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Physicochemical and Catalytic Properties of the System Chromium Oxides–Oxygen–Water

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This paper describes investigations of various chemical, electrical, and catalytic properties of materials, obtained by calcination of chromic oxide gel. Samples of four different preparations of chromic oxide gel, whereof one contained additions of magnesium, were annealed for 5 hr in air at various temperatures between 100° and 700°. As shown by differential thermal, thermogravimetric, and X-ray analyses, dehydration first results in the formation of X-ray-amorphous monohydrate, which is stable over a wide range of temperatures between 280–360°. Simultaneously with dehydration the oxidation of the material takes place. The oxidation increases with increasing temperature of annealing. The O/Cr ratio, corresponding to maximal oxidation at 350°, amounts to about 2. It has been shown by applying various methods of chemical analysis that the excess charges are present in such material in the form of hexavalent chromium, the proper formula being thus $Cr_2O_3 \cdot CrO_3$ and not CrO_2. At 400° crystallization of Cr_2O_3 occurs, the oxide being at first considerably oxidized on the surface. This oxidation decreases on annealing at still higher temperatures. Addition of magnesium has no influence on the oxidation state of the amorphous material, but greatly increases the amount of excess charges in crystalline Cr_2O_3.

Measurements of the electrical conductivity and thermoelectric power indicate that the conduction mechanism is similar in the amorphous material and in the crystalline oxide. Changes of electrical conductivity and of its activation energy are related to the changes of concentration of Cr^{6+} ions.

The catalytic activity in H_2O_2 decomposition has been determined and specific rate constants, k, frequency factors k_0, and activation energies, E, of the reaction have been computed. The reaction exhibits a compensation effect, which hints at the changes of energy states of active centers with the temperature of annealing. This is consistent with the results of electrical conductivity measurements, since changes of activation energy of electrical conductivity are parallel to changes of activation energy of the reaction. The experiments reveal a correlation between rate constants, k, and surface concentration of Cr^{6+} ions, whereas discussion of the reaction mechanism shows that frequency factors k_0 rather than rate constants k should be related to this concentration.

The catalytic properties of chromium oxide have been extensively studied in the last few years from various viewpoints. T. W. Rode (*1*) has carried out detailed studies of the chemical properties of this oxide, aiming at the explanation of the mechanism of various processes taking place in the course of its formation. The objective of that research was also to find a correlation between the mode of preparation of the starting material and the chemical properties of the resulting chromic oxide. On the other hand Voltz and Weller have, in a series of papers (*2*) investigated the electronic properties of chromic oxide and tried to explain its catalytic activity in terms of the electronic theory of catalysis.

It is a well-known fact that chromic oxide gel, when heated in air, is oxidized to a large extent (*3*). The presence of chromium ions in various valence states enables an easy exchange of electrons between the oxide and adsorbed reactants of the catalytic reaction, the oxide being in position to accept electrons as well as to give them up. The chromium ions of higher valence can act as acceptor centers, whereas chromium ions of lower valence possess donor properties. Roginski (*4*) considers all such substances as being good catalysts for the redox reactions. It has been considered therefore of interest to investigate from this point of view the catalytic properties of the products of calcination of chromic oxide gels and to investigate what is the influence on these properties of the processes taking place in the course of decomposition of the gel and its oxidation. The decomposition of hydrogen peroxide has been chosen as the test reaction for comparison of the catalytic activity.

EXPERIMENTAL

1. Materials. The starting chromic oxide gels were prepared in the following way:

Ammonium hydroxide (1 *N*) was added at a constant rate of 10 ml/min to the hot (80–90°C) solution of 1 *N* chromium nitrate and ammonium nitrate. The reaction was carried out with continuous stirring until the solution showed the required value of pH, which amounted to 8 for preparation I, 6–7 for preparation II, and 11–12 for preparations III and IV.

In the case of preparation IV with additions of magnesium, magnesium nitrate was first added to the solution of chromium nitrate and ammonium nitrate in the appropriate quantity and precipitation carried out in the same manner as described above. The analysis revealed that the gel contains 0.055 moles of magnesium/mole of chromium oxide.

The resulting gels were allowed to stand for 2 hr, then decanted, filtered when hot, and repeatedly washed with distilled water until the filtrate showed no ammonia to be present. The preparations were then dried at 100°C for 10 hr in air.

Samples of each preparation were then annealed for 5 hr in air at various temperatures between 100°C and 700°C and quenched to room temperature.

2. Differential thermal analysis. The DTA was carried out against alumina as standard. The rate of heating was 12°/min. The weight of samples was about 0.3 g.

3. Thermogravimetric analysis. The analysis was carried out at 1 atm of air. The rate of heating was 2.5°/min. The weight of sample was similar to that used in the DTA.

4. X-ray analysis. The starting material and samples annealed at various temperatures were examined by the powder method of X-ray diffraction, using a 57.4-mm camera. CuK_α radiation was employed.

5. Chemical analyses. In order to determine the surface concentration of Cr^{6+} ions the sample was for 1 hr treated with water and then filtered. The amount of extracted chromate ions in the filtrate was determined colorimetrically with diphenylcarbazide.

The total amount of excess charges was determined by the Bunsen-Rupp method. As the solubility of preparations varied considerably with the temperature of annealing, it was necessary to determine the amount dissolved simultaneously with the determination of excess charges. The experimental procedure was as follows: A sample of approximately 0.5 g was placed in a specially designed flask (*5*), connected with a second flask containing the KI solution. Conc. HCl (30 ml) was then added to the sample and the contents boiled for a definite time, ranging from 1 to 30 min. The amount of iodine evolved was titrated with 0.01 *N* thiosulfate. It is equivalent to the amount of excess positive charges of chromium in the dissolved part of the sample, which oxidized chloride ions. Simultaneously, nondissolved powder was filtered, washed with water, dried, and the amount dissolved in HCl determined, while the filtrate was analyzed colorimetrically for the content of chromate ions. When time of analysis was short, the amount of excess charges found iodometrically was small, whereas the filtrate contained a large amount of chromate ions. On prolonging the time of analysis the amount of iodine evolved increased and the amount of chromate ions in the filtrate decreased. Eventually, for longer times of analysis, no chromate ions could be detected in the filtrate. This is illustrated in Table 1, which shows detailed results of analysis for samples of preparation III, annealed at 100°, 200°, and 300°. Apparently, the reaction taking place when the gel is boiled in concentrated HCl consists of two steps. In the first step the sample is dissolvel in HCl, in the second, chloride ions are oxidized to chlorine by chromium ions of higher valence. The second step is probably slower than the first one so that chromium ions of higher valence remain in the filtrate after the first minutes of boiling and are consumed by the second step only after a longer duration of analysis.

TABLE 1

RESULTS OF THE BUNSEN-RUPP ANALYSIS OF SAMPLES OF PREPARATION III, ANNEALED AT 100°, 200°, AND 300°

	Temperature of annealing					
	100°		200°		300°	
	Amount of active oxygen, mg/g, equivalent to					
Duration of analysis (min)	Iodine evolved	Cr^{6+} ions in the filtrate	Iodine evolved	Cr^{6+} ions in the filtrate	Iodine evolved	Cr^{6+} ions in the filtrate
1	1.71	0.00	0.64	41.20	0.96	33.08
3	3.48	0.00	4.57	47.90	4.07	23.70
5	6.10	0.00	10.62	49.82	11.21	27.55
10	13.33	0.00	29.90	27.08	21.90	31.51
20	17.29	0.00	—	—	70.90	0.00
30	21.00	0.00	62.40	0.00	70.90	0.00

The total amount of excess charges in the part of the sample dissolved in the given time was calculated as the sum of the amount found iodometrically and that found as chromate ions in the solution. It was then plotted as a function of the amount of sample dissolved and the experimental results extrapolated to 100% dissolution.

6. Surface area. The surface areas were calculated from the adsorption of argon at liquid nitrogen temperature.

7. Electrical conductivity. For measurements of electrical conductivity small cubes with sides of about 1 cm, compressed under about 50 atm, were used. The measurements were made using a Wheatstone bridge operated with 1000 c/sec ac and an oscillograph as the zero-point instrument. Details of the apparatus and experimental procedure have been described elsewhere (*6*).

8. Catalytic activity. The measurements of the kinetics of catalytic decomposition of hydrogen peroxide have been carried out in the apparatus represented in Fig. 1. It was essentially similar to that used by Nachman, Maxim, and Braun (*8*). It consisted of the reaction vessel (A, 20 cm^3), two burettes (50 cm^3, B; and 10 cm^3, C) and a manometer (D). The burettes and the manometer were filled with water. Oxygen liberated as the result of hydrogen peroxide decomposition increased the pressure in the apparatus, which was indicated by the manometer. The manometer was leveled back every 30 sec by running water out from the burette. The volume of water run out in order to level the manometer is the measure of the volume of oxygen liberated in the given period of time. Thus the

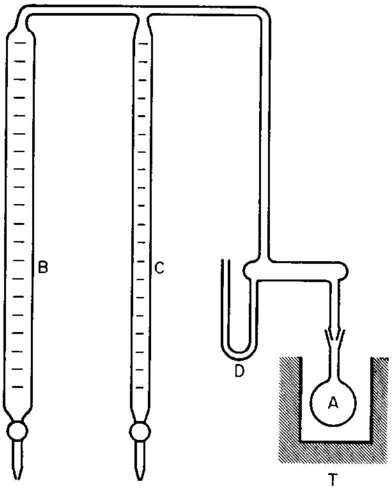

FIG. 1. Apparatus for determination of catalytic activity in H_2O_2 decomposition. A, reaction vessel; B, 50 cm^3 burette; C, 10 cm^3 burette; D, manometer; T, thermostat.

decomposition of hydrogen peroxide was always investigated at the same atmospheric pressure. The provision of two burettes of different volumes enabled the measurement of slow as well as rapid reactions. The reaction vessel was inserted into a Vobser thermostat; 10 mg of catalyst was placed in the reaction vessel and maintained for 10 min in the thermostat in order to bring it to the reaction temperature. In another vessel 10 ml of 30% solution of hydrogen peroxide was kept in the thermostat. The solution of hydrogen peroxide was then quickly poured into the reaction vessel, vigorously stirred and then the vessel attached to the apparatus. The manometer was leveled and the time measurements began. The experiments were carried out for 30 min at 20°, 25°, 30°, 35°, and 40°C with each catalyst.

RESULTS AND DISCUSSION

1. *Differential Thermal Analyses*

The results of differential thermal analyses of all four preparations of the chromic oxide gels are represented in Fig. 2. All preparations show similar behavior, analogous to that observed by T. W. Rode (*1*). Reference to the data of thermogravimetric and chemical analyses, presented below, indicates the following interpretation. The first endothermic peak beginning at 20° and attaining a minimum at about 180° corresponds to the loss of water by the highly hydrated gel, which leads to the formation of the trihydrate. This phase has in fact been identified by Hantsch and Torke (*7*). The decomposition of trihydrate to monohydrate may be responsible for the second endothermic peak, which begins at about 240°. As clearly seen from the thermogravimetric curves this phase is stable over a wide range of temperatures between 280° and 360°. Its formation has been reported by Simon *et al.* (*9*) and its properties as a definite chemical compound have been investigated by T. W. Rode (*1*) and Laubengayer and McCune (*10*). The end of the second endothermic peak is difficult to ascertain, because an exothermal effect superimposes on it in the temperature range 280–320°, due to the oxidation of the gel (cf. Fig. 5). This exothermic peak does not appear in all cases. It is best seen in the case of preparations I and III, is very small in the case of preparation II, and does not appear at all in the case of

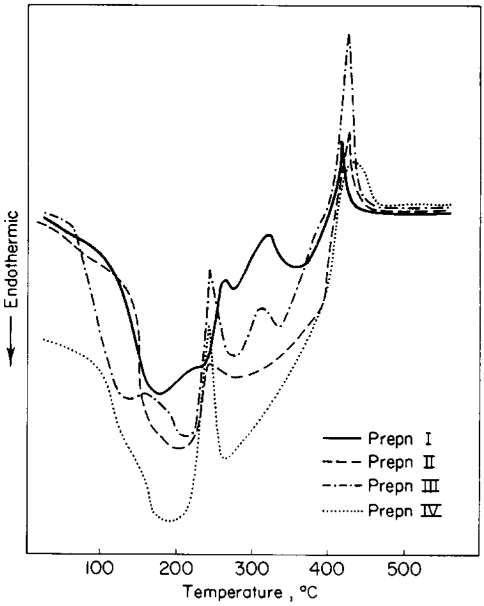

FIG. 2. Differential thermal analysis of chromic oxide gels.

preparation IV. The reason for that must probably be looked for in the relative intensities of simultaneously proceeding endothermal dehydration and exothermal oxidation. In the case of preparation IV the dehydration proceeds further than in the case of other preparations and the big heat consumption probably swamps the exothermal effect. The next big exothermal effect at 420° may evidently be ascribed to the formation of crystalline Cr_2O_3. This sudden liberation of heat, known as the "glow phenomenon" was first observed by Berzelius (*11*).

2. Thermogravimetric Analyses

Figure 3 shows the results of thermogravimetric analyses. There is clear evidence of the formation of the monohydrate, which is stable in the broad region of temperatures between 280° and 360°. The inflection on the dehydration curves in the region of trihydrate may be taken as a hint that also this compound is formed as the intermediate stage of the dehydration. The break in the region of the pentahydrate is observed only in the case of preparation I.

It is interesting that the dehydration of preparation IV, containing magnesium, proceeds in a way different from that followed by pure chromic oxide preparations. Apparently the presence of magnesium ions influences the stability of the monohydrate so that it is not formed as an intermediate stage of the dehydration.

3. X-Ray Analyses

Samples annealed at temperatures lower than 350° displayed no X-ray diffraction patterns. Sample annealed at 350° gave a few diffused lines, which, however, could not have been assigned. First lines of rhombohedral Cr_2O_3 appeared in diffrac-

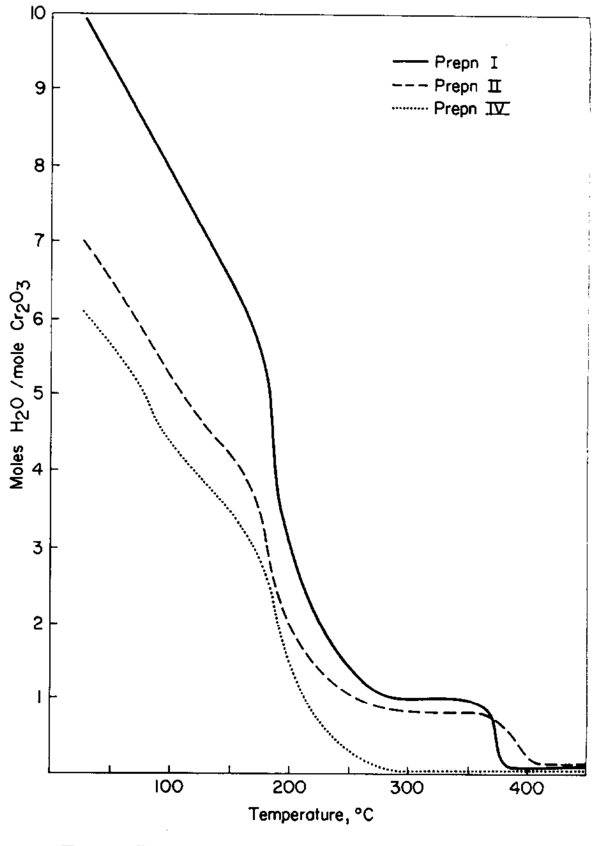

FIG. 3. The dehydration of chromic oxide gels.

tion photographs of a sample annealed at 400°. Samples prepared at higher temperatures showed an increasing number of sharper and sharper lines and at 700° gave the full diffraction pattern of Cr_2O_3.

Some workers (*10*) have noted that preparations of hydrous chromic oxide, prepared similarly to ours give several slightly broadened X-ray diffraction lines. As we have considered the X-ray analysis only as complementary, aiming at the detection of the formation of crystalline Cr_2O_3, we have not carried out detailed X-ray examinations of low-temperature samples.

4. Chemical Analyses

The determination of the amount of chromate ions, which could have been extracted with water aimed at the estimation of the surface oxidation of samples. Samples of chromic oxide gels annealed at 100° and higher temperatures are practically insoluble in water and it may be assumed that on treating them with water only chromate ions pass into the solution. As the diffusion in the solid is very slow at room temperature it seems justified to assume that only those chromate ions are washed out, which are present in the surface layers of grains.

The results of the experiments are summarized in Fig. 4, which shows the amount of water-extracted chromate ions, expressed in terms of equivalent amount of active oxygen, plotted as a function of the temperature of annealing. The surface oxidation increases on increasing the temperature of annealing, attains a maximum at 300–350°, depending on the preparation, and then decreases. It corresponds to 0.03–0.61 of the monolayer of close-packed oxygen ions in the case of pure chromic oxide preparations and up to 4.6 atomic layers in the case of preparation IV, doped with magnesium.

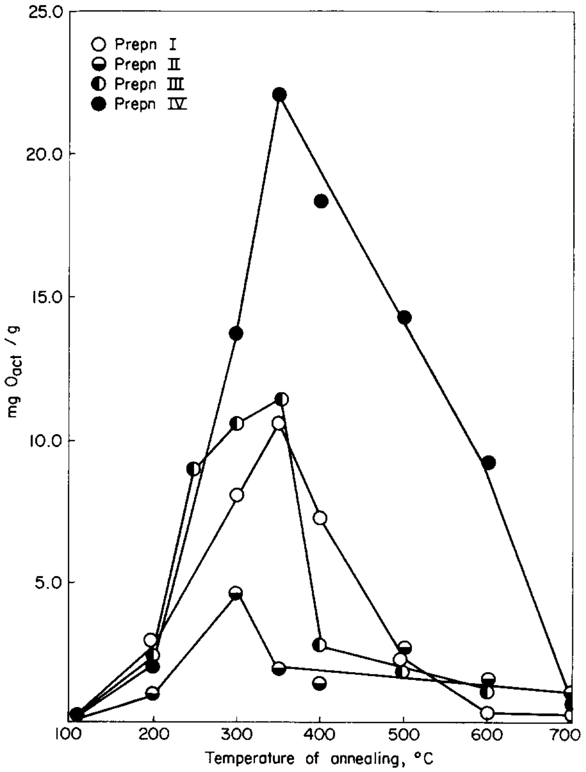

FIG. 4. The amount of water-extractable chromate ions, expresed in terms of mg of active oxygen/g sample, as a function of the temperature of annealing.

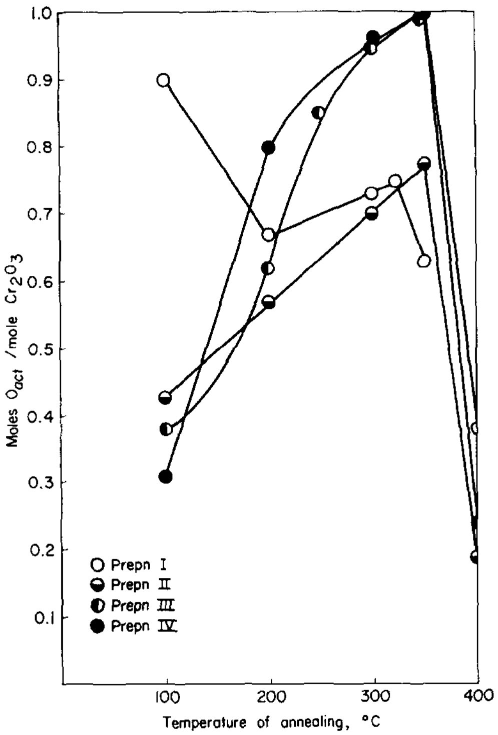

FIG. 5. The total amount of excess charges of chromium, expressed in terms of moles of active oxygen/mole Cr_2O_3, as a function of the temperature of annealing.

Figure 5 shows the total amount of excess charges of chromium expressed in terms of moles of active oxygen per mole of Cr_2O_3. The oxidation of samples increases with the increasing temperature of annealing and attains a maximum at about 320° for preparation I, and 350° for other preparations. At these temperatures the O/Cr ratio amounts to 1.87 for preparation I, 1.89 for preparation II, and 2.0 for preparations III and IV.

The only exception is the sample of preparation I, annealed at 100°, which in spite of the low temperature of annealing shows a very high oxidation, corresponding to an O/Cr ratio of about 1.95 (*12*). The origin of this phenomenon is not yet clear and we would not like to attach to it greater significance.

The results of analyses of samples annealed at temperatures higher than 400° are summarized in Table 2. However, owing to their limited solubility it is impossible to apply the extrapolation method and to calculate the total amount of excess charges. It seems that the results represent only the amount of excess charges present in the surface layers of crystallites. Unfortunately no conclusions can be drawn as regards the oxidation state of the bulk phase.

TABLE 2
RESULTS OF THE BUNSEN-RUPP ANALYSIS

Temperature of annealing (°C)	*Amount of active oxygen* (mg/g) Preparation I	II	III	IV
500°	3.0	3.0	3.5	20.2
600°	1.0	2.6	2.4	18.3

The data for preparations III and IV presented in Fig. 5 and in Table 2, indicate that doping with magnesium has no influence on the oxidation of the preparation at temperatures up to 350°; at higher temperatures, however, it increases the amount of excess charges considerably.

It is appropriate to raise at this point the question as to in what form are the excess charges present in the bulk phase of the gel. The phenomenon of oxidation of chromic oxide gel on heating it in air was observed by many authors. It was investigated more thoroughly by Rothaug (*13*), who boiled the heated samples in water and found that the extract contains Cr^{6+} and Cr^{3+} ions in the proportion corresponding to chromic chromate. He assumed therefore that chromic oxide gel gets oxidized on heating to $Cr_2O_3 \cdot 3CrO_3$. In view of our experiments it seems, however, that Rothaug determined only the surface oxidation of the gel. Investigating the problem of the preparation of chromic oxide Dominé-Bergès (*14*) found that the total O/Cr ratio rises on heating the gel to the value of about 2 and suggested that CrO_2 is formed, i.e., that Cr^{3+} ions are oxidized to Cr^{4+} ions. The same conclusion was reached by Scheve (*15*) on the basis of some analytical and magnetic measurements. In our previous papers (*12*, *16*) we have also tried to explain the experimental results on the assumption that Cr^{4+} ions appear as the result of heating the gel in air. On the other hand Rode, Kazanski, and Pietcherskaia (*17*) recently carried out measurements of the paramagnetic resonance and concluded that only Cr^{3+} and Cr^{6+} ions are present in the dehydrated samples of chromic oxide gel.

The problem of the changes of oxidation states of chromium ions in the course of thermal dehydration of chromic oxide gel is of great importance to catalysis. The products of dehydration are widely used as catalysts and their outstanding catalytic activity may be due to the presence of chromium ions of various valences. In order to find a direct answer to this disputable problem we have carried out the following series of experiments.

Samples of preparation III, annealed at 100–350° were totally dissolved in boiling concentrated sulfuric acid and the amount of chromate ions was determined colorimetrically. The results are given in column II of Table 3. Column III in this table shows the amount of excess charges as determined by the Bunsen-Rupp method, and column IV, the amount of water-extractable chromate ions. For simplicity all data are expressed in terms of moles of active oxygen per mole of Cr_2O_3.

TABLE 3

RESULTS OF VARIOUS CHEMICAL ANALYSES OF PREPARATION III

Temperature of annealing (°C)	Moles of active oxygen per mole of Cr_2O_3 corresponding to		
	Cr^{6+} ions after dissolution in H_2SO_4	The total amount of excess charges	Cr^{6+} ions in the water extract
100°	0.00	0.38	0.000
200°	0.42	0.62	0.008
250°	0.70	0.85	0.030
300°	0.81	0.95	0.035
350°	0.95	1.00	0.046

Data summarized in Table 3 show that in the sample annealed at 100° the excess charges are present in form of Cr^{4+} or Cr^{5+}. At the same time this rules out the possibility that large amount of chromate ions, detected after dissolution in sulfuric acid samples annealed at higher temperatures, are due to the oxidation of chromium ions by boiling sulfuric acid. In samples annealed at 200°, 67% of excess charges are already present in the form of Cr^{6+}, and in samples annealed at 350°, 95%.

Thus it seems that on annealing at lower temperatures Cr^{3+} is oxidized to Cr^{4+} as an intermediate step in the oxidation to Cr^{6+}. On raising the temperature of annealing more and more chromium is oxidized to the valence of 6 and at 350°, when a maximal oxidation is attained, practically all excess charges are in the form of Cr^{6+}. Although such samples have the stoichiometric composition of CrO_2, their structure is better represented by the formula $Cr_2O_3 \cdot CrO_3$.

Detailed analysis of the results of the Bunsen-Rupp determination lends further support to this conclusion. The results obtained with preparation III, which are given in Table 1, may serve as an example. The fact that chromate ions appear in the filtrate in the case of samples annealed at 200° and 300°, but not in case of sample annealed at 100°, seems to indicate that they were present in these samples.

5. *Surface Area*

The changes of specific surface areas of preparations I–IV on annealing at various temperatures are shown in Fig. 6. The surface areas of samples annealed at temperatures lower than 350°, i.e. in the temperature range wherein X-ray-amorphous products of dehydration are formed, differ very much from each other. This is because such properties of gels as surface area are extremely sensitive to the mode of preparation and even small differences in the conditions of precipitation may greatly change the surface area. Samples annealed at higher temperatures, when crystalline Cr_2O_3 is formed, have surface areas of the same order, slowly decreasing as the temperature of annealing is increased.

6. *Electrical Conductivity*

An example of the results of the measurements of electrical conductivity is shown in Fig. 7, wherein electrical conductivities of samples of preparation III, annealed at various temperatures, are plotted as a function of the reciprocal of the abso-

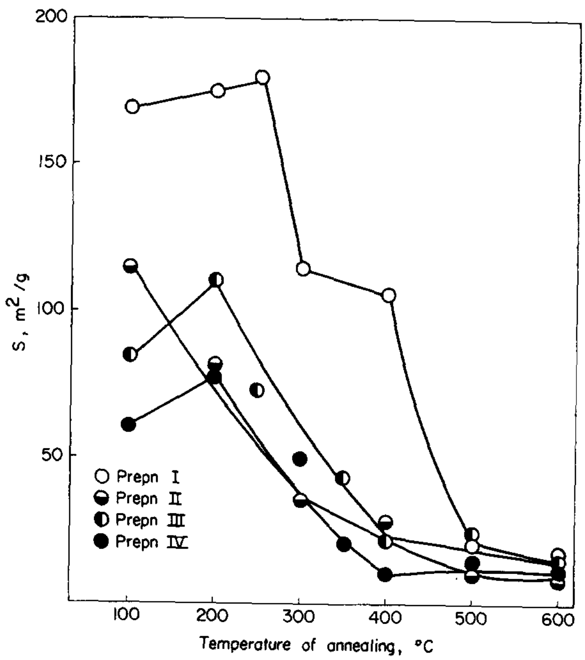

FIG. 6. Specific surface area as a function of the temperature of annealing.

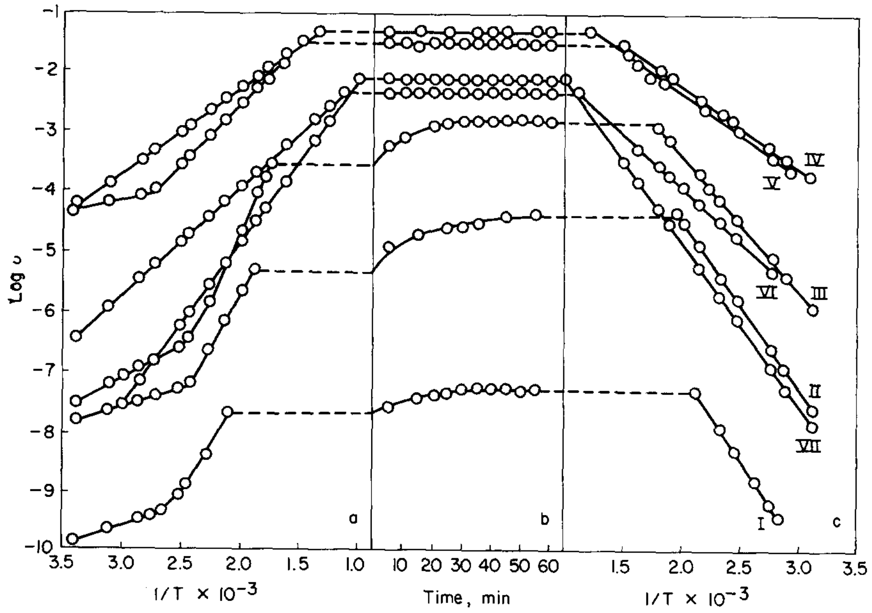

FIG. 7. Changes of the logarithm of electrical conductivity: a, on heating; b, on keeping sample at the temperature of previous annealing; c, on cooling and on subsequent heating.

lute temperature. All measurements were carried out at 1 atm of air. The sample was first heated to the temperature of previous annealing and the conductivity measured on heating (Fig. 7a). The sample was then kept at this temperature until the conductivity attained a constant value. Isothermal changes of conductivity with time are represented in Fig. 7b. After a constant value of the conductivity had been attained the sample was subsequently cooled to room temperature and heated again to the temperature of annealing, the conductivity being measured on cooling as well as on heating (Fig. 7c). A similar picture was obtained with other preparations.

The changes of conductivity on keeping the sample at the temperature of preannealing may be due either to the loss of water readsorbed or taken up again after annealing or to some rearrangement of the structure of the gel taking place on additional heat treatment. The values of electrical conductivity measured afterwards on cooling and on heating were already consistent with each other and it can be assumed that they truly reflect the electrical properties of the material. These properties strongly depend on the temperature of annealing, which is illustrated in Fig. 8.

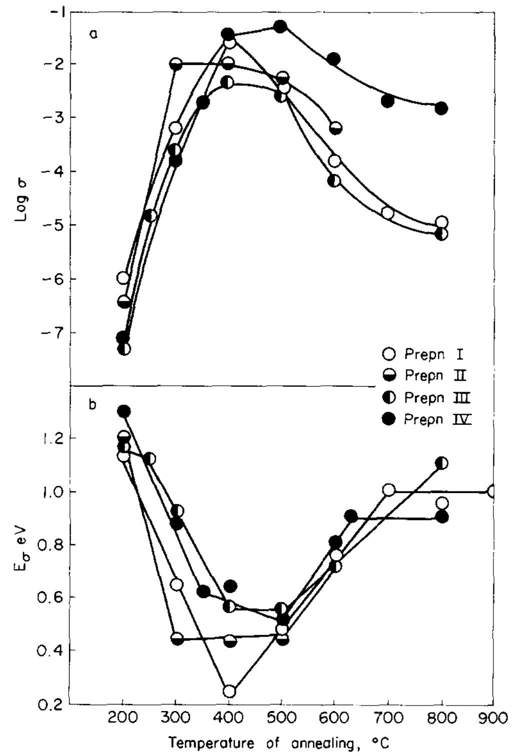

FIG. 8. a. Electrical conductivity as measured at 200°. b. Activation energy of electrical conductivity, both as a function of the temperature of annealing.

Figure 8a shows the values of electrical conductivity of various preparations, as measured at 200°, plotted as a function of the temperature of annealing. Figure 8b represents the dependence of the activation energy of the conductivity, calculated from the formula $\sigma = \sigma_0 \exp(-E/2kT)$, on the temperature of annealing.

Samples annealed at 200° are poor conductors. The conductivity rises on raising the annealing temperature, reaches a maximum for samples annealed at 400°, and then decreases for samples annealed at still higher temperatures. The activation energy shows the reverse behavior. It decreases in the temperature range 200–400°, passes through a minimum at 400° and increases at higher temperatures, attaining at about 700° a plateau of 0.9–1.0 eV.

As discussed previously the formation of a crystalline phase of Cr_2O_3 occurs at about 400°. This temperature coincides with the temperature of maximum on the conductivity curve and minimum on the activation energy curve. The formation of the new phase, however, is not accompanied by any discontinuity of the conductivity or its activation energy, which could have been expected if the conductivity mechanisms were different in the amorphous phase, and in crystalline Cr_2O_3. Thus it seems reasonable to conclude that a similar mechanism is responsible for the conductivity in both these substances.

Further evidence for this assumption is lent by the measurements of the thermoelectric power. All samples annealed between 200° and 700° showed the same sign of the thermoelectric power, indicating *p*-type conductivity.

Crystalline Cr_2O_3 is a *p*-type semiconductor. There are however different opinions as to the origin of the conductivity in this oxide. Hauffe and Block (*18*) found that the conductivity of Cr_2O_3 is independent of the pressure of oxygen and concluded that the defect structure of the cationic lattice cannot be in this case the cause of the observed *p*-type conductivity. Later Hauffe and Wagner (*19*) suggested that Cr_2O_3 may be an intrinsic semiconductor. More recent experiments by Voltz and

Weller (*2*) showed, however, that chemisorption of oxygen does change the conductivity of Cr_2O_3 and they assumed that at least in the surface layers the conductivity is due to cation deficiency.

Formation of each vacancy in the cationic lattice must be accompanied by the appearance of a Cr^{6+} ion. Such an ion constitutes an acceptor level in the energy spectrum of Cr_2O_3, increasing its electronic conductivity according to the general equation:

$$\tfrac{3}{2}O_2 = Cr_2O_3 + 2Cr_{\square}\ ,\ ,\ ,\ + 6\oplus$$

If it is now assumed that the conduction mechanism is essentially the same in the amorphous phase and in the crystalline oxide, the following interpretation of the conductivity curves could be suggested. On raising the temperature of annealing the oxidation of the gel increases, which results in the increase of the concentration of Cr^{6+} acceptor centers and consequently in the increase of conductivity. At 400° the crystallization of Cr_2O_3 occurs. The lattice of the oxide immediately after formation is probably highly disordered and the material shows high conductivity. On annealing at higher temperatures the lattice becomes more and more ordered, the concentration of Cr^{6+} ions rapidly decreases and so does the conductivity.

As is seen from Fig. 8 doping with magnesium has practically no influence on the electric conductivity in the region, wherein only X-ray-amorphous phase exists, but greatly increases the conductivity of samples, which consist of crystalline Cr_2O_3. Magnesium ions substitute Cr^{3+} ions in the lattice of Cr_2O_3, which must be accompanied by the formation of additional Cr^{6+} ions. Increase of the concentration of acceptor levels is followed by an increase in conductivity. Obviously there can be no substitution of this kind in the amorphous gel and doping with magnesium does not influence its conductivity.

The difference in conductivity of doped and pure oxide increases with the increasing temperature of annealing. This may be easily understood if we remember that the concentration of cationic vacancies and consequently the concentration of Cr^{6+} ions in pure oxide decreases, when the lattice gets more and more ordered on heating samples at higher and higher temperatures. This cannot be the case in magnesium-doped samples, wherein the concentration of Cr^{6+} ions is related to the concentration of magnesium ions, which in turn is independent of the temperature of annealing.

It may be now taken as generally accepted (*20*) that the conductivity of polycrystalline oxides is determined by the surface conductivity of grains. It seems therefore interesting that samples of all preparations annealed below 400° show similar conductivity although their surface areas differ very much from each other.

7. Catalytic Activity in H_2O_2 *Decomposition*

The analysis of experimental data has been carried out on the assumption that the decomposition of H_2O_2 is a first order process. As the maximal conversion observed after 30 min never exceeded 0.05, it may be assumed in the first approximation that the reaction runs at the constant concentration of H_2O_2. At such conditions the integration of the first order equation gives

$$v = v_0 + kt \tag{1}$$

where v represents the volume of oxygen evolved and v_0, the volume of oxygen evolved to the moment at which the time measurements started. In all experiments except those with samples annealed at 100° the linear dependence of the volume of oxygen evolved on time has been observed in accordance with Eq. (1). The rate constants have been computed from the slope of v vs. t plots.

Comparison of the catalytic activity of various preparations of catalysts is permissible only if the measrements are carried out in the kinetic region of the reaction. In such case we would expect the rate constant to be proportional to the amount of catalyst used in the experiment. Figure 9 shows the volume of oxygen evolved as a function of time for three different amounts of the same catalyst. The proportionality of the rate constant to the mass of the

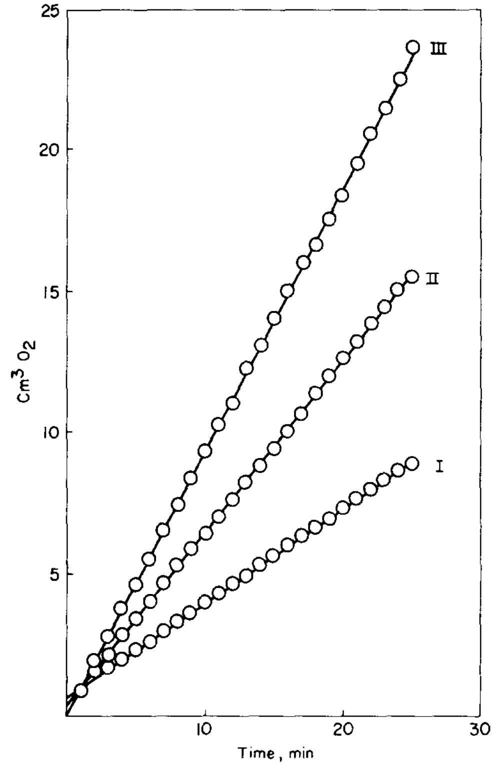

FIG. 9. The amount of oxygen evolved in H_2O_2 decomposition at 20° as function of time. Catalyst: samples of preparation I annealed at 300°. Curve I—5 mg of catalyst, $k = 0.336$; curve II—10 mg of catalyst, $k = 0.616$; curve III—15 mg of catalyst, $k = 0.940$.

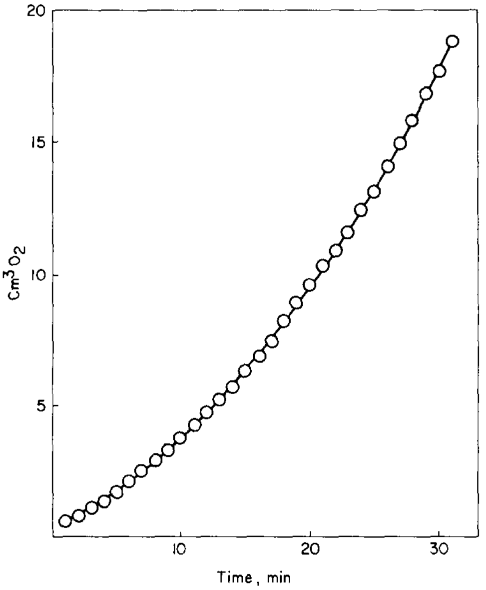

FIG. 10. The amount of oxygen evolved in H_2O_2 decomposition at 20° as function of time. Catalyst: sample of preparation I annealed at 100°.

catalyst indicates that the reaction is proceeding in the kinetic region.

The question may also be raised as to whether the reaction is in fact heterogeneous or a homogeneous one, catalyzed by small amounts of the oxide dissolved in the course of the reaction. This is probably the case with samples annealed at 100°, for which the increase of the reaction rate with time is observed (Fig. 10). It may be assumed in this case that the reaction is heterogeneous only at the beginning of the experiment, the homogeneous reaction contributing to a greater and greater extent as the reaction proceeds, owing to the dissolution of the sample in the course of the reaction. By similar arguments, the validity of Eq. (1) in the case of samples annealed at higher temperatures may be taken as evidence that the reaction is heterogeneous.

In order to prove this conclusion we have carried out the following series of experiments. Ten milligrams of catalyst was added to 10 ml of 30% solution of hydrogen peroxide and after the kinetics of decomposition had been measured the solution was allowed to stand for 24 hr. This period was sufficient for the decomposition of hydrogen peroxide to come to its end. The sample was then filtered, the filtrate added to 10 ml of fresh 30% solution of hydrogen peroxide and the kinetics of decomposition followed again. If the decomposition were a homogeneous process catalyzed by chromium ions in the solution, we would expect the activity of the filtrate to be of the same order as the activity of the sample, allowing for the dilution of the peroxide in the former case. The experiments showed that the activity of the filtrate is negligible in comparison with the activity of the sample. These results prove that the measured rate of decomposition is the rate of heterogeneous catalytic reaction.

Figure 11a shows the dependence of rate constants of hydrogen peroxide decomposi-

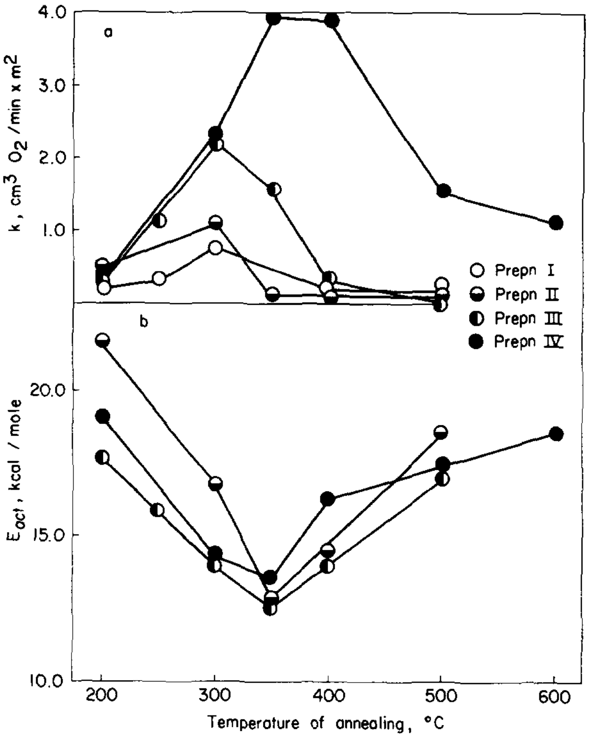

FIG. 11. a. Specific rate constants "k" of H_2O_2 decomposition. b. Activation energy of this reaction, both as function of the temperature of annealing.

tion, calculated per unit surface area, on the temperature of annealing for all four preparations. The catalytic activity increases at first with the increasing temperature of annealing, passes through a maximum at 300° in the case of preparations of pure chromic oxide and at 350° for magnesium-doped preparation and then decreases. Corresponding changes of the activation energy of the decomposition are represented in Fig. 11b.

Interesting results may be obtained by examining the correlation between the frequency factors and the activation energies. It is illustrated in Fig. 12, which shows that the compensation effect is exhibited by catalysts obtained by annealing chromic oxide gels. Experimental points obtained with all four preparations fall on two straight lines, whereof one passes through points corresponding to samples annealed at temperatures lower than 350° and the other through points obtained with samples annealed at 400° and higher temperatures. On this latter line also fall experimental points obtained with crystalline Cr_2O_3 (denoted on Fig. 12 as preparation V), prepared in the following way: Cr_2O_3 was first obtained by decomposition of ammonium chromate at high temperatures (800°), cooled, washed until all chromate ions were removed and then heated in air at 100–350° for 5 hr.

As in all cases of reactions showing a compensation effect (*21*) the relation between k_0 and E can be expressed by the formula

$$\log k_0 = (E/a) + b \qquad (2)$$

with two different numerical values of the constant b—one characterizing samples composed of amorphous hydrous chromic oxide and the second characterizing crystalline Cr_2O_3. The only two points which deviate from this rule are those obtained with magnesium-doped samples, annealed at high temperatures.

The decomposition of hydrogen peroxide

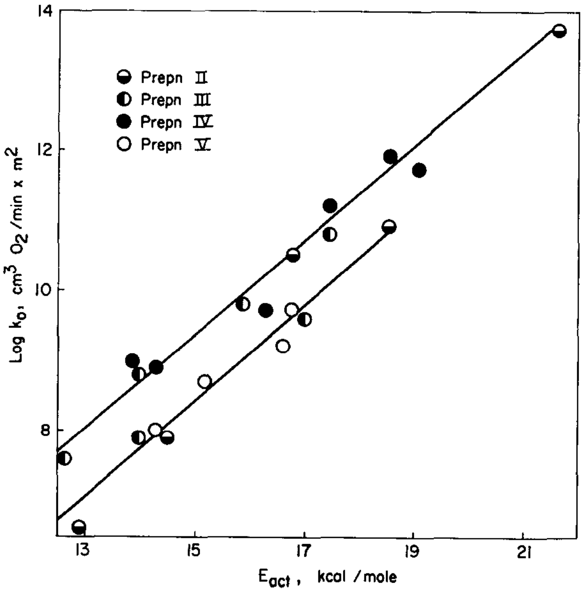

FIG. 12. Compensation effect for decomposition of H_2O_2. Curve I—samples annealed at temperatures up to 350°; curve II—samples annealed at temperatures higher than 350°.

on metallic surfaces was first interpreted by Weiss (*22*) in terms of a radical mechanism. He considered that parts of the metallic surface donate electrons, becoming thus charged and acting in this state in turn as electron acceptors. Proceeding along similar lines Roginski (*4*) also suggested a radical mechanism for the decomposition of hydrogen peroxide on semiconductors, but assumed that two kinds of active centers—donors and acceptors—must be present on the surface for the catalyst to be active.

In the case of chromic oxide, donor centers are formed of Cr^{3+} ions and acceptor centers of Cr^{6+} ions. Voltz and Weller (*2*) suggested on the basis of a very scarce experimental material that the catalytic activity of chromic oxide in hydrogen peroxide decomposition may be attributed to the presence of Cr^{6+} ions on the surface of oxide grains. In view of our results it may be concluded that a relation exists between the amount of Cr^{6+} ions present on the surface and the value of rate constant "k" (cf. Figs. 4 and 11a). This would imply that the rate-determining step of the decomposition involves acceptor centers, their concentration being the main factor influencing the rate of the reaction. Steps wherein donor centers take part must thus proceed faster and have no influence on the over-all rate.

The compensation effect in catalysis is usually explained (*21*) by assuming that the reaction takes place on active centers of various activation energies. It would mean that Cr^{6+} active centers are characterized by different energetic states depending on the temperature of annealing. This conclusion is consistent with the results of electrical conductivity measurements. As shown previously, Cr^{6+} ions are also responsible for the conduction in the amorphous phase. The parallelism in the changes of the activation energy of the electrical conductivity and the activation energy of H_2O_2 decomposition indicate that energy levels of Cr^{6+} ions change with temperature of annealing in such a way, as required for Eq. (2) to be observed.

It must however, be emphasized that there is no theoretical ground for deriving the correlation between the rate constant "k" and the concentration of Cr^{6+} active centers. In fact, the question may be raised as to which of the quantities: k, k_0, or E should be taken as a measure of the catalytic activity. Assuming Roginski's mechanism one can derive a kinetic equation showing a linear dependence of the rate of decomposition on the concentration of Cr^{6+} active centers. In such a case, however, k_0 rather than k should be related to this concentration. The experimental results do not reveal any such simple relation.

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