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Abstract

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DEHYDROCYCLIZATION OF *n*-HEPTENES ON AN ALUMINA–CHROMIA–POTASSIUM CATALYST

The mechanism of the dehydrocyclization reaction of paraffin hydrocarbons and the role of olefins in it have repeatedly been discussed in the literature ([1–3]). At the same time, no single point of view can be established on the question of the aromatization of the olefin hydrocarbons themselves and, in particular, on the question of the influence of the position of the double bond in them on this reaction. This is explained by the absence of systematic studies and by differences in the conditions under which the experiments were carried out, the catalysts used, and the starting hydrocarbons. Thus, according to Hogg, Fereis, and Zoidemberg ([5]), heptene-1 and heptene-2 are aromatized at 465° on chromium oxide with practically the same yield of toluene, whereas hexene-1 under these conditions forms 1.7 times more benzene than hexene-2. According to Goldwasser and Taylor ([6]), heptene-1 and heptene-3 (423°, chromium oxide) are aromatized practically identically. Platt and Tarasova ([2]) found that on an aluminovanadium catalyst at 400–480° heptene-1 gives more aromatics than heptene-3.

The appearance of such a sensitive analytical method as gas–liquid chromatography makes it possible to examine in greater detail the question of the mechanism of dehydrocyclization of aliphatic hydrocarbons. In this connection we decided, using *n*-heptenes as an example, to determine the influence of the position of the double bond on the yield of toluene.

For this purpose, experiments were carried out on the aromatization of heptene-1, heptene-2, and heptene-3 at 450° and a space velocity of 1.63 hr^{-1} on an alumina–chromia–potassium catalyst (4 cm^3) previously reduced with hydrogen (at 550°), the composition and some properties of which were published in ([7]). The experimental procedure did not differ from that described earlier ([7]). Each experiment was conducted for 75 min with periodic sampling of the catalyzate. Analysis of the catalyzates was performed with a capillary gas–liquid chromatograph with a flame-ionization detector on columns with tributyrate of triethylene glycol. The toluene content was determined on a 10 m column, and

the heptenes on a 40 m column. The composition of the starting hydrocarbons is given in Table 1. Since cracking of the hydrocarbons under the experimental conditions was very

Table 1

Composition of the starting heptenes (content of the principal substance and impurities in weight percent)

Starting substance	Heptane	Heptene-1	Heptene-2 cis	Heptene-2 trans	Heptene-3 cis	Heptene-3 trans	Total principal substance
Heptene-1	0.8	98.2	0.0	0.0	0.2	0.8	98.2
Heptene-2	1.8	0.0	80.5	17.7	0.0	0.0	98.2
Heptene-3	0.0	3.5	0.2	1.8	61.0	33.5	94.5

small (in all, about 2 wt.%), the decrease in catalyzate yield in the first sampling is explained mainly by consumption of material in filling the apparatus, by adsorption on the catalyst, and by wetting of the walls of the cold parts of the reactor. It may therefore be considered that the change in the composition of the catalyzate reflects sufficiently accurately the change in the yields of the reaction products.

As a result of the investigation it was found that in the initial period of the reaction, i.e., during the first 5 min of the experiment, aromatization of heptene-3 proceeds best (see Table 2). The decrease in the aromatizing activity of the catalyst with time,

Table 2

Results of experiments on the aromatization of *n*-heptenes. 450°, space velocity 1.63 h^{-1}

Starting substance	Time of catalyst sampling from start of experiment, min	n_D^{20}	heptane	heptene-1	heptene-2 cis	heptene-2 trans	heptene-3 cis	heptene-3 trans	benzene	heptadienes	dimers
Heptene-1	5	1.4427	18.1	1.1	2.5	4.5	1.9	4.8	2.3	Traces	64.7
Heptene-1	15	1.4360	15.2	1.3	2.8	5.5	2.2	5.8	1.7	»	65.5
Heptene-1	30	1.4330	16.2	1.5	3.9	6.1	2.5	6.7	1.7	»	61.4
Heptene-1	45	1.4313	15.5	1.8	4.2	6.7	3.1	7.3	0.8	»	60.6
Heptene-1	75	1.4235	16.2	2.8	6.2	10.1	4.7	11.5	1.1	1.1	46.3
Heptene-2	5	1.4260	18.7	2.9	4.7	8.0	4.2	9.5	1.0	Traces	51.0
Heptene-2	15	1.4160	13.2	3.5	9.5	14.6	5.4	12.7	1.0	0.9	39.0
Heptene-2	30	1.4120	4.1	6.5	15.0	21.8	10.8	25.6	—	3.0	13.2
Heptene-2	45	1.4100	1.6	6.4	29.0	26.1	8.4	22.3	—	4.0	2.2
Heptene-2	75	1.4050	1.7	6.9	22.8	26.6	8.4	22.8	0.6	6.3	3.8
Heptene-3	5	1.4440	15.5	0.9	1.8	3.3	1.5	4.0	3.2	Traces	70.0
Heptene-3	15	1.4307	14.6	1.9	3.6	6.3	4.1	8.8	2.4	»	58.3
Heptene-3	30	—	15.2	2.2	4.5	8.9	4.4	11.2	1.1	—	52.5
Heptene-3	45	1.4150	8.7	4.5	9.6	16.5	9.6	20.5	1.2	3.0	26.4
Heptene-3	60	1.4098	2.9	5.2	11.6	20.4	15.7	29.1	0.5	5.6	9.0

apparently caused by coke deposition, was least pronounced during aromatization of heptene-1 (see Fig. 1). The catalyst was deactivated most strongly in the course of the experiment on aromatization of heptene-2. If the content of toluene in the catalyzate is extrapolated to the start of the reaction, it follows that the initial aromatization rates of heptenes-1 and -2 are close to one another. Analysis of the gas evolved during regeneration for CO_2 and H_2O showed that during aromatization of heptenes-2 and -3 more coke is formed than from heptene-1 under identical experimental conditions.

It should be noted that, along with dehydrocyclization and coke deposition, migration of the double bond proceeded intensively during aromatization of the heptenes. The composition of the heptene fraction of the catalyzate was thermodynamically equilibrated, or close to it. This, to a certain extent, should have leveled the yields of toluene, coke, and other reaction products. Nevertheless, the observed difference may be due to the fact that in the initial layers of the catalyst the nonisomerized hydrocarbon reacts. Another possible explanation of this fact will be discussed at the end of the present article.

Fig. 1. Change in the content of toluene in the catalyzates during experiments on aromatization of heptenes. 450°, space velocity 1.63 h^{-1}. 1 —heptene-1; 2 — heptene-2; 3 —heptene-3 (dashed line —extrapolated portions of the curves)

As follows from the data of Table 2, the hydrogenating ability of the catalyst is less sensitive to poisoning than its aromatizing activity. Thus, when the toluene content in the catalyzates decreases by 17-18%, the heptane content either does not change (heptene-3) or decreases by only 2% (heptene-1). The heptane content in the heptene-2 catalyzate decreases somewhat more strongly.

When the chromatograms of the heptene catalysts were examined (see, for example, Fig. 2), peaks were found which, judging by their positions, could apparently be assigned only to dienes. Indeed, after the catalyst was treated with maleic anhydride, they disappeared. The heptene aromatization catalysts contained appreciable amounts of such hydrocarbons (up to 6 wt.%), apparently mainly heptadienes. It turned out that, as the toluene content in the catalyst decreased, the heptadiene content increased. Under otherwise equal conditions, more heptadienes were obtained from heptenes-2 and -3. An experiment on the aromatization of heptene-3 in a helium stream showed that in this case the yield of dienes increases and catalyst poisoning decreases somewhat. The ratio of the yields of heptadienes and toluene was clarified by a series of experiments in which constant flow rates of heptene-1 and helium were maintained (respectively, 20 ml of liquid and 3000 ml of gas at N.T.P. per 1 hr), but the amount of catalyst in the catalytic tube was varied. In individual experiments, 1, 2, 3, 5, 10, and 20 cm^3 of catalyst were taken. Thus, as a result of the study, it was determined, on the one hand, how the yields of toluene, heptadienes, and heptane vary along the catalyst bed and, on the other hand, the effect of the nominal contact time on the change in the yields of these products.

Fig. 2. Chromatogram of the heptene-1 aromatization catalyst. Experiment at

Fig. 2 chromatogram

Figure 1: Fig. 2 chromatogram

Fig. 3 plot

Figure 2: Fig. 3 plot

450° and a space velocity of 4 hr^{-1}; column length 10 m. 1 —cracking products, 2 —heptane, 3 —heptene-1 + heptene-3, 4 —trans-heptene-2, 5 —cis-heptene-2, 6 —hexadienes, 7 —benzene, 8 —heptadienes, 9 —toluene

In Fig. 3 one of the graphs obtained in this work is shown, illustrating the influence of the nominal contact time on the yield of the reaction products in its initial periods, i.e., over the time interval from the 2nd to the 5th min from the start of each experiment. The yield of toluene, at short contact times, i.e., near the origin, has, as it were, an "induction" period; in the region of contact times up to 0.5 sec the yield of heptadienes exceeds the yield of toluene. Under these conditions, dienes can be obtained from heptene-1 in a yield of about 5 wt.% with an insignificant content of toluene in the catalyst. The heptadiene-yield curve passes through a maximum at a nominal contact time equal to 1.5 sec. This same contact time corresponds to the inflection point on the toluene-yield curve.

Fig. 3. Influence of the nominal contact time on the content of the main reaction products in heptene-1 aromatization catalysts. 450°, catalyst sampling was carried out from the 2nd to the 5th min of the experiment. 1 —toluene, 2 —heptane, 3 —heptadienes

The mutual arrangement of the yield curves of heptadienes and toluene is very similar to that which has repeatedly been observed for analogous curves of the dependence of the yields of aromatics and olefins on contact time in the dehydrocyclization of alkanes, for example, the yield curves of toluene and heptenes in the dehydrocyclization of *n*-heptane ([8]).

The characteristic form of the initial sections of the yield curves of toluene and heptadienes indicates the possibility that heptadienes are an intermediate product in the dehydrocyclization reaction of heptenes, just as the heptenes themselves may possibly prove to be intermediate products in the dehydrocyclization of heptane. In this case it should be assumed that the dehydrocyclization reaction of paraffinic hydrocarbons on chromium catalysts is a multistage process proceeding through the formation of olefins, dienes, and, possibly, trienes. However, it is not excluded that the difference noted above in the yields of toluene and coke in the aromatization of heptenes-1, -2, and -3, with a thermodynamically equilibrium composition of the heptene fraction of the catalysts, is explained by a feature of the reaction mechanism. In this case it may be assumed that dehydrocyclization on an alumina–chromia–potassium catalyst proceeds through the formation of an intermediate activated complex of the or-

ganic molecule with the catalyst. Such a complex is dehydrogenated stepwise, and at each stage of dehydrogenation of the complex a dynamic equilibrium is established between it and the corresponding olefinic hydrocarbons in the gas phase. A detailed elucidation of the mechanism of the dehydrocyclization reaction will require its further experimental study.

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