Academician A. A. BALANDIN, I. D. ROZHDESTVENSKAYA, and A. A. SLINKIN

![Fig. 1](figure)

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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

Academician A. A. BALANDIN, I. D. ROZHDESTVENSKAYA, and A. A. SLINKIN

THE EFFECT OF DIFFERENT GAS TREATMENTS ON THE CATALYTIC AND MAGNETIC PROPERTIES OF A CHROMIUM OXIDE CATALYST

It is known that treatment of chromium oxide with various gases leads to a change in its catalytic and semiconducting properties ($^{1-3}$). It is of interest to compare the change in the magnetic and catalytic properties of chromium oxide as a function of the conditions of its thermal treatment. Turkevich (^{4}) studied the magnetic and catalytic properties of amorphous and crystalline chromium oxide treated with hydrogen in the dehydrocyclization reaction of heptane. He showed that amorphous and crystalline samples of chromium oxide, sharply differing in catalytic activity, are identical in magnetic properties, being antiferromagnets. In most works, for chromium oxide obtained by various methods, values of the magnetic susceptibility (χ) are given that lie within the range $18–26 \cdot 10^{-6}$ ($^{4-6}$). For chromium oxide treated with hydrogen at 1000°, a value $\chi = 59.0 \cdot 10^{-6}$ was obtained (^{5}). As will be shown below, this is apparently connected with the presence of ferromagnetic impurities in the sample. Among ferromagnetic oxygen compounds of chromium, crystalline chromium dioxide is known, with $\chi = 6.0 \cdot 10^{-1}$, and chromium monochromate, with $\chi = 3.5 \cdot 10^{-1}$ (^{7}).

Fig. 1

In addition, it was of interest to study the effect of treatment of chromium oxide with atomic hydrogen on its catalytic properties. Up to now there has been very little information on the action of atomic hydrogen on the activity of catalysts. In 1952 a paper appeared (^{8}) in which the activating action of atomic hydrogen on a tungsten catalyst for ammonia synthesis was studied. This catalyst had considerably greater activity than one reduced in the usual way; however, its activity was very unstable.

The starting substances, the method of preparing chromium hydroxide, and the apparatus for carrying out the kinetic experiments were the same as in

([9]). To prepare the catalysts, chemically pure chromium nitrate was used. The conditions of thermal treatment of the initial hydroxide are presented in Scheme I, and the results of measurements of χ in Table 1 (the numerals Ia and IIa denote samples obtained from chromium nitrate of "pure" grade).

Experiments on treating the catalyst with atomic hydrogen were carried out in the apparatus shown in Fig. 1. Hydrogen obtained by electrolysis

potassium hydroxide solution, was purified of oxygen by passing it over Pd-asbestos at 180° and of moisture by passing it through columns with dehydrated silica gel. Pure hydrogen entered the discharge tube 1, made of molybdenum glass. Aluminum electrodes 2 on tungsten leads were sealed into it. A voltage of 10,000–12,000 V was applied to the electrodes.

Scheme I

Cr_2O_3 (VII) $Cr(OH)_3$
$\nwarrow$ H, 0.5 h $\swarrow$ H_2, 500°, 10 h $\downarrow$ N_2, 500°, 10 h $\searrow$ air, 500°, 10 h
Cr_2O_3 (VIII) $\xleftarrow{H,\ 6\ h}$ Cr_2O_3 (I) Cr_2O_3 (II)
$\swarrow$ H, 20 h $\downarrow$ air, 500°, 10 h
Cr_2O_3 (IX) Cr_2O_3 (V)

An insert 3, ending in ground joint 11, was fitted into the discharge tube by means of a ground joint; into this insert entered the lower ground joint of cup 4 containing the catalyst sample. The cup had a mesh bottom. The insert was provided with a seal-in for a thermocouple and was connected through cock 5 with a vacuum pump and a vacuum gauge. The cup with the catalyst was located at a distance of 15 cm from the discharge. The catalyst charge was 0.7 g. Reduction of the catalyst proceeded as follows. The discharge tube was evacuated to a pressure of 10^{-3} mm, the tightness was checked, after which the system was filled with pure hydrogen. Then continuous pumping of the hydrogen passing through the cup with the catalyst was begun, so that a pressure of the order of 1-2 mm was maintained in the system, and voltage was applied to the electrodes. Atomic hydrogen from the discharge tube was drawn through the catalyst for a certain time, after which the voltage was switched off, the system was filled with hydrogen, and the catalyst in the cup, by means of a cable and cock with pulley 6, was raised into the catalytic tube 7 until the upper ground joint of cup 10 came into contact with the ground portion of tube 9. In this operation the pocket with the thermocouple touched the upper layer of the catalyst. In a continuous

Table 1

Dependence of χ on temperature for various Cr_2O_3 preparations

Catalyst No.	$\chi \cdot 10^6$ at 20°C	$\chi \cdot 10^6$ at 50°C	$\chi \cdot 10^6$ at 80°C	$\chi \cdot 10^6$ at 160°C	$\Delta°, K$	μ_B	Catalyst No.	$\chi \cdot 10^6$ at 20°C	$\chi \cdot 10^6$ at 50°C	$\chi \cdot 10^6$ at 80°C	$\chi \cdot 10^6$ at 160°C
I	24.0	25.3	24.4	23.3			VI	24.4	25.2	23.4	23.0
II	23.8	25.0	23.6	22.9			VII	92.0	–	–	–
III	340.0	–	–	–			Ia	96.0	–	–	–
IV	28.0	–	25.8	24.0	500	3.7	IIa	21.8	–	22.1	20.8
V	22.8	24.3	23.3	22.8							

stream of hydrogen, entering from above through cock 8, the catalytic tube was transferred from the ground joint of the discharge tube to the ground joint of the receiver, the furnace heating was switched on, and the experiment was carried out at a definite temperature. Before each experiment the catalyst was regenerated in a stream of molecular hydrogen at 500° for 2 h in order to remove reaction products from its surface.

As is evident from the data of Table 1, catalysts I and II, obtained by treatment of the hydroxide with hydrogen and nitrogen, respectively, are antiferromagnets with a Néel temperature of about 50°C. Sample IX, obtained from I by treatment with atomic hydrogen, is likewise antiferromagnetic. On the other hand, treatment of the hydroxide with air under the same conditions (temperature 500°C) leads to the appearance of appreciable ferromagnetism (sample III). This appearance of ferromagnetism has two features. 1) It is not associated with the presence of ferromagnetic impurities in the sample, since treatment of the initial hydroxide with hydrogen and even with atomic hydrogen does not lead to the appearance of fer-

Table 2

Catalyst no.	Decomposition of iso-C_3H_7OH: reaction temp. °C	Decomposition of iso-C_3H_7OH: V_{0H2}, ml/min	Decomposition of iso-C_3H_7OH: V_{0H2O}, ml/min	Decomposition of C_3H_7OH: % reacted	Decomposition of iso-C_3H_7OH: Δ, °C	Decomposition of iso-C_3H_7OH: ε_{H2}, kcal/mol	Decomposition of iso-C_3H_7OH: ε_{H2O}, kcal/mol	Dehydrogenation of C_6H_{12}: reaction temp. °C	Dehydrogenation of C_6H_{12}: V_{0H2}, ml/min	Dehydrogenation of C_6H_{12}: Δ, °C	Dehydrogenation of C_6H_{12}: ε_{H2}	Q	Q	Q	S, m^2/g
I	241–295	4.0–10.7	0.3–2.6	6.4–49.3	22	9.5	23.1	335–395	11.1–32.8	0	14.5	66.3	22.8	41.5	55
II	250–295	4.3–10.5	0.3–2.0	5.7–45.6	22	10.3	24.3	331–403	6.0–25.8	0	15.8	66.1	22.1	41.5	28
III	280–328	3.1–9.8	2.2–6.6	41.0–75.4	107	10.4	26.7	337–444	10.1–36.5	49	31.8	65.4	24.3	52.7	35

Catalyst no.	Decomposition of iso-C_3H_7OH: reaction temp, °C	Decomposition of iso-C_3H_7OH: V_{0H2}, ml/min	Decomposition of iso-C_3H_7OH: V_{0H2O}, ml/min	Decomposition of iso-C_3H_7OH: % reacted	Decomposition of iso-C_3H_7OH: Δ, °C	Decomposition of iso-C_3H_7OH: ε_{H2}, kcal/mol	Decomposition of iso-C_3H_7OH: ε_{H2O}, kcal/mol	Dehydrogenation of C_6H_{12}: reaction temp, °C	Dehydrogenation of C_6H_{12}: V_{0H2}, ml/min	Dehydrogenation of C_6H_{12}: Δ, °C	Dehydrogenation of C_6H_{12}: ε_{H2}	Q	Q	Q	S, m^2/g
IV	280–326	3.8–9.6	1.9–8.0	33.0–65.5	6	11.8	19.2	348–410	10.4–36.4	0	24.4	62.2	26.9	44.7	55
V	246–286	4.6–11.3	0.6–2.7	11.0–18.5	36	14.3	20.8	378–450	5.0–40.6	22	26.5	60.1	21.1	50.8	25
Ia	260–302	5.2–13.8	0.8–3.0	12.0–48.6	22	14.5	20.3	362–456	6.5–42.4	0	26.7	57.0	23.9	52.1	56
IIa	252–294	3.7–11.0	0.50–3.5	12.0–27.0	10	21.3	27.1	339–381	0.3–2.5	0	17.6	60.0	27.0	33.9	56
VI	299–356	4.1–8.6	1.2–3.1	20.5–26.7	–	0.6	14.3	438–466	8.0–28.3	0	22.3	57.4	26.6	56.9	–
VII	300–363	3.8–11.1	1.2–4.5	25.3–47.0	–	10.0	13.8	436–483	8.0–23.0	0	25.4	55.7	26.0	57.0	–
IX	305–364	4.5–9.1	1.4–4.1	24.0–30.6	–	8.6	12.7	438–486	4.3–17.1	0	30.8	54.5	23.7	65.3	35

romagnetism, whereas $Cr(OH)_3$ obtained from reagent-grade $Cr(NO_3)_3$ and treated with hydrogen (sample Ia) exhibits ferromagnetism caused by the presence of impurities in the initial salt. 2) Ferromagnetism appears only under a definite temperature treatment of the hydroxide with air and decreases sharply when ferromagnetic sample III is heated in air at 600° (sample VI). Heating sample III in a stream of H_2 leads to the disappearance of ferromagnetism and to the appearance of paramagnetic sample IV. We believe that the appearance of ferromagnetism is apparently due to the formation of small amounts of chromium dioxide in the oxide under a definite regime of thermal treatment of the initial hydroxide.

The catalytic properties of the preparations obtained were tested in the reactions of decomposition of isopropyl alcohol and dehydrogenation of cyclohexane. The results are given in Table 2, from which it is evident that samples of chromium oxide obtained from the same hydroxide but subjected to different gas treatments possess different catalytic properties, namely different activity V_0 and selectivity of action, different values of the activation energy ε (kcal/mol), and different values of the bonding energy of the indexed atoms with the catalyst surface Q (kcal). The antiferromagnetic catalysts I and II have analogous catalytic properties both in the decomposition reaction of isopropyl alcohol and in the dehydrogenation reaction of cyclohexane. (The different catalytic properties of preparations Ia and IIa are connected with the presence of ferromagnetic impurities in the former.) On considering Table 2, particular attention is drawn to the fact that the ferromagnetic catalyst III and the antiferromagnetic catalyst IX, obtained from the hydroxide under completely different conditions, nevertheless lead to identical changes in the course of the reactions studied. Indeed, for both catalysts the dehydrogenation of cyclohexane is strongly suppressed and the dehydration of isopropyl alcohol is enhanced. This makes it possible to suppose that catalysts III and IX have the same chemical structure of the surface.

The acceleration of the dehydration of isopropyl alcohol is apparently connected with the formation on the surface of centers of the type

$$> \mathrm{Cr} - \mathrm{OH},$$

similar to the centers

$$> \mathrm{Al} - \mathrm{OH}$$

on the surface of Al_2O_3 (^{10}).

In catalyst IX, the formation of hydro-

···hydroxyl groups is associated with chemisorption of atomic hydrogen (12), and in catalyst III—with the interaction of CrO_2 with hydrogen liberated at the first moment of the reaction. The presence of such an interaction is confirmed by the large exothermic effect (Δ, °C) observed upon adsorption of isopropyl alcohol and cyclohexane on the surface of catalyst III. The formation of hydroxyl groups promoting the alcohol dehydration reaction also occurs in catalyst IV as a result of the reduction of CrO_2 by hydrogen.

The strong influence of OH groups on the dehydrogenation of cyclohexane was also demonstrated by treating chromium oxide (sample I) with water vapor, followed by regeneration in a stream of H_2 at 500°. Such a catalyst was completely inactive in the cyclohexane dehydrogenation reaction. Water also deactivates chromium oxide for deuterium-hydrogen exchange (13).

Regarding the relationship between the magnetic and catalytic properties of the studied samples of oxide-chromium catalyst, the following may be said. Different gas treatments of chromium oxide lead to samples with different magnetic properties. However, the magnetic data, as well as the electrical data, characterize the bulk properties of the samples and in a number of cases do not reflect changes in the chemical structure of the surface. In the present work it is precisely the change in surface properties that has the decisive influence on the course of the chemical reaction; therefore, it does not appear possible in the investigation carried out to establish a simple relationship between the magnetic and catalytic properties of oxide-chromium catalysts.

The use of the magnetic-susceptibility method in the present work proved very effective in that it was possible to detect a new phase, namely chromium dioxide in oxidized chromium oxide. The use of X-ray and electron-diffraction methods of investigation showed the presence of crystalline α-Cr_2O_3 in all the studied samples. These methods failed to detect CrO_2 because of their considerably lower sensitivity. Experiments on the treatment of chromium oxide with atomic hydrogen showed that this treatment leads to sharp deactivation of the catalyst with respect to the dehydrogenation of cyclohexane. On the other hand, in the decomposition of isopropyl alcohol, treatment with atomic hydrogen promotes the dehydration reaction, as already indicated above. Such a change in catalytic properties is apparently due to the chemical interaction of atomic hydrogen with the catalyst surface, with the formation of hydroxyl groups. This interaction proceeds very intensively in the first minutes, as evidenced by the difference in the catalytic properties of samples I and VII, and is sharply retarded upon further treatment. It is interesting to note the constancy of the activity of the samples treated with atomic hydrogen during a given experiment and upon passing from experiment to experiment in the reactions studied.

Zelinsky Institute of Organic Chemistry
Academy of Sciences of the USSR

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CITED LITERATURE

1. S. E. Voltz, S. Weller, *J. Am. Chem. Soc.*, **75**, 5227 (1953).
2. S. Weller, S. E. Voltz, *J. Am. Chem. Soc.*, **76**, 4695 (1954).
3. P. B. Weisz, C. D. Prater, K. D. Rittenhouse, *J. Chem. Phys.*, **21**, 2236 (1953); R. Chaplin, P. R. Chapman, R. H. Griffith, *Nature*, **172**, 77 (1953); P. R. Chapman, R. H. Griffith, J. D. F. Marsh, *Proc. Roy. Soc.*, A **224**, 419 (1954).
4. J. Turkevich, *J. Chem. Phys.*, **12**, 345 (1944).
5. W. H. Albrecht, E. Wedekind, *Zs. anorg. u. allgem. Chem.*, **210**, 105 (1933).
6. S. Bhatnagar, A. Camenron et al., *J. Chem. Soc.*, **1939**, 1433.
7. T. V. Rode, Doctoral dissertation, IOKh, Academy of Sciences of the USSR, Moscow, 1957.
8. S. L. Kiperman, N. A. Rybakova, M. I. Temkin, *ZhFKh*, **26**, 621 (1952).

9. A. A. Balandin, I. D. Rozhdestvenskaya, *ZhFKh*, **34**, No. 6 (1960).

10. K. V. Topchieva, K. Yu. Yun-Pin, I. V. Smirnova, in: *Surface Chemical Compounds and Their Role in the Phenomena of Adsorption and Catalysis*, Moscow, 1957.

11. A. M. Rubinshtein, A. A. Slinkin, *Izv. AN SSSR, OKhN*, 1958, No. 9, 1054.

12. O. Glemser, U. Hauschild, *G. Lutz, Zs. anorg. Chem.*, **269**, 93 (1952).

13. S. E. Voltz, S. Weller, *J. Am. Chem. Soc.*, **75**, 5231 (1953).

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