CHEMISTRY

M. I. ROZENGART and Academician B. A. KAZANSKII

1958

SovietRxiv

Abstract

Full Text

CHEMISTRY

M. I. ROZENGART and Academician B. A. KAZANSKII

DEHYDROCYCLIZATION OF *n*-HEPTANE ON ALUMINA-CHROMIA CATALYSTS

One of the distinctive features of alumina-chromia catalysts for the aromatization of paraffinic hydrocarbons is their short working cycles, caused by the need for regeneration after several hours of operation. This is connected with the deactivation of the catalysts by carbonaceous deposits (“coke”) formed on their surface during the working period.

Our experiments on the dehydrocyclization of *n*-heptane showed that it is possible to prepare catalysts that would operate continuously, without regeneration, for a long time, up to 27 hr, giving an average yield of aromatics over this period of 67 wt. %. After 100 hr of operation with periodic regenerations, the duration of the working period for them decreased to 10-12 hr and did not change appreciably during the subsequent 115-117 hr of operation. After 215-217 hr of operation, the surface area of the catalysts decreased threefold, and the pore volume one and a half times. At the same time, the total yield of reaction products and the yield of toluene from the heptane passed over the catalyst changed only slightly. One reason for this phenomenon, it may be supposed, is the fact that under the conditions used by us (515°, space velocity 0.3 hr^{-1}) the dehydrocyclization reaction on active catalysts proceeds not in the kinetic but in the diffusion region. Experiments with catalyst samples of different grain size confirmed this assumption.

Experimental Part

The experiments were carried out in a vertical block furnace, in which two reaction tubes of refractory glass with an internal diameter of 18 mm were placed simultaneously. Into the tube, above the catalyst layer, there was inserted a liner of external diameter 15.5 mm, made from a tube of the same glass sealed at both ends. The temperature was measured with a chromel-alumel thermocouple, the hot junction of which was placed in the block. Heptane was fed by means of a syringe (1). The reaction products were collected in a receiver cooled with water and in a coil trap connected with it, placed in a Dewar vessel with a mixture of dry ice and acetone.

Commercial standard heptane was treated, as usual, with concentrated sulfuric acid and then distilled on a column with an efficiency of 24 theoretical plates.

The heptane obtained had the following constants: b.p. 98.4°/760 mm, n_D^{20} 1.3878, d_4^{20} 0.6834.

The alumina-chromia catalysts, promoted with potassium ion, had the same composition (chromium oxide 15, aluminum oxide 82, potassium oxide 3 mol. %), differing somewhat in the method of preparation. Catalysts 149 and 162 were used in grains of diameter 3–5 mm, catalyst 187 in grains of diameter 0.5–1 mm and 3–5 mm.

The aromatics content in the catalyzates was calculated from the refractive index on the basis of a curve for the dependence of the refractive index of heptane-toluene mixtures on their composition, and in some cases was determined by dispersion analysis. Numerous analyses of catalyzates obtained by aromatization of individual hydrocarbons (*n*-hexane, *n*-heptane, *n*-octan-

cyclohexane, methylcyclohexane) on different catalysts in the course of our investigations confirmed the sufficient accuracy of the refractometric method for determining aromatics. As we found, the difference in the aromatic content determined from the refractive index and dispersometrically, taking into account the compounds of uncertain bromine numbers, was less than 5%, if the bromine number in the case of heptane did not exceed 15.

Long-duration tests of the catalysts* (catalyst 149 was tested for 217 h, catalyst 162 for 215 h) were carried out with 20 ml of catalyst at 510°. The refractive index and the yield were determined for catalysts collected over 4 h. The catalysts were regenerated after the refractive indices of the catalysts collected over 4 h had fallen to 1.4500 or somewhat lower. Regeneration with air was carried out at the experimental temperature, measured by a thermocouple in the block; before and after regeneration the catalyst was purged with nitrogen for 5 min. To activate freshly charged catalysts it is necessary to carry out one to three two-hour runs with subsequent regenerations, after which the catalyst acquires high activity. Table 1 gives the results of several

Table 1

Aromatization of *n*-heptane on catalysts 149 (series of runs 380) and 162 (series of runs 382) at 515° and a space velocity of 0.3 h^{-1}

Catalyst	Run no.	Operating time, h	n_D^{20}	Bromine number	Yield of catalyst, wt. % (calculated on n-C_7H_{16})	Yield of aromatics, wt. % (calculated on n-C_7H_{16})	Yield of unsaturated compounds, wt. % (calculated on n-C_7H_{16})
Catalyst 149	6	1—4	1.4680	10.1	84	67	5
Catalyst 149	6	5—8	1.4685	10.9	87	70	6
Catalyst 149	6	9—12	1.4659	9.6	86	68	5
Catalyst 149	6	13—16	1.4704	13.9	77	64	7
Catalyst 149	6	17—20	1.4580	19.0	77	55	9
Catalyst 149	6	Average				65	
Catalyst 149	8	1—4	1.4735	—	78	65	
Catalyst 149	8	5—8	1.4768	—	76	66	
Catalyst 149	8	9—11	1.4547	—	85	58	
Catalyst 149	8	Average				63	
Catalyst 149	15	1—4	1.4571	8.8	94	66	5
Catalyst 149	15	5—8	1.4601	9.8	91	67	5
Catalyst 149	15	9—10	1.4492	12.5	82	52	6
Catalyst 149	15	Average				64	
Catalyst 162	4	1—4	1.4843	4.1	79	73	2
Catalyst 162	4	5—8	1.4882	3.6	79	75	2
Catalyst 162	4	9—12	1.4796	6.0	84	74	3

Catalyst	Run no.	Operating time, h	n_D^{20}	Bromine number	Yield of catalyst, wt. % (calculated on n-C_7H_{16})	Yield of aromatics, wt. % (calculated on n-C_7H_{16})	Yield of unsaturated compounds, wt. % (calculated on n-C_7H_{16})
Catalyst 162	4	13—16	1.4756	7.9	81	68	4
Catalyst 162	4	17—20	1.4703	8.6	81	65	4
Catalyst 162	4	21—24	1.4645	10.8	76	59	5
Catalyst 162	4	25—27	1.4529	13.3	83	55	7
Catalyst 162	4	Average				67	
Catalyst 162	7	1—4	1.4739	—	85	71	—
Catalyst 162	7	5—8	1.4632	—	84	64	—
Catalyst 162	7	9—12	1.4535	—	82	55	—
Catalyst 162	7	Average				63	
Catalyst 162	10	1—4	1.4681	5.6	78	63	3
Catalyst 162	10	5—8	1.4650	8.0	82	64	4
Catalyst 162	10	9—12	1.4480	12.2	78	48	6
Catalyst 162	10	Average				58	

runs with prolonged operating periods, runs with the same catalysts after the duration of the operating periods had decreased, and also the final tests of catalysts 149 and 162.

As is seen from Table 1, catalyst 149 in run no. 6 retained high activity for 20 h of continuous operation without regeneration; the average yield of aromatics over this period was 65%, calculated on the heptane passed. Subsequently the operating period decreased to 10—11 h, and the yield

* The following took part in carrying out the long-duration, round-the-clock tests: O. D. Sterligov, P. S. Pavlova, A. A. Frolov, V. A. Obodova, G. S. Taits, and T. V. Vasina. Z. F. Kuznetsova also took part in this and in a number of other sections of the work.

aromatics—up to 63%. The working period of catalyst 162 in experiment No. 4 was 27 h, with an average aromatics yield of 67%. Then the working period of the catalyst, as in the preceding case, decreased to 12 h, and the average aromatics yield fell to 58%. The content of unsaturated compounds in the catalyzates, as is evident from the bromine numbers, is small and changes only slightly, increasing at the end of the working period simultaneously with the drop in aromatics yield.

The results of distillation and analysis of the catalyzates obtained with catalyst 149 at the beginning, in the middle, and at the end of its operation also indicate a systematic decrease in the toluene content during the test, from 71 wt.% for the mixture of catalyzates from the first six experiments to 69% for the mixture of catalyzates from the last five experiments. At the same time, a small amount of benzene is formed (about 3%). The content of organic substances in catalyzates 149 and 162 after an 8-hour working period and subsequent purging with nitrogen for 20 min at the temperature of the experiment was 4%. The content of organic substances in catalyst 149 was determined both during its testing by analysis of the gases leaving during regeneration and by combustion of a sample taken at the end of the test; in catalyst 162, it was determined only by the latter method*.

Measurement of the surface area of catalysts 149 and 162 was carried out by adsorption of benzene vapor from an air stream according to the method described for oxide catalysts by A. M. Rubinshtein and A. V. Afanas' eva ([2]). It was found that the surface area of catalyst 149 decreased during the entire test period, with 14 regenerations, from 217 to 69 m^2/g, and that of catalyst 162 (9 regenerations) from 332 to 107 m^2/g. The pore volume of catalyst 162, calculated from the adsorption of benzene vapor in an exsiccator over pure benzene, changed from 0.265 to 0.175 cm^3/g. Such a change in the physical structure of our catalysts is characteristic of alumina or catalysts prepared on its basis that have been subjected to high temperature, sometimes in combination with water vapor ([3], [4]), which could have formed in the first moments of regeneration and at the beginning of experiments after regeneration.

Experiments with two samples of catalyst 187 of different grain size were carried out at different space velocities at 510° for 4 h, followed by regenerations. The space velocity was varied by changing the amount of catalyst charged into the tube (2.11; 4.39; and 8.78 g) at

Table 2

Aromatization of heptane at 510° on catalyst 187 with an experiment duration of 4 h and a heptane feed rate of 6.5 ml per hour

No. of experiment	Catalyst weight, g	Weight velocity, h^{-1}	n_D^{20}	Bromine number of catalyzate	Yield, wt.% (based on C_7H_{16}): catalyzate	Yield, wt.% (based on C_7H_{16}): aromatics	Yield, wt.% (based on C_7H_{16}): unsaturated
Grains 0.5-1 mm	**Grains 0.5-1 mm**	**Grains 0.5-1 mm**	**Grains 0.5-1 mm**	**Grains 0.5-1 mm**	**Grains 0.5-1 mm**	**Grains 0.5-1 mm**	**Grains 0.5-1 mm**
414[1]	8.78	0.48	1.4424	14.4	78	45	6.9
414[2]	8.78	0.48	1.4452	–	79	47	–
421	4.39	1.08	1.4277	16.5	88	39	8.9
423	4.39	1.16	1.4270	16.8	89	38	9.2
425	2.11	2.25	1.4089	17.2	96	24	10.1

No. of experiment	Catalyst weight, g	Weight velocity, h^{-1}	n_D^{20}	Bromine number of catalyzate	Yield, wt.% (based on C_7H_{16}): catalyzate	Yield, wt.% (based on C_7H_{16}): aromatics	Yield, wt.% (based on C_7H_{16}): unsaturated
Grains 3-5 mm	**Grains 3-5 mm**	**Grains 3-5 mm**	**Grains 3-5 mm**	**Grains 3-5 mm**	**Grains 3-5 mm**	**Grains 3-5 mm**	**Grains 3-5 mm**
413[1]	8.78	0.50	1.4417	18.3	76	43	8.5
413[2]	8.78	0.50	1.4389	–	79	42	–
417	4.39	1.09	1.4183	19.7	91	31	11.0
424	4.39	0.97	1.4175	–	93	31	–
426	2.11	2.08	1.4038	–	96	18	–
427	2.11	2.08	1.4058	16.1	94	19	9.5

at the same rate of heptane feed (6.5 ml/hour). In parallel experiments with samples of different grain size, equal catalyst charges were each time loaded into both tubes. Since the bulk specific weight of the 0.5-1 mm sieve fraction of catalyst 187 was 1.02, and that of the 3-5 mm sieve fraction was 0.88, the space velocities in the parallel experiments differed; however, the weight velocities, i.e., the amount, expressed in grams, of liquid passed per gram of catalyst per

* Determination of organic substances by combustion was carried out in the microanalysis laboratory of the Institute of Organic Chemistry, Academy of Sciences of the USSR, headed by V. A. Klimova.

Fig. 1. Aromatization of heptane on catalyst 187 with different grain diameters (1—0.5-1 mm, 2—3-5 mm) at 510° and different weight velocities

Figure 1: Fig. 1. Aromatization of heptane on catalyst 187 with different grain diameters (1—0.5-1 mm, 2—3-5 mm) at 510° and different weight velocities

hour, were practically identical in the parallel experiments. The results of these experiments are given in Table 2 and in Fig. 1.

With an increase in the weight velocity of heptane from 0.5 to 2.15 hour^{-1}, the catalyst yield increased in parallel experiments with catalysts of different grain size practically identically, from 78 to 96%; the yield of aromatics on the catalyst of 0.5-1 mm grain size decreased from 46 to 24%, while on the sample of 3-5 mm grain size the yield of aromatics changed from 42.5 to 18.5%. Both curves of the dependence of the yield of aromatics on the weight velocity of heptane run in the same direction; the curve for the coarser sample lies lower. The yield of unsaturated compounds increased in the first case from 6.9 to 10.1%, and in the second from 8.5 to 9.5%.

Fig. 1. Aromatization of heptane on catalyst 187 with different grain diameters (1—0.5-1 mm, 2—3-5 mm) at 510° and different weight velocities

From the results obtained it follows that the grain size of the catalyst affects the yield of aromatics. According to existing views ($^{5-7}$), the dependence of the yield of reaction products on the grain size of the catalyst is evidence that the reaction proceeds in the so-called diffusion region, i.e., that its rate is influenced by diffusion of the components of the reaction mixture. Consequently, the aromatization reaction of heptane on the promoted alumina-chromium catalyst proceeds in the diffusion region.

It should be noted in this connection that the influence of catalyst grain size has also been observed for the dehydrogenation reactions on an alumina-chromium catalyst of *n*-butane (^{8}) and cyclohexane (^{9}). This phenomenon, which is apparently common to various reactions of saturated hydrocarbons on alumina-chromium catalysts, is explained, evidently, by the fact that at the relatively high temperatures (450-550°) at which these transformations proceed on oxide catalysts, the reaction rates become equal to or exceed the diffusion rates of hydrocarbons in the catalyst.

Institute of Organic Chemistry
named after N. D. Zelinsky
Academy of Sciences of the USSR

Received
26 XII 1957

CITED LITERATURE

1. A. M. Levit, L. Kh. Freidlin, *Zav. lab.*, **16**, 244 (1950).
2. A. M. Rubinshtein, V. A. Afanas' ev, *Izv. AN SSSR, OKhN*, 1956, 1294.
3. I. E. Neimark, L. Kh. Freidlin, A. I. Rastrenenko, N. V. Borunova, *Izv. AN SSSR, OKhN*, 1956, 784.
4. L. Kh. Freidlin, A. A. Balandin, N. V. Borunova, A. E. Agronomov, *Izv. AN SSSR, OKhN*, 1956, 913.
5. V. A. Roiter, *Khim. nauka i prom.*, **2**, 210 (1957).
6. G. K. Boreskov, *Catalysis in the Production of Sulfuric Acid*, 1954, pp. 66–87.
7. E. Wheeler, in: *Catalysis: Questions of Theory and Methods of Investigation*, IL, 1955, pp. 479–563.
8. R. W. Blue, V. C. Holm et al., *Ind. and Eng. Chem.*, **44**, 2710 (1952).
9. R. B. Weisz, E. W. Swegler, *J. Chem. Phys.*, **59**, 823 (1955).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.