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Abstract

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The Effect of Additions of Potash and Phosphoric Acid on the Aromatizing Activity of Chromium Oxide

In our previous works (^{1}) it was shown that alkaline and alkaline-earth elements have a promoting effect on the aromatizing activity of an alumina-chromium catalyst in the reactions of dehydrocyclization of *n*-heptane and dehydrogenation of cyclohexane. Since in a two-component alumina-chromium catalyst the active component is chromium oxide, it was of interest to study the effect of additions on the catalytic activity of pure chromium oxide in hydrocarbon-conversion reactions, especially since Rubinshtein, Pribytkova, and Slinkin (^{2}) found an inhibiting effect of an addition of potassium to pure chromium oxide in the reactions of dehydration and dehydrogenation of isopropyl alcohol.

Experiments carried out at 450° and at a space velocity of 0.8 hr^{-1} showed that an addition of potash (0.25 wt. % K_2O) completely suppresses the dehydrocyclization reactions of *n*-heptane, reduces the formation of unsaturated compounds by a factor of 7, and almost completely stops the secondary cracking and isomerizing action of the catalyst. This addition had an identical effect on the dehydrogenation of cyclohexane to benzene, completely suppressing the reaction. However, when a mixture of *n*-heptane with *n*-heptene-1 was passed over a catalyst to which potash had been added, toluene was formed; its yield was only 2.5 times lower than the yield of toluene from the same mixture on a catalyst consisting of pure chromium oxide under the same conditions.

In order to determine whether the inhibiting effect of potash is not a specific consequence of its alkaline nature, we studied the action of additions of phosphoric acid (0.14 wt. %) on chromium oxide under the same conditions. It proved to be almost identical with the action of potash. The introduction of phosphoric acid suppressed the reaction of dehydrocyclization of heptane, the reaction of dehydrogenation of cyclohexane to benzene, and reduced by approximately half the formation of toluene from a heptane-heptene mixture. The introduction of both additions also reduced the hydrogenating ability of the catalyst.

The experiments described lead to the conclusion that the promoting action of the alkaline element potassium on an alumina-chromium catalyst in the hydrocarbon reactions described cannot be attributed solely to interaction of the alkaline additive with chromium oxide, but has a more complex nature and, apparently, is a consequence of the interaction of all three components—chromium oxide, aluminum oxide, and the alkaline additive—one form of which is described in the cited work (^{2}). The fact that heptane and cyclohexane cease to aromatize on pure chromium oxide after the introduction of potash or phosphoric acid, while heptene continues to aromatize, may be explained by assuming that the additives used in the present work affect the first stage of catalysis—activated adsorption. It may be supposed that the additives hinder the adsorption of saturated hydrocarbons on the active centers of the chromium catalyst, but to a considerably lesser extent affect the adsorption of the more active olefin molecules. Clarification of the details of this phenomenon requires further investigation.

Experimental Part

The apparatus, the experimental procedure, and the analysis of the catalyst were the same as in the works cited above (^{1}). In experiments with a heptane-heptene mixture, because of the high concentration of olefins, the content of aromatics in the catalyzates was determined by the dispersiometric method. The catalyzates from all experiments were also analyzed by gas-liquid chromatography. Two samples of pure chromium oxide were synthesized from reagent-grade chromium nitrate. The finally washed samples, dried in a drying cabinet, were heated in a stream of air to 535° and, after cooling, were screened on sieves.

For the experiments, 5.5 ml (8.1 g, grain diameter 0.5-1.0 mm) of each sample was taken. With a fresh catalyst, in order to stabilize it, a 2-hour experiment on the aromatization of heptane was carried out at 535°, followed by regeneration. The remaining experiments, in order to reduce side reactions, were carried out at 450° and a space velocity of 0.8 h^{-1}. Before an experiment the catalyst was heated in a stream of hydrogen to 535° and then kept for one hour at this temperature in order to reduce hexavalent chromium to trivalent chromium. Then, without stopping the flow of hydrogen, the catalyst was cooled to 450°, and to displace the hydrogen nitrogen from a cylinder was passed through for 3-4 min, after which the experiment was carried out. At the end of the experiment the catalyst was purged with nitrogen and regenerated with air; the duration of regeneration was equal to the duration of the experiment. The order of the experiments was as follows: first, experiments with heptane; then with cyclohexane; and finally with the heptane-heptene mixture.

The first catalyst sample, regenerated after this, was removed from the tube and impregnated with a solution of potash, taken in such an amount that the potassium content in the catalyst corresponded to 0.25 wt. % K_2O. The catalyst was dried in a drying cabinet, and, for stabilization, a 1-hour experiment with heptane at 535° was carried out with it, followed by the remaining experiments in the same order as with the sample of pure chromium oxide. The second catalyst sample was impregnated with a solution of H_3PO_4. Phosphoric acid was taken in an amount stoichiometrically equal to the potash, which amounted to 0.14 wt. % H_3PO_4 on the catalyst.

The initial heptane and cyclohexane were obtained by purification of commercial reagents (1). Heptene-1 was synthesized by pyrolysis of heptanol-1 acetate and was twice distilled on a column with an efficiency of 40 theoretical plates. The initial hydrocarbons had the following constants:

	b.p., °C/760 mm	n_D^{20}	d_4^{20}
n-Heptane	98.4	1.3878	0.6837
Cyclohexane	80.7	1.4256	0.7786
n-Heptene-1	93.6	1.3995	0.697

Since we had a relatively small amount of heptene at our disposal, the experiments were carried out with a heptane–heptene mixture having the following constants: n_D^{20} 1.3928; d_4^{20} 0.690. Bromine number 78.2. The mixture contained heptene: 46 wt. % by preparation, 48% by bromine number.

Preliminary experiments carried out at 535° showed that the pure chromium oxide prepared by us is poisoned at this temperature during the aromatization process. Table 1 gives the experiments at 450° with chromium oxide both pure and with additives. The average catalyst yield in the experiments with heptane was 88%, and in the experiments with the mixture somewhat lower, 84%.

The introduction of potassium into pure chromium oxide completely suppressed the heptane aromatization reaction, and on the chromatogram of the catalyzate from experiment 3 no peak corresponding to toluene was observed. Chromatography of the catalyzate from experiment 4, carried out on a catalyst with an addition of phosphoric acid, showed the presence of traces of toluene. It is possible that this difference is explained by a greater

activity of the second sample of pure chromium oxide, as is evident from the results of experiments 1 and 2.

The yield of unsaturates from heptane decreased upon introduction of a potassium additive from 11 to 1.6%, and upon introduction of a phosphoric acid additive from 13 to 3%. A considerable part of the unsaturates obtained on catalysts with additives apparently consists of cracking products. Unfortunately, we were unable to determine the content of heptene-1 in the catalyzates. It turned out that with dinonyl phthalate as the stationary phase in gas–liquid chromatography, *n*-heptane and heptene-1 are not separated.

Table 1

Experiments on aromatization over chromium catalysts

No.	Substance	Sample no. and additive to Cr_2O_3	Passed, ml	Yield, wt.% based on passed hydrocarbon: aromatics	Yield, wt.% based on passed hydrocarbon: unsaturates
1	Heptane	No. 1 without additive	12.5	10	10.8
2	»	No. 2 » »	13.3	14	12.5
3	»	No. 1 + 0.25% K_2O	13.3	0	1.6
4	»	No. 2 + 0.14% H_3PO_4	8.4	1	3.4
5	Cyclohexane	No. 1 without additive	11.1	52	1.6
6	»	No. 2 » »	8.9	51	1.1
7	»	No. 1 + 0.25% K_2O	8.5	0	0.3
8	»	No. 2 + 0.14% H_3PO_4	10.4	1	1.5
9	Mixture C_7H_{16} + C_7H_{14}	No. 1 without additive	8.9	17	19.9
10	Same	No. 1 + 0.25% K_2O	8.9	6	34.5
11	» »	No. 2 + 0.14% H_3PO_4	8.5	8	41.0

Aromatization of cyclohexane also ceased after the introduction of potash and phosphoric acid into the chromium catalyst. It is possible that in the experiments with cyclohexane the unsaturates are, for the most part, products of slight cracking. Introduction of potassium decreased their yield from 1.6 to 0.3% (catalyst sample 1), whereas introduction of phosphoric acid increased the yield of unsaturates from 1.1 to 1.5% (sample 2).

In the aromatization of the heptane-heptene mixture over pure chromium oxide, the yield of aromatics was 17 wt.% based on the mixture, or 35% based on the heptene passed. Introduction of additives decreased the yield of aromatics by approximately a factor of 2.5. It should be noted that the total yield of unsaturates and aromatics in aromatization of the mixture over pure chromium oxide (experiment 9) is less than the content of heptene in the initial mixture. This is apparently due to the fact that during the aromatization process part of the heptene was hydrogenated by hydrogen evolved in the dehydrocyclization reaction. In experiment 10 (potash additive), the sum of unsaturates and aromatics was 41%, i.e., hydrogenation of heptene with potassium added to pure chromium oxide practically does not occur. In experiment 11 the total yields of these hydrocarbons amounted to 49%; in other words, upon introduction of phosphoric acid, hydrogenation of heptene practically ceases, within the experimental error. Comparison of the chromatograms showed that introduction of potassium sharply decreases the yield of cracking and isomerization products of heptene. Conversely, introduction of phosphoric acid slightly increased cracking and, as might have been expected, intensified isomerization of heptene.

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CITED LITERATURE

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2. A. M. Rubinshtein, N. A. Pribytkova, A. A. Slinkin, *Kinetics and Catalysis*, **1**, No. 1, 129 (1960).

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

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