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Abstract

Full Text

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STRUCTURE AND CATALYTIC PROPERTIES OF CHROMIUM-SILICA-GEL CATALYSTS

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The dehydrating and dehydrocyclizing action of `Cr$_{2}$O$_{3}$` has in most cases been studied using aluminochromium catalysts. However, the possibility of using silica gel as a support for `Cr$_{2}$O$_{3}$` has repeatedly attracted the attention of investigators (`1-3`).

In studying the aromatization of paraffinic hydrocarbons on various catalysts, including chromium-silica-gel catalysts, we observed that one type of these catalysts—namely, a chromium-silica-gel catalyst preliminarily treated with ethyl alcohol—strongly changes its stability during the aromatization of *n*-heptane depending on the nature of the gas in whose stream the fresh sample was heated before the experiment. This circumstance led us to study in greater detail the influence of preparation methods on the dehydrating action and structural characteristics of these catalysts, in the hope of shedding light on the causes affecting the stability of oxide catalysts during dehydrocyclization.

It turned out that a chromium-silica-gel catalyst preliminarily treated with alcohol and heated before the experiment in a stream of air was rapidly poisoned during the dehydrocyclization of heptane, possessed antiferromagnetic properties, and showed sharp `Cr$_{2}$O$_{3}$` lines on X-ray patterns. The very same preparation of catalyst, reduced with alcohol but preliminarily heated in a stream of hydrogen, was not poisoned practically during a two-hour experiment on the aromatization of *n*-heptane, and proved to be paramagnetic and X-ray amorphous.

Fig. 1. Adsorption of a paraffinic hydrocarbon on crystalline `Cr$_{2}$O$_{3}$`

(plane III): *a*—`O$^{2-}$` ions; *b*—`Cr$^{3+}$` ions; *v*—C atoms; *g*—possible sites of bond closure.

On the basis of such a difference in the structural characteristics of these two samples, one may make an assumption about the causes of the difference in some of their catalytic properties, in particular, their stability during the experiment. It is generally accepted that the aromatization of paraffinic hydrocarbons proceeds by a doublet-sextet mechanism (4,5), which requires a definite spatial arrangement of chromium atoms in the form of sextets (4-6). The antiferromagnetism of the first sample is associated with the presence of crystalline `Cr$_{2}$O$_{3}$`, in which each `Cr$^{3+}$` ion (in the plane) is surrounded by three other `Cr$^{3+}$` ions with oppositely directed resultant spins, all of them together forming a continuous network of sextets in the plane (III) (6). Paraffin molecules that fall on two neighboring sextets of `Cr$^{3+}$` ions can in this case be adsorbed in such a way (see Fig. 1) that, along with intramolecular closure of C—C bonds leading to aromatization of the paraffinic hydrocarbon, the formation of a new intermolecular C—C bond also becomes possible; this should lead to the creation on the catalyst surface of chains or a network of hydrocarbon molecules (i.e., a polymer), which are converted into coke.

The paramagnetic properties of the second sample indicate the absence of antiferromagnetic interaction. This may be due to the fact that the sextets of Cr^{3+} ions in this case do not form a continuous network, but are scattered over the surface of the support. As a result, the formation of intermolecular C—C bonds, leading to coke deposition, is greatly hindered.

Since poisoning of the catalyst during the aromatization experiment is caused by the deposition of coke on its surface, the difference noted above in the structure of the catalysts should affect their stability during the experiment, which was indeed found experimentally.

Experimental Part

The catalytic experiments were carried out by the procedure described earlier (7). Catalyst 1 was prepared from coarse-pore KSK silica gel after complete removal of Cl and SO_4 ions. A dry silica-gel charge heated to 110° was impregnated with an aqueous CrO_3 solution, calculated to give 15 mol.% Cr_2O_3 in the finished catalyst. The preparation was dried and then reduced with ethanol. A catalyst sample (20 cm^2) was heated to 535° in an air stream (catalyst 1A), after which an experiment with heptane was carried out; the yield of aromatics was 35 wt.%; the catalyst had a high initial activity, but was rapidly poisoned during the experiment (see Fig. 2). At the same time, its activity in the dehydrogenation of cyclohexane changed hardly at all during a two-hour experiment. After regeneration the catalyst almost completely restored its initial activity and was again rapidly poisoned during the experiment.

Fig. 2. Change in the refractive index of catalysts during the experiment: 1—catalyst 1B, heated in an H_2 stream; 2—catalyst 2B, heated in an H_2 stream; 3

Fig. 2. Change in the refractive index of catalysts during the experiment: 1—catalyst 1B, heated in an H_2 stream; 2—catalyst 2B, heated in an H_2 stream; 3—catalyst 1A, heated in an air stream (*a*—fresh sample, *b*—after regeneration); 4—catalyst 1B after regeneration; 5—catalyst 2A, heated in an air stream

Figure 2: Fig. 2. Change in the refractive index of catalysts during the experiment: 1—catalyst 1B, heated in an H_2 stream; 2—catalyst 2B, heated in an H_2 stream; 3—catalyst 1A, heated in an air stream (*a*—fresh sample, *b*—after regeneration); 4—catalyst 1B after regeneration; 5—catalyst 2A, heated in an air stream

—catalyst 1A, heated in an air stream (*a*—fresh sample, *b*—after regeneration); 4—catalyst 1B after regeneration; 5—catalyst 2A, heated in an air stream.

Catalyst 1B (after treatment with alcohol and drying, heated to the experimental temperature in a hydrogen stream) behaved differently from the preceding one. The yield of aromatics on a fresh sample of catalyst 1B was 56%. The sample lost almost no activity during the two-hour experiment, as is evident from the small change in the refractive index of the catalyzate with time (see Fig. 2). After the very first regeneration with air, the activity of catalyst 1B decreased and it began to be poisoned rapidly during the experiment, so that the yield of aromatics in the experiment after regeneration and in subsequent experiments was approximately 35%.

Thus, heating individual samples of catalyst 1 in an air stream in all cases led to a decrease in the stability of the catalyst in the dehydrocyclization process. To clarify the reasons for this phenomenon, we carried out further experiments.

First of all, catalysts 2A and 2B were prepared, analogous to catalysts 1A and 1B, but on silica gel from which metal oxides had been removed by repeated boiling with fresh portions of concentrated HCl and subsequent washing with HCl, HNO_3, and water. As can be seen from the data in Table 1, the difference in the behavior of catalysts 2A and 2B is analogous to that observed for catalysts 1. Thus it was established that the difference in the properties of the catalysts heated beforehand in an air stream or in H_2 did not depend on impurities of oxides of other metals contained in the silica gel. In view of the fact that CrO_3 was thoroughly purified by recrystallization, it may be assumed that the observed difference in the behavior of the catalysts is due to the nonidentity of their structure and phase composition as a result of different genesis. Therefore we investigated the influence of

methods of preparation on these properties of the catalysts by X-ray and magnetochemical methods, preparing a series of catalyst 2 specimens (for convenience they are numbered with Roman numerals); the conditions of their preparation are presented in the scheme. The magnetic susceptibility of the paramagnetic catalysts was determined by the Faraday method in the temperature range 20-160° and at field strengths from 3000 to 5000 oersted, and that of the diamagnetic ones by the Gouy method. To measure the magnetic properties of the reduced samples, they

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SiO$_{2}$—CrO$_{3}$ I (dried in air at 130°)

          treated with air, 515°, 1 h
Cr$_{2}$O$_{3}$—SiO$_{2}$ II

Cr$_{2}$O$_{3}$—SiO$_{2}$ VII  $\leftarrow$ treated with air, 515°, 1 h $\leftarrow$  Cr$_{

        ↓ treated with H$_{2}$, 515°, 1 h
Cr$_{2}$O$_{3}$—SiO$_{2}$ III

        ↓ treated with air, 515°, 1 h
Cr$_{2}$O$_{3}$—SiO$_{2}$ IV  $\rightarrow$ treated with H$_{2}$, 515°, 1 h $\rightarrow$

        ↓ treated with O$_{2}$, 515°, 1 h
Cr$_{2}$O$_{3}$—SiO$_{2}$ V

From SiO$_{2}$—CrO$_{3}$ I:
        ↓ treated with H$_{2}$, 515°, 1 h
Cr$_{2}$O$_{3}$—SiO$_{2}$ VIII

          treated with air, 515°, 1 h
Cr$_{2}$O$_{3}$—SiO$_{2}$ IX
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were annealed in glass ampoules in a stream of hydrogen. Phase analysis was carried out from X-ray diffraction patterns obtained in RKD cameras with radiation of the copper K_{α} series (Ni filter).

The initial dry silica gel washed free of Fe was diamagnetic at 20°, with $\chi \cdot 10^6 = -0.29$; after treatment at 515° in a stream of H_2, $\chi \cdot 10^6 = -0.45$; the initial preparation of catalyst 2—specimen I (silica gel with CrO_3 deposited on it)—was also diamagnetic, $\chi \cdot 10^6 = -0.1$. The susceptibility of all these samples did not depend on the field strength in the interval studied. Table 2 gives data on the phase composition and magnetic properties of the catalysts I-IX studied. From the data of Table 2 it is evident that

Table 1

Aromatization of n-heptane and cyclohexane at atmospheric pressure on Cr_2O_3—SiO_2 *catalysts*

Experiment No.	Catalyst No.	Substance	Temp., °C	Space velocity, h^{-1}	Yield based on hydrocarbon passed, wt.%: catalyst	Yield based on hydrocarbon passed, wt.%: aromatics
1	1A	*n*-Heptane	535	0.19	65	36
2	1A	*n*-Heptane	535	0.19	74	41
3	1A	Cyclohexane	535	0.14	63	58
4	1A	Cyclohexane	535	0.17	65	50
5	1A	*n*-Heptane	510	0.18	71	33
6	1A	*n*-Heptane	510	0.18	66	31
7	1B	*n*-Heptane	535	0.18	61	56
8	1B	*n*-Heptane	535	0.18	65	34
10	1B	*n*-Heptane	535	0.18	70	35
11	2A	*n*-Heptane	510	0.18	66	21
12	2A	*n*-Heptane	510	0.18	70	25
13	2B	*n*-Heptane	510	0.18	64	54
14	2B	*n*-Heptane	510	0.18	73	27
15	2B	*n*-Heptane	510	0.18	72	27

Note. Each subsequent experiment with a given catalyst was carried out after regeneration.

Table 2

Phase composition and magnetic properties of the catalysts

Catalyst no.	Catalytic phase	Relation to the Curie–Weiss law	$\chi \cdot 10^6$ at 20°C	$\chi \cdot 10^6$ at 83°C	$\chi \cdot 10^6$ at 160°C
I	Amorphous	Diamagnetic	−0.10	−0.10	−0.10
II	Amorphous	Obeys	13.2	11.3	10.1
III	Amorphous	Obeys	13.2	11.5	10.3
IV	Cr_2O_3	Does not obey	7.5	7.4	7.0
V	Cr_2O_3	Does not obey	7.8	7.6	7.0
VI	Cr_2O_3	Does not obey	8.3	8.1	7.6
VII	Cr_2O_3	Does not obey	7.7	7.6	7.0
VIII	Cr_2O_3	Does not obey	7.3	7.4	6.9
IX	Cr_2O_3	Does not obey	6.7	6.9*	6.5**

* Measured at 60°.
** Measured at 120°.

that the samples studied are divided into two groups. 1) X-ray-amorphous, paramagnetic catalysts—samples II and III*—the temperature dependence of whose susceptibility obeys the Curie–Weiss law, which made it possible to calculate the magnetic moment, found to be equal to 3.2 μB for both samples; and 2) samples IV–IX, antiferromagnetic, all the lines in whose X-ray diffraction patterns were identified as Cr_2O_3 lines.

Thus, sample VIII, obtained from sample I by heating in a stream of H_2 without preliminary treatment with alcohol, contains crystalline Cr_2O_3, as do samples V and VI; whereas sample III, obtained by heating sample II in a stream of H_2, is X-ray-amorphous and paramagnetic. It may be assumed that in the first case Cr_2O_3 is reduced directly to Cr_2O_3, while in the second—during treatment with alcohol—some intermediate chromium compound is formed, stable in a hydrogen atmosphere but forming crystalline Cr_2O_3 upon heating in an air stream. It is possible that this intermediate compound is chromium silicate, formed during treatment of the catalyst with alcohol, or else nonstoichiometric chromium oxides, which may be obtained in the reduction of CrO_3 with alcohol in the absence of other mineral acids.

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* The Cr-containing phase in them is in a state of very high dispersion. An X-ray-amorphous structure in the present case may also result because the rays reflected from very small crystals are completely scattered by the amorphous SiO_2 support.

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

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