# THE VALENCE STATE OF CHROMIUM IONS CONTAINED IN THE ACTIVE SITES OF DEHYDROCYLIZATION OF PARAFFIN HYDROCARBONS ON ALUMINOCHROMIUM CATALYSTS

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An investigation of the development (increase in activity in the initial period of operation) of a catalyst, containing oxides of metals of variable valence, is a convenient method for the study of the role of the valence state of ions of these metals in the catalytic conversions of hydrocarbons. For example, in the dehydrocyclization of n-hexane, on an oxidized aluminochromiumpotassium catalyst, a gradual increase in the activity is observed, associated with the reduction of $Cr^{6+}$ ions [1, 2], as well as $Cr^{3+}$ ions [3] by the first portions of the hydrocarbon. This indicates that dehydrocyclizing activity is possessed by chromium ions of lower oxidation states than 3 +. However, the conclusions drawn in [3] are not entirely unambiguous, since during the preparation of the catalyst, the possibility of the formation of chromium ions in it in an oxidation state greater than 3 + was not excluded. In this case the appearance of dehydrocyclizing activity might be ascribed to the formation of $Cr^{3+}$ ions, and not $Cr^{2+}$ in the reduction of the catalyst by the hydrocarbon. And yet, there was no strict evidence that the hydrocarbon is capable of reducing chromium ions to $Cr^{2+}$. Evidently, a final solution of the problem will necessitate dehydrocyclization on an aluminumchromium catalyst that would be known to contain only $Cr^{3+}$ ions before the beginning of the experiment, and would not contain adsorbed oxygen, and also to ascertain that under the conditions of the experiment (550°) the hydrocarbon is capable of reducing chromium ions to $Cr^{2+}$.

## EXPERIMENTAL METHOD

The catalysts were prepared in a box equipped with supply lines for the delivery of $NH_4OH$, distilled water, $N_2$, He, and for the connection of a water jet pump with filtering funnel. During the work, $N_2$ or He was continuously passed through the box with an excess gas pressure in the box of 30-50 mm of water.

A catalyst with 14% chromium (20% $Cr_2O_3$) was produced by coprecipitation of $Cr^{3+}$ and $Al^{3+}$ hydroxides with ammonia from a solution of their chlorides. The precipitate obtained was repeatedly washed and filtered until $Cl^-$ ions disappeared in the filtrate. A catalyst with 0.3% chromium (here and henceforth mass %) was produced by impregnating $Al_2O_3$ with a solution of $CrCl_3$, followed by treatment with a solution of ammonia and washing free of $Cl^-$ ions. A silica gel-chromium catalyst with 0.3% Cr was produced by impregnating silica gel washed free of iron ions with a solution of chromic acid.

The distilled water used for the preparation of the catalysts was boiled for 3-4 h in a stream of $N_2$ to remove dissolved oxygen. The $Al_2O_3$ used to prepare the catalysts with 0.3% Cr was calcined at 550°C in a reactor and cooled in a stream of He, and then the reactor was transferred in hermetically sealed form to a box. Grade "high purity" helium, used to purge the box and as a carrier gas, contained no more than $5 \cdot 10^{-4}$ vol. % $O_2$.

The loading of the catalyst into the reactors was also performed in the box. The filled reactors were hermetically sealed with stoppers with stopcocks, and then extracted from the box. Before connection of the reactors to the catalytic setup, all open volumes that were in contact with the atmosphere were thoroughly purged with helium, which excluded the possibility of penetration of atmospheric oxygen to the catalysts.

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The amount of the catalyst loaded was determined at the end of the testing after oxidative regeneration.

Experiments on the dehydrocyclization of n-hexane were conducted at 550° in a stream of He (80 ml /min) in a pulsed catalytic setup [4], connected to a capillary column with an efficiency of 20,000 theoretical plates and a flame-ionization detector. In certain experiments the catalyst was preliminarily reduced in the setup itself in a stream of $H_2$ at 550° for 30 min, and then purged with helium for 1 h. For each experiment we took a new portion of catalyst, into which 5-10 pulses of n-hexane, $\sim 0.05\ \mu l$ each time, were successively introduced with the aid of a separator of the gas flow mounted in front of the reactor, as a result of which when $\sim 0.5\ \mu l$ of hexane was admitted to the closed device, only one-tenth of this amount reached the catalyst.

The dispersion between the amounts of n-hexane introduced in each pulse was 20%. Therefore, the summary yields of hydrocarbons were considered constant if the difference between them was no more than 20% rel.

## DISCUSSION OF RESULTS

All the catalysts exhibited a pronounced development when the dehydrocyclization of n-hexane was conducted with them in a pulsed system at 550° (Tables 1 and 2). The number of pulses necessary for the establishment of constant activity of the catalyst was the greatest for samples with a higher chromium content (compare experiments 1-4 and 6-7) and was decreased with decreasing amounts of the catalyst used (compare experiments 1-4). At the same time, when dehydrocyclization was conducted on preliminarily reduced samples, the yield of benzene and its content in the effluent hydrocarbons were high from the very first pulse (experiments 5, 8) and did not increase in the subsequent pulses.

Table 2 cites more detailed information on the composition of the conversion products of n-hexane, as well as the summary yields of hydrocarbons, for two typical experiments. Experiment 2 was conducted with a catalyst heated in a stream of He at 550°, experiment 5 with the same catalyst, but preliminarily reduced with $H_2$. In experiment 2, after the introduction of the first pulse of n-hexane, neither hexane itself nor its conversion products were detected among the hydrocarbons emerging from the reactor. In subsequent admissions of n-hexane, the summary yield of hydrocarbons increased, and benzene appeared in them. The mixture of hydrocarbons emerging from the catalyst at first contained only benzene and cracking products of n-hexane. The unreacted n-hexane appeared among them only when the fourth pulse was introduced. The indicated patterns were observed in all the experiments with a sample of the unreduced catalyst weighing more than 0.2 g, which, as might have been expected, is associated with the reduction of $Cr^{3+}$ ions to $Cr^{2+}$.

The theoretical possibility of the formation of $Cr^{2+}$ in the case of reduction of a chromium oxide catalyst with hydrocarbon was demonstrated for the example of a silica gel-chromium catalyst, containing 0.3% Cr. The selection of this catalyst was due to the fact that as was shown in [5], after reduction with CO, the band characteristic of $Cr^{2+}$ distinctly appears in its UV spectrum. In this work the catalyst was reduced with propane at 550°, since propane forms less coke in comparison with its higher homologs [6]. When propane was admitted, after 20-30 sec the catalyst acquired a blue color, while in the case of a longer reduction, it became appreciably covered with coke. In the spectrum of the reduced (but not coked)

TABLE 1. Change in the Yields of Benzene on Aluminochromium Catalysts in Experiments on the Dehydrocyclization of n-Hexane (Pulsed system, 550°, helium velocity 80 ml/min, size of pulse 0.05 $\mu$l)

| Expt. No. | Catalyst | | Pulse No. | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Cr, % | g | 1 | 2 | 3 | 4 | 5 | 6 | 7–10 |
| 1 | 14 | 0,48 | 0 | 0,02 | 0,2 | 2 | 30 | 30 | 90 |
| 2 | 14 | 0,26 | 0 | 0,4 | 30 | 80 | 90 | 80 | |
| 3 | 14 | 0,24 | 0 | 10 | 80 | 80 | 80 | 90 | |
| 4 | 14 | 0,13 | 10 | 70 | 70 | 80 | 90 | | |
| 5 | 14* | 0,13 | 60 | 50 | 60 | 50 | | | |
| 6 | 0,3 | 1,7 | 0 | 0,2 | 8 | 21 | 15 | 13 | |
| 7 | 0,3 | 1,0 | 0 | 1 | 12 | 8 | 7 | 7 | |
| 8 | 0,3* | 1,0 | 40 | 35 | 30 | 35 | 20 | | |

*The catalyst was reduced before the experiment with hydrogen at 550°, and then purged with helium at the same temperature.

TABLE 2. Summary Yields of Hydrocarbons and Their Composition in Experiments on the Dehydrocyclization of n-Hexane on an Aluminochromium Catalyst, Containing 14% Cr (Pulsed system, 550°, He velocity 80 ml/min, size of pulse 0.05 μl)

| Hydrocarbons | Experiment 2, unreduced catalyst | | | | | | Experiment 5, catalyst reduced with $H_2$ | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | pulse No. | | | | | | | | | |
| | 1 | 2 | 3 | 4 | 5 | 6 | 1 | 2 | 3 | 4 |
| Summary yield of hydrocarbons | 0 | 0,5 | 30 | 80 | 100 | 90 | 100 | 80 | 100 | 80 |
| Hydrocarbon composition: | | | | | | | | | | |
| n-hexane | 0 | 0 | 0 | 0,4 | 0,5 | 0,7 | 32 | 32 | 38 | 28 |
| products of n-hexane cracking | 0 | 21 | 3 | 4 | 4 | 5 | 4 | 4 | 4 | 4 |
| benzene | 0 | 79 | 97 | 96 | 95 | 95 | 63 | 63 | 57 | 66 |

sample, a band characteristic of $Cr^{2+}$ was detected. This fact, as well as the available literature data [7, 8], indicates that at 500-550°, hydrocarbons are actually capable of reducing chromium in chromium oxide catalysts to the oxidation state 2 +. It can therefore be assumed with good probability that the reduced summary yields of hydrocarbons in the case of the introduction of the first two to three pulses of n-hexane to the unreduced aluminochromium catalyst (see Table 2) are associated with the consumption of hydrocarbons for the reduction of $Cr^{3+}$, evidently to $Cr^{2+}$. Unfortunately, the $CO_2$ and $H_2O$ formed in this case could not be detected in view of the insensitivity of the flame-ionization detector to these substances. At the same time, when dehydrocyclization was conducted on a preliminarily reduced sample, the summary yields of hydrocarbons were high and constant when all four pulses of n-hexane were introduced (see Table 2, experiment 5).

Since a sharp increase in the yields of benzene was observed simultaneously with the reduction of $Cr^{3+}$, it might be thought that the active centers of dehydrocyclization are formed during the process of reduction. Evidently when the amount of the catalyst taken is increased, the amount of the hydrocarbon necessary for its reduction also increases. As can be seen from Table 1, this leads to a lengthening of the period of formation of the activity of the catalyst. The appearance of a small amount of benzene (yield 10%) after the introduction of the first pulse of hexane in experiments with the smallest samples of the catalysts (0.13 g, experiment 4) is explained by the fact that the amount of hydrocarbon introduced in one pulse proved to be sufficient not only for the reduction of $Cr^{3+}$, but also for the subsequent participation in the dehydrocyclization reaction. At the same time, in experiments with preliminarily reduced samples already containing $Cr^{2+}$, the yield of benzene and its content among the other hydrocarbons were higher and constant from the very beginning of the experiment (experiments 5 and 8), which confirms the conclusion drawn.

Attempts to treat the results obtained as the participation only of $Cr^{3+}$ ions in the reaction under consideration proved far less successful. For example, the low initial yields of benzene can be explained by a ratio of the rate constants of oxidation of hexane (in the reduction of $Cr^{3+}$ to $Cr^{2+}$) and its dehydrocyclization (on other, unreduced $Cr^{3+}$ ions) unfavorable for its formation. Moreover, in the reduction of the catalyst, water vapors are formed, which, as is well known [1], poison aluminochromium dehydrocyclization catalysts. Actually, when one pulse of n-hexane is introduced into an unreduced sample (weight of the sample 0.2 g or more), not even traces of benzene are formed. This could be only in the case of the total absence of active centers of dehydrocyclization on the catalyst or in the case when the rate of oxidation of hexane with at least 1000 times greater than the rate of its dehydrocyclization (according to the sensitivity of the analysis). The latter seems rather improbable to us, since in certain experiments (experiment 7), in the case of admission of the first pulse, small quantities of unoxidized hydrocarbons emerged from the catalyst in the form of cracking products of n-hexane, but benzene, as before, was not detected among them. As for the influence of water vapors, they could be formed only after the introduction of the first portion of n-hexane and therefore could in no way influence the activity of the initial catalyst. Thus, all these facts: the absence of dehydrocyclizing activity in the unreduced catalyst, its appearance after the reduction of the catalyst with hydrogen and hydrocarbon, and, finally, the parallelism between the increase in the yields of benzene and the summary yields of hydrocarbons — are evidence in our opinion in support of the participation of $Cr^{2+}$ ions in the active centers of dehydrocyclization.

Turning to experiments with reduced catalysts, let us note that traces of $O_2$ ($5 \cdot 10^{-4}$ vol. %) and He did not produce any significant oxidation of the reduced sample. This follows from the fact that after reduction with hydrogen, followed by purging with helium, the catalyst was not developed with respect to the reaction studied. Evidently, the unreduced samples could not be oxidized to a greater degree when helium was passed through the box, and then through the reactor during its heating. Consequently, the formation of chromium ions in an oxidation state greater than 3 could not be so significant as to be the cause of the development of the unreduced samples.

Thus, the development of aluminochromium catalysts is observed not only in the case of reduction of $Cr^{6+}$, but also for the reduction of $Cr^{3+}$, which is associated with the formation of the active sites of dehydrocyclization, evidently including $Cr^{2+}$ ions. Hexane readily reduces $Cr^{3+}$ ions at 550°, and thus, itself prepares the centers for subsequent dehydrocyclization.

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## CONCLUSIONS

In an investigation of aluminochromium catalysts in a pulsed system, it was found that the catalysts containing chromium only in the oxidation state 3 + do not catalyze the dehydrocyclization of paraffin hydrocarbons.

When several successive pulses of n-hexane are introduced, the activity of such catalysts increases, which is explained by the formation of $Cr^{2+}$ ions in the active centers of dehydrocyclization, the existence of which in the reduced catalysts is demonstrated with the aid of the UV spectra.

## LITERATURE CITED

1. M. I. Rozengart, K. M. Gitis, and B. A. Kazanskii, Neftekhimiya, 4, 406 (1964).
2. M. I. Rozengart, Z. F. Kuznetsova, and K. M. Gitis, Neftekhimiya, 5, 17 (1965).
3. K. M. Gitis, K. I. Slovetskaya, M. I. Rozengart, and A. M. Rubinshtein, Kinetika i Kataliz, 11, 1189 (1970).
4. E. S. Mortikov, M. I. Rozengart, and B. A. Kazanskii, Izv. Akad. Nauk SSSR, Ser. Khim., 99 (1968).
5. L. K. Przheval'skaya, V. A. Shvets, and V. B. Kazanskii, Kinetika i Kataliz, 11, 1310 (1970).
6. L. A. Novikova, M. I. Rozengart, N. F. Kononov, N. G. Ivanova, T. V. Zueva, and B. A. Kazanskii, Neftekhimiya, 6, 531 (1966).
7. H. Z. Krauss and H. Stach, Z. Anorgan. und Allgem. Chem., 366, 34 (1969).
8. H. Z. Krauss and H. Stach, Inorg. and Nucl. Chem. Letters, 4, 393 (1968).