of the catalysts.

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