

The Mechanism of Low-Temperature Doping of Chromium Oxide with Altrivalent Ions

JERZY DEREŃ AND JERZY HABER

From the Department of Surface Phenomena, Research Institute of Physical Chemistry, Polish Academy of Sciences, Kraków, Poland

and

The Department of Physical Chemistry, Pedagogical Institute, Katowice, Poland

Received April 28, 1964

The investigations described in this paper aim at the explanation of the influence of low-temperature doping with altrivalent ions on physicochemical and catalytic properties of chromium oxide. The preparations were obtained by coprecipitation of chromium oxide gel with different amounts of magnesium and titanium hydroxides, respectively, and subsequent annealing in air at various temperatures between 400° and 600°C. Independently of the type of addition the DTA curves exhibited at about 400° a strong exothermic effect indicating the formation of Cr₂O₃ lattice. X-ray diffraction photographs showed in all cases only the lines of rhombohedral Cr₂O₃.

Owing to chemisorption of oxygen at the surface of Cr₂O₃ crystallites a thin surface layer is formed, wherein the O/Cr ratio amounts to 2.6–3.0 and which contains all the doping agent introduced. Magnesium increases the concentration of excess charges in this layer, whereas titanium decreases it. This effect however, cannot be explained in terms of a substitution mechanism and some other mechanism must be invoked to account for the influence of doping agent on the adsorptive properties of Cr₂O₃. The incorporation mechanism begins to operate only at 650–700°. This model is consistent with the results of electrical conductivity measurements.

A close correlation has been found between the specific rate constants of hydrogen peroxide decomposition and the surface concentration of Cr⁶⁺ ions. The activity of Cr⁶⁺ active centers is independent of the type and amount of doping agent, but decreases slightly with increasing temperature of annealing.

It is noteworthy that all properties, if plotted against the amount of doping agent change in such a way, as predicted by the electronic theory of solids, although substitution of altrivalent ions in the sense considered in this theory does not take place.

In our previous paper (1) we have described the investigation of various chemical, electrical, and catalytic properties of materials, obtained by low-temperature calcination of chromic oxide gels. One of the preparations contained the addition of magnesium oxide, introduced by coprecipitating magnesium and chromium hydroxides. The results of this investigation showed that the influence of the addition of magnesium on various physicochemical properties of the resulting material becomes considerable in the case of preparations calcined at temperatures higher than 400°, which is the

temperature of the formation of Cr₂O₃ lattice. Annealing at still higher temperatures was followed by the decrease of differences in the behavior of pure and doped preparations so that only small differences were exhibited by samples annealed at 600°. At still higher temperatures the properties of doped preparations begin again to diverge from those of pure preparations.

It is the basic concept of the electronic theory of catalysis that doping of semiconducting oxides with altrivalent metal ions changes their electronic state thus modifying their adsorptive and catalytic proper-

ties. The comparison of these theoretical considerations with experimental evidence is however permissible only when the basic assumption of the theory is fulfilled, namely that the doping agent forms a solid solution in the investigated oxide. It usually requires sintering at comparatively high temperatures in order to secure the formation of a homogeneous solid solution. Doped preparations of Cr_2O_3 prepared in such a way have been a subject of several investigations (2), carried out from the viewpoint of the theory of solids. They are, however, of lesser interest to catalysis because of their small surface area.

It seems that two ranges of the sintering temperature may be distinguished, wherein doping affects physicochemical and catalytic properties of semiconducting oxides. When sintering is carried out at lower temperatures the doping agent penetrates only into a thin surface layer, the properties of this surface layer being thus changed considerably and differing from the properties of the bulk phase. Being catalytically active such preparations are of great interest to catalysis. At high temperatures a homogeneous solid solution is formed, but the preparations have small surface area.

The present research aims at a closer investigation of the influence of low-temperature doping on the physicochemical and catalytic properties of chromium oxide. Divalent magnesium ions and tetravalent titanium ions have been chosen as the doping agent. The high-temperature doping with the same ions is being investigated and will be published separately.

EXPERIMENTAL

1. Materials

The starting chromic oxide gels were prepared in the same way as Preparation III, described in our previous paper (1), with magnesium nitrate or titanium chloride added to the solution in proper quantities. This method was chosen in order to enable the comparison of the results obtained for doped oxide with those obtained previously in the case of pure chromic oxide.

The resulting gels were allowed to stand for 2 hr, then decanted, filtered when hot, and repeatedly washed. The preparations were then dried at 120° for 10 hr in air, annealed for 5 hr in air at every 20° in the temperature range 400 – 600° , and quenched to room temperature.

The purity of starting materials was checked using the method of semiquantitative spectrographic analysis. The Q24 quartz spectrograph of medium resolving power was used. The analysis showed that the preparations contained only small traces of few elements: Mn—0.001%; Ni—0.001%; Cu—0.0001%; and Na—0.1%.

The starting preparations were examined by the method of differential thermal analysis.* All preparations showed similar behavior analogous to that observed previously (1). The big exothermal effect known as the "glow phenomenon" and ascribed to the formation of Cr_2O_3 lattice appeared in all cases practically at the same temperature of about 400° .

2. The Determination of the Concentration of Doping Agent

The amount of doping agent has been determined using the polarographic titration. The experimental procedure was as follows. The solution of 8-oxychinoline was titrated with the help of specially prepared standard solutions of magnesium and titanium salts, respectively. The samples of all preparations were dissolved in 80% sulfuric acid and the amount of magnesium and titanium determined. The following results were obtained:

Preparation A	11.6 at.% Mg
Preparation B	4.9 at.% Mg
Preparation C	6.3 at.% Ti
Preparation D	13.4 at.% Ti

3. X-Ray Analysis

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.

*The authors are indebted to Dr. L. Stoch for carrying out the differential thermal analyses.

4. Chemical Analysis

a. Determination of surface concentration of Cr^{6+} ions. Preliminary experiments showed that on treating the samples with water practically only Cr^{6+} ions pass into solution. After 0.5 hr the extraction comes to its end. 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 layer.

The determination of the surface concentration of Cr^{6+} ions was carried out by treating a sample with distilled water at room temperature for 1 hr. The sample was then filtered and the amount of chromate ions in the filtrate was determined colorimetrically with diphenylcarbazide.

b. Determination of the concentration of excess charges. The analysis is aimed at the determination of the amount of excess charges in this part of the sample which dissolves in boiling conc. HCl. A sample of approximately 0.5 g was placed in a specially designed flask (3), connected with a second flask containing the KI solution. Conc. HCl (30 ml) was then added and the contents boiled for 30 min. The amount of iodine evolved was titrated with 0.01 *N* thiosulfate. Simultaneously nondissolved powder was filtered and the total amount of chromium ions in the filtrate was determined in the following way. First the chloride ions were removed by precipitating with a 2% solution of silver nitrate and filtering away the silver chloride. Then 10 ml of 10% solution of sodium persulfate was added and the solution boiled on the water bath for 0.5 hr in order to oxidize all chromium ions into chromate ions. The latter were then determined colorimetrically and the results recalculated as the amount of sample dissolved on boiling in conc. HCl.

The apparatus also enabled the determination of the concentration of excess charges after chemisorbed oxygen had been removed from the surface (3). The samples were outgassed at the temperature of their previous annealing at 10^{-6} mm Hg, boiled in the outgassed HCl without having been exposed to air, and the procedure described above was followed.

5. Surface Area

The specific surface areas were calculated from the adsorption of nitrogen at liquid nitrogen temperature.

6. Electrical Conductivity

Details of the apparatus and experimental procedure have been described elsewhere (4).

7. Catalytic Activity

In order to compare the catalytic activity of samples measurements of the kinetics and activation energy of hydrogen peroxide decomposition have been carried out. The apparatus and experimental procedure were similar to that used in our previous investigation (1). As previously a linear dependence of the volume of oxygen evolved on time has been observed. The rate constants have been computed from the slope of v vs t plots. A special series of experiments has been carried out to check that the measured rate constants are really the rate constants of the heterogeneous catalytic reaction and not of the homogeneous reaction catalyzed by small amounts of chromium ions dissolved in the course of experiment.

RESULTS AND DISCUSSION

Diffraction photographs of all samples exhibited only the lines of rhombohedral Cr_2O_3 . The higher was the temperature of annealing the sharper were the lines, showing that the lattice becomes more and more ordered. The process of ordering of the lattice is accompanied by considerable changes of the specific surface area. This is shown in Fig. 1, wherein surface area has been plotted as a function of the temperature of annealing for all four preparations. For comparison the surface areas of samples of pure Cr_2O_3 [Preparation III from ref. (1)] are also given. The greatest changes of surface area are observed in the low temperature range, wherein it decreases rapidly with increasing temperature of annealing. It may also be noted that surface areas of samples annealed at these temperatures differ very much from each other, whereas at higher temperatures they approach a common level except for Preparation D. It

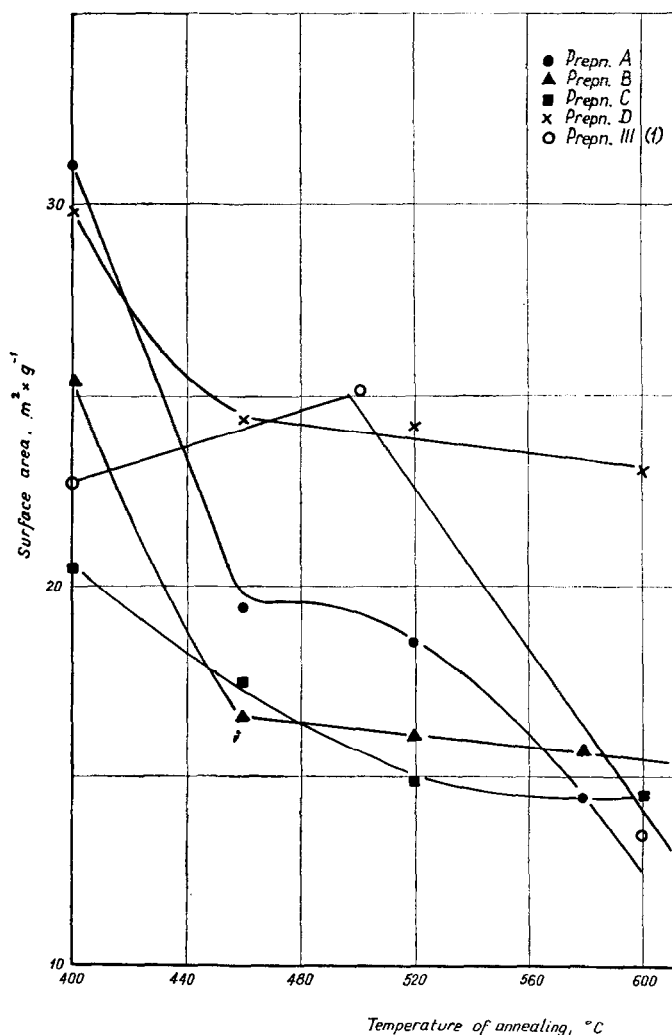


Fig. 1. Specific surface area as a function of the temperature of annealing.

seems that the origin of these differences observed at low temperatures may be looked for in the "biography" of preparations. Although all precautions were taken to maintain identical conditions on precipitating the gels, the presence of the addition may cause a considerable local change of the pH in the vicinity of the molecules of doping agent hydroxide.

The results of chemical analyses are represented in Fig. 2, which shows the amount of excess charges, expressed in terms of the amount of Cr^{6+} ions (on the right scale) or in terms of equivalent amount of active oxygen (on the left scale) plotted as a func-

tion of the temperature of annealing. The addition of magnesium strongly increases the amount of excess charges in samples annealed at low temperatures, whereas addition of titanium slightly depresses this amount. However, as the temperature of annealing is increased the amount of excess charges in magnesium-doped samples rapidly decreases so that beginning from about 550° all samples show practically the same amount of excess charges independently of the type and amount of the addition. It may be interesting to mention that on annealing at still higher temperatures (700° – 1200°) the amount of excess charges again

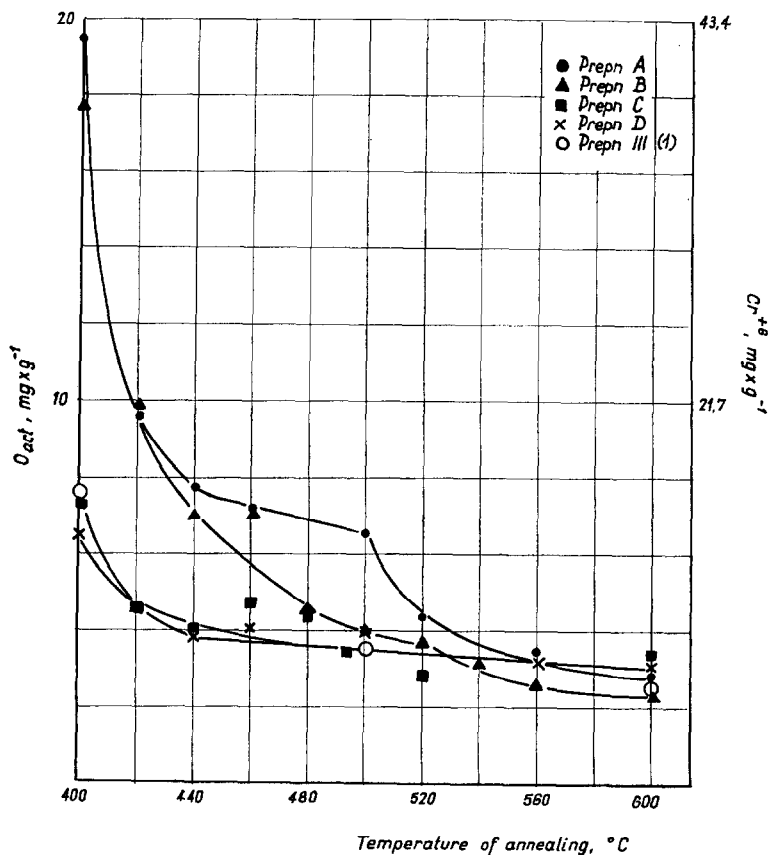


Fig. 2. The amount of excess charges of chromium as a function of the temperature of annealing.

begins to diverge, increasing in the case of magnesium-doped samples and decreasing in titanium-doped samples. Detailed discussion of these further experiments will be the subject of a separate publication.

It must be emphasized that the results summarized in Fig. 2 represent only the excess charges present in these parts of samples, which were dissolved in HCl in the course of analysis. The amount of sample dissolved is shown in Fig. 3, wherein the total amount of chromium dissolved in the course of analysis is plotted as a function of the temperature of annealing. The shapes of curves on Figs. 2 and 3 are similar and calculations show that independently of the type and amount of the doping agent the O/Cr ratio varies in narrow limits between 2.6 and 3.0.

The analysis showed also that in samples annealed in the temperature range

400–580° almost the whole amount of magnesium introduced passes into solution on boiling the samples in HCl. At temperatures higher than 600° this amount decreases so that in the case of samples annealed at 700° practically no magnesium can be detected in the solution. The amount of magnesium dissolved is shown in Fig. 4, plotted as per cent of the total magnesium introduced against the temperature of annealing.

The question may be raised at this point as to what is the composition of the remaining nondissolved parts of samples. They have been dissolved in 80% sulfuric acid and their composition determined. It turned out that in all samples, independently of the temperature of annealing and the type of addition, the O/Cr ratio amounted to about 1.5.

Interesting conclusions may be drawn

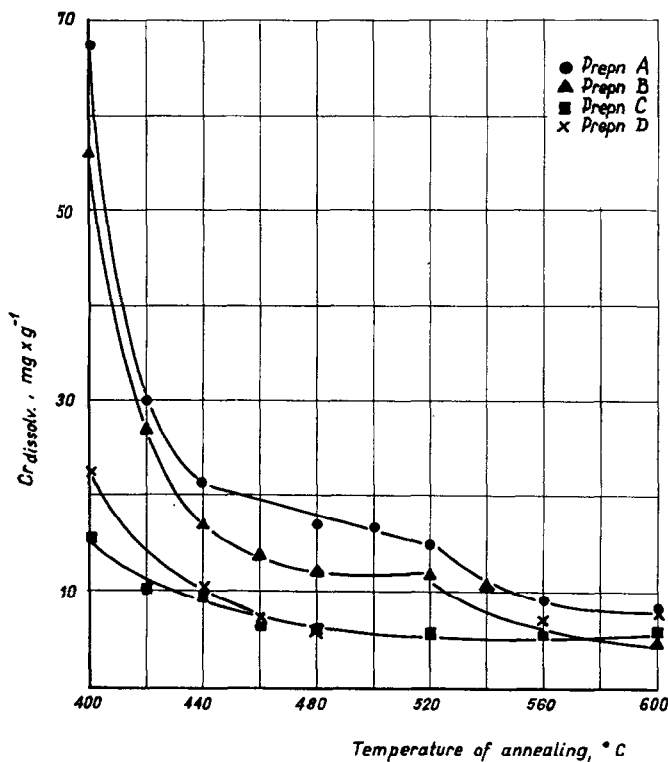


Fig. 3. The total amount of chromium dissolved in the course of analysis as a function of the temperature of annealing.

from the relation between the amount of excess charges and the specific surface area of samples. Let us assume for the moment that all excess charges correspond to the chemisorbed O²⁻ ions and calculate the

coverage obtained in respect to the hexagonal close-packed layer of oxygen ions taken as full coverage. The results of these calculations are shown in Table 1.

It may be seen from the data summarized

TABLE 1
THE COVERAGE OF THE SURFACE BY OXYGEN EQUIVALENT TO THE AMOUNT OF EXCESS CHARGES FOUND IN THE SAMPLE

Temperature of annealing (°C)	Preparation							
	A		B		C		D	
	Mg O _{act} per m ²	Fraction of monolayer	Mg O _{act} per m ²	Fraction of monolayer	Mg O _{act} per m ²	Fraction of monolayer	Mg O _{act} per m ²	Fraction of monolayer
400	0.63	1.51	0.70	1.68	0.35	0.83	0.22	0.52
420	0.35	0.84	0.45	1.08	0.24	0.57	0.12	0.28
440	0.33	0.79	0.38	0.90	0.22	0.54	0.15	0.36
460	0.38	0.91	0.36	0.87	0.22	0.54	0.16	0.39
480	0.35	0.84	0.27	0.65	0.27	0.65	0.15	0.36
500	0.34	0.81	0.24	0.58	0.22	0.54	0.16	0.39
520	0.23	0.56	0.23	0.55	0.19	0.45	0.14	0.35
540	0.21	0.51	0.20	0.48	0.22	0.53	0.14	0.35
560	0.22	0.52	0.16	0.39	0.22	0.53	0.14	0.35
580	0.21	0.50	0.16	0.38	0.22	0.53	0.13	0.32
600	0.22	0.52	0.16	0.37	0.22	0.53	0.13	0.32

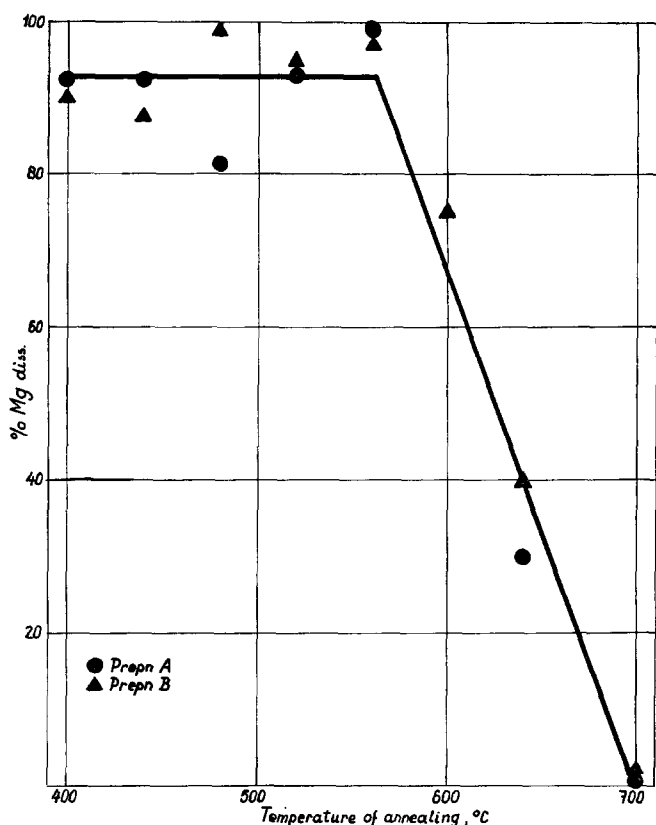


Fig. 4. The amount of magnesium dissolved in the course of analysis, expressed in terms of per cent of the total amount of magnesium introduced, as a function of the temperature of annealing.

in this table that except for magnesium-doped samples annealed at 400° the amount of excess charges in the dissolvable parts of samples corresponds to only partial coverage of the surface with oxygen ions. Thus it seems that in all cases the appearance of chromium ions of higher valence may be reasonably explained in terms of oxygen chemisorption. The presence of magnesium increases the amount of chemisorption at lower temperatures, whereas titanium decreases it. At higher temperatures all samples independently of the amount and type of doping agent tend to display similar activity towards the chemisorption of oxygen.

Further support to this conclusion is lent by the results of the determination of excess charges carried out in vacuum. They are summarized in Table 2 for samples of Preparation A. Samples were outgassed at the temperature of their previous annealing

TABLE 2
THE EFFECT OF OUTGASSING ON THE AMOUNT OF EXCESS CHARGES IN THE SAMPLE

Temperature of outgassing (°C)	Time of outgassing (hr)	Mg O _{out} per gram
400	0	18.6
	2	14.8
	3	8.0
	6	0.0
500	0	6.6
	3	0.7
600	0	2.5
	3	0.0

so that column 1 of Table 2 represents the temperature of outgassing as well as the temperature of annealing. In column 2 the time of outgassing is given and in column 3

the amount of excess charges, expressed in terms of milligrams of active oxygen per gram of sample. It may be seen that active oxygen can be completely removed by outgassing the sample, the time of outgassing being shorter the higher is its temperature. As it does not seem plausible that the equilibration of the bulk of the sample could take place at a temperature as low as 400° the results suggest that the excess charges were due to oxygen chemisorbed at the surface.

Figure 5 shows the surface concentration of Cr⁶⁺ ions as determined by the extraction

with water, plotted as a function of the temperature of annealing [Fig. 5(a)] and as a function of the amount of doping agent [Fig. 5(b)]. Addition of magnesium increases the surface concentration of Cr⁶⁺ ions, the latter being proportional to the amount of magnesium. Addition of titanium has an opposite effect, slightly decreasing the surface concentration of Cr⁶⁺ ions. This effect of the doping agent is strongest in the case of samples annealed at 400° and markedly decreases on raising the temperature of annealing.

The shape of the curves represented in

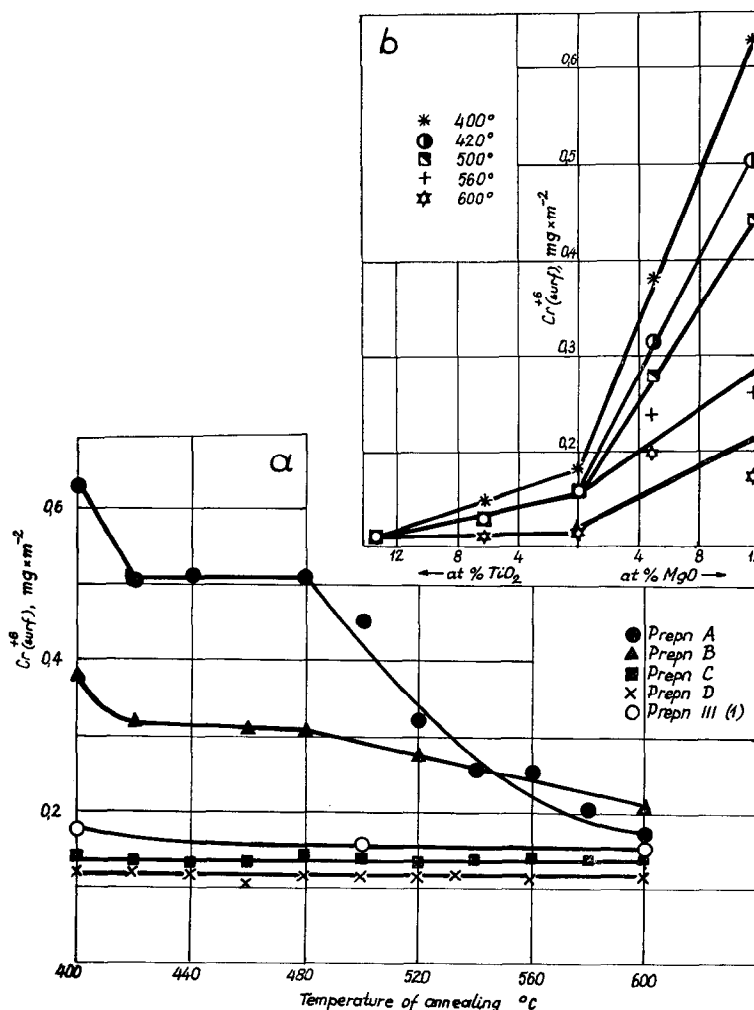
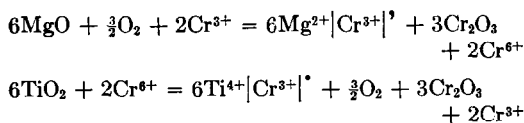


FIG. 5. The surface concentration of Cr⁶⁺ ions as a function of (a) the temperature of annealing; (b) the amount of the doping agent.

Fig. 5(a) is very similar to that of the temperature dependence of the total amount of excess charges (Fig. 2); only the absolute values amount to about one-third of the total concentration of excess charges. It is of course probable that water washes out only a fraction of the surface chromate ions. As, however, mentioned before, the extraction comes to its end after about 0.5 hr and the concentration of chromate ions in the solution does not increase even after 30 hr of extraction. Thus it seems justified to assume that practically all surface chromate ions are washed out in water. In such a case we must conclude that the excess charges form on the surface of Cr_2O_3 a diffused barrier layer extending a few crystal layers into the bulk of the crystallites. On treating the sample with water only the outermost surface layer can be dissolved, whereas on boiling in HCl the whole thin surface layer is taken off. The composition of this layer varies between CrO_3 and Cr_5O_{13} and it contains practically the whole amount of the introduced doping agent.

As discussed above, in the case of samples annealed at low temperatures addition of magnesium considerably increases and addition of titanium decreases both the total and surface concentration of excess charges. One would be tempted to explain such influence of additions simply in terms of incorporation of altrivalent ions into surface layer of the host lattice of chromium oxide according to the following equations:



The substitution of trivalent chromium ions by divalent magnesium ions should entail the increase of the concentration of free holes, whereas the substitution of tetravalent titanium ions should affect this concentration in the opposite direction.

However, if we assumed that such substitution of dopes into the surface layer had taken place, we would come to the conclusion that the decrease of the concentration

of excess charges in the surface layers of magnesium-doped samples, taking place on increasing the temperature of annealing, is due to the increasing diffusion of magnesium ions into the bulk. The change of the concentration of excess charges in samples A and B between 400° and 520° amounting approximately to 15 mg $\text{O}_{\text{act}}/\text{g}$ (cf. Fig. 2) would require 60 mg Mg/g , i.e. about 75% of the introduced amount to diffuse away from the surface layers into the bulk. This is incompatible with the results presented in Fig. 4, which show that the amount of dissolvable magnesium begins to decrease at about 560° , whereas at lower temperatures practically all of the introduced magnesium ions remain in the surface layers.

The second alternative is that at 400° only a part of the magnesium ions are substitutionally incorporated into the surface layer. In such a case, however, we should expect that on increasing the temperature of annealing more and more of the magnesium is incorporated into surface layers of grains, which must entail the increase of the concentration of excess charges and not its decrease as observed on Fig. 2. A different mechanism has to be invoked, whereby the presence of magnesium and titanium ions modify the adsorptive properties of the surface. Its nature however is not yet clear.

As mentioned before, the amount of magnesium ions in the surface layer of Cr_2O_3 crystallites begins to decrease at about 600° and at 700° no magnesium can be dissolved by boiling in HCl. At the same time the properties of magnesium- and titanium-doped samples again begin to diverge. It may be also noted that this temperature range coincides with that of the beginning of the reaction between MgO and Cr_2O_3 (5). This is probably when the incorporation mechanism starts to operate.

This picture is further supported by the results of electrical conductivity measurements, shown in Fig. 6. Figure 6(a) shows the electric conductivity as measured at 200° plotted as a function of the amount of doping agent for samples annealed at 400°

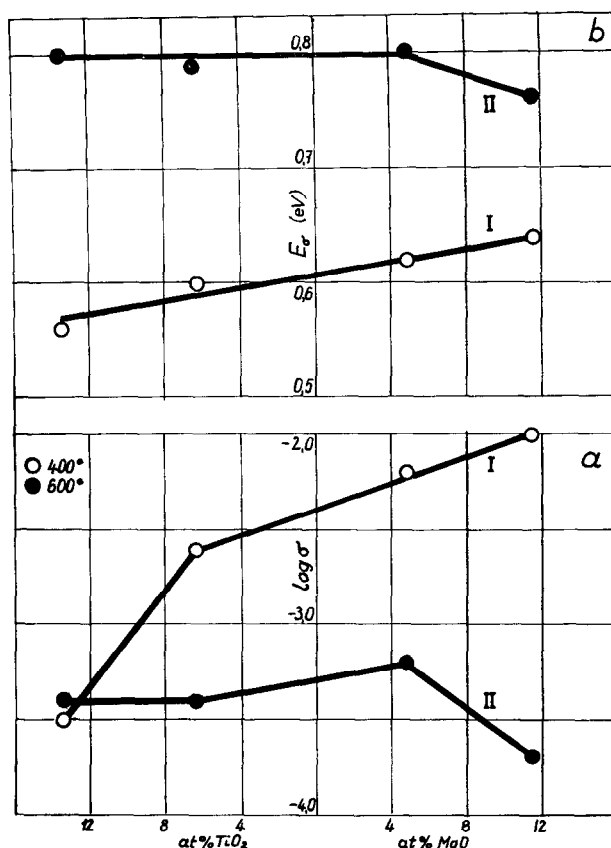


FIG. 6. (a) Electrical conductivity as measured at 200°, (b) activation energy of electrical conductivity, both as a function of the amount of doping agent for samples annealed at 400° and 600°.

(curve I) and 600° (curve II). Figure 6(b) represents the corresponding activation energies of the conductivity, calculated from the formula $\sigma = \sigma_0 \exp(-E/2kT)$. In the case of samples annealed at 400° a rapid increase in conductivity is observed passing from Preparation D to Preparation C and then to Preparation B, which may be related to oxygen coverage increasing in the same order. Oxygen coverage in the case of samples annealed at 600° does not display such a trend and neither does the electrical conductivity.

Figure 7 shows the specific rate constants of hydrogen peroxide decomposition, calculated per unit surface area, plotted as a function of the temperature of annealing [Fig. 7(a)] and as a function of the amount of doping agent [Fig. 7(b)]. In the case of

samples annealed at low temperatures the addition of magnesium considerably increases the rate constant, whereas the addition of titanium has a much smaller effect in the opposite direction. The influence of additions on the rate constants decreases with increasing temperature of annealing.

The comparison of Figs. 5 and 7 shows that a close correlation exists between the specific rate constant of hydrogen peroxide decomposition and surface concentration of Cr^{6+} ions. This is in agreement with our previous conclusions (1) that the rate-determining step of the decomposition involves Cr^{6+} acceptor centers. In the limits of experimental error the rate constant per unit surface concentration of Cr^{6+} ions is independent of the type and amount of doping agent, but decreases slightly with

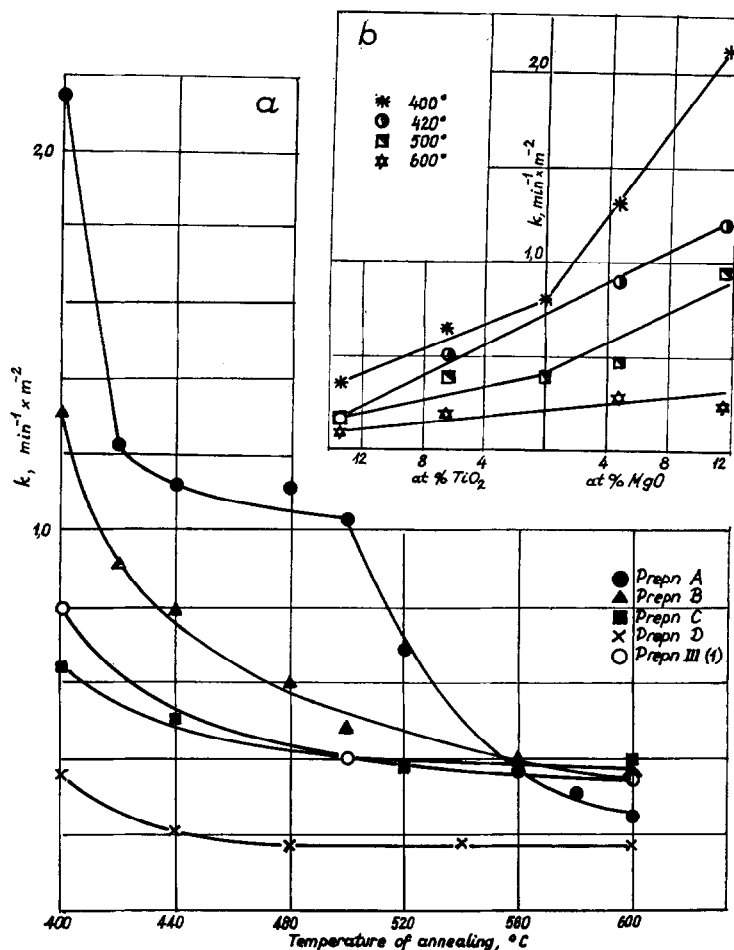


Fig. 7. Specific rate constants of H_2O_2 decomposition as a function of (a) the temperature of annealing, (b) the amount of doping agent.

increasing temperature of annealing, which may indicate that energy levels of Cr^{6+} active centers change with temperature of annealing. The changes of activation energy of the electrical conductivity with temperature of annealing may be taken as evidence that this is really the case.

One interesting feature must be emphasized here. As shown by Figs. 5(b) and 7(b), many properties, if plotted as functions of the amount of doping agent, change in the manner predicted by the simple electronic theory of catalysis. This is very often taken as evidence of the validity of predictions based on the assumption that altrivalent ions are substitutionally built

into the lattice and modify the electronic state of the solid, which in turn influences its catalytic activity. The results presented above clearly show that this may not be the case. Similar graphs are obtained, although other evidence shows that the influence of altrivalent ions cannot be explained by simple substitution of these ions into the host lattice. It seems that this may be a more general situation which very often has not received enough attention.

REFERENCES

1. DEREŃ, J., HABER, J., PODGÓRĘCKA, A., AND BURZYK, J., *J. Catalysis* **2**, 161 (1963).
2. HAUFFE, K., AND BLOCK, J., *Z. Physik. Chem.*

- (*Leipzig*) **198**, 232 (1951); FISCHER, W. A., AND LORENTZ, G., *Z. Physik. Chem. (Frankfurt)* **18**, 265, 308 (1958); SZABÓ, Z. G., AND SOLYMOŠI, F., *Acta Chim. Acad. Sci. Hung.* **25**, 161 (1960).
3. DEREŃ, J., HABER, J., AND SŁOCZYŃSKI, J., *Chemia Analit.* **6**, 659 (1955).
4. DEREŃ, J., HABER, J., AND WILKOWA, T., *Z. Physik.* **155**, 453 (1959).
5. DEREŃ, J., AND HABER, J., unpublished results.