The Electron Paramagnetic Resonance Absorption of Chromium Ions Dispersed on Silica-alumina. II. The Variation in the Spectrum under Several Chemical Treatments

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The structural change in chromium ions with the variation in the chemical composition of the supporting material was examined by the authors in a preceding report (Part I of this series)[1] through the analysis of the line shape in the γ-absorption on the electron paramagnetic resonance (EPR), which has been attributed to Cr^{5+} ions. This paper will be concerned mainly with the spectral change in the EPR of the same materials under several chemical treatments.

A few investigators have examined the behavior of the EPR spectra of chromium ions dispersed on silica-alumina under the influence of chemical reagents. Pecherskaya and Kazanskii[2-5] have reported on a series of experiments on this problem, attaching importance to the catalytic activity in the polymerization of ethylene. They have considered that Cr^{5+} ions are the catalytic-active sites. They have also examined the influence of the chemical composition of the supporting materials on the EPR spectra and the catalytic activity.

On the other hand, Cossee and Van Reijen[6] have investigated a similar substance by means

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[1] A. Matsumoto, H. Tanaka and N. Goto, This Bulletin, 38, 45 (1965).

[2] Yu. I. Pecherskaya, V. B. Kazanskii and V. V. Voevodskii, 2nd International Congress on Catalysis (Paris), 1960, paper no. 108.

[3] F. M. Bukanaeva, Yu. I. Pecherskaya, V. B. Kazanskii and V. A. Dzis'ko, *Kin. i Kat.*, 3, 358 (1962).

[4] V. B. Kazanskii and Yu. I. Pecherskaya, ibid., 4, 244 (1963).

[5] G. K. Boreskov, F. M. Bukanaeva, V. A. Dzis'ko, V. B. Kazanskii and Yo. I. Pecherskaya, ibid., 5, 434 (1964).

[6] P. Cossee and L. L. Van Reijen, 2nd International Congress on Catalysis (Paris), 1960, paper no. 82.

of EPR and magnetic susceptibility under the influence of hydrogen, sulfur dioxide, benzene, etc. They think that reduction at a relatively low temperature produces mainly Cr^{4+} ions, and they discussed the influence of the supporting materials as well as the methods of reduction. However, they did not very much consider the nature of active sites in the polymerization of ethylene. Recently they also reported on interesting work on the same sort of material in relation to the catalytic-active sites in the dehydrogenation reactions.7)

The authors intend in this paper to demonstrate the influence of the chemical composition of the supporting materials on the variation in EPR spectra under the action of air, water vapor, cyclohexane. The effect of evacuation will also be investigated. Then, with these results added to those of Part I, the relation between the stability of the $3d^1$ state or chromium ions and the catalytic activity in the polymerization of ethylene and in the decomposition of hydrogen peroxide will be discussed.

Experimental

Materials and Treatment.—The supporting materials and the method of preparing dispersed samples were the same as those described in Part I. The calcination of samples was carried out in a stream of dry air at 500°C for 4 or 17 hr. Immediately after the calcination, the measurement of the EPR and the chemical treatments were started. The samples used in the experiment are listed in Table I.

The Measurement of the EPR Spectra.—The EPR spectra were observed with the K-band superheterodyne spectrometer described in the preceding paper. When the measurement was performed at elevated temperatures, a cavity equipped with a heater was employed. A small quantity of coal powder was fixed in the cavity as a standard of the relative intensity of the EPR absorption.

A silica tube which contained the sample was inserted into the cavity and connected with a vacuum system. The cavity had previously been heated at a fixed temperature. After evacuation for several minutes, each reagent was introduced and the measurement of EPR was started. Dry air was conducted from a flask containing phosphorus(V) oxide. Water vapor was then introduced from a glass tube in which a small quantity of deaerated water had been sealed off. Ethylene was taken from the same material as those used in the polymerization experiment in this laboratory. The reaction of cyclohexane was followed in the open air.

In some cases samples were treated outside the cavity and were measured in an ordinary cavity at room temperature. Especially the evacuation of the samples not calcined was carried out in another tube at room temperature for 24 hr. with an oil diffussion pump, and then the samples were transferred into a tube for measurement and sealed off. When the samples not calcined were evacuated, a color change occurred, even at room temperature.

The Oxidation Number.—The oxidation number was determined by the iodometry described in Part I.1) When the determination was carried out after reduction with cyclohexane, the samples were dried, with evacuation, at room temperature. After treatment with ethylene, however, it was impossible to determine the oxidation number because the polymer covered the samples.

The Polymerization of Ethylene.—The activity in the polymerization of ethylene was determined at 135°C by means of the decrease in the pressure of ethylene starting from 1 atm. and from 40 kg./cm² without a solvent. About 200 mg. of the sample calcined was placed in a glass tube dipped in an oil bath at 135°C; then, after the air had been removed with a rotary vacuum pump for five minutes, ethylene was introduced up to 1 atm. The volume of the system was about 600 cc. (N.T.P.). Then the decrease in the pressure was observed. Some of the samples were taken out during this treatment and their EPR spectra measured.

When the experiment was performed starting from 40 kg./cm², about 500 mg. of the sample was placed in a stainless steel autoclave (100 cc.). After the repeated replacement of the atmosphere with nitrogen, the autoclave was heated to 135°C and ethylene was introduced up to 40 kg./cm². The decrease in the pressure was observed, and after a definite time the weight of the polymer produced was measured. The volume of the system was about 125 cc. (N.T.P.).

Decomposition of Hydrogen Peroxide.—The decomposition of hydrogen peroxide was investigated at 30°C, using an apparatus which was similar to that of Deren et al.8) About 100 mg. of the sample was placed in an ampoule and 30 cc. of 30% hydrogen peroxide was added. By running water out from the burettes connected to the system, a manometer was balanced and the volume of the generated oxygen was determined nearly continuously. The decomposition proceeded linearly with time. The measurement was continued for about an hour.

Results

The Variation in EPR Absorption in the Atmospheres of Different Gases.—*The Appearance of the γ-Absorption by Evacuation and Its Disappearance with Air and Water Vapor.*—Impregnated samples which had merely been dried at 120°C in open air gave a broad so-called β-absorption of EPR without a sharp line of γ-absorption or with only a very weak one. When these materials were evacuated, the γ-absorption appeared and increased, even at room temperature. This absorption, however, was more affected by air and water vapor than that of the calcined samples. Figures 1

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7) L. L. Van Reijen, W. M. H. Sachtler, P. Cossee and D. M. Brouwer, 3rd International Congress on Catalysis (Amsterdam), 1964.

8) J. Deren, J. Haber, A. Podgorecka and J. Burzyk, *J. Cat.*, 2, 161 (1963).

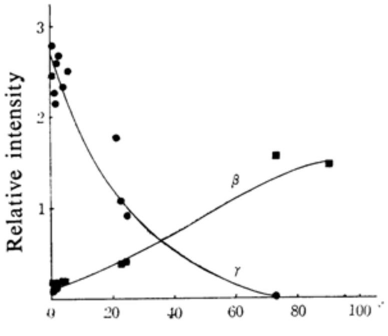

Fig. 1. The variation of the intensity of EPR absorptions in dry air. Sample No. 5, not heat treated and evacuated, at room temperature. (The unit of the intensity is not the same in two absorptions.)

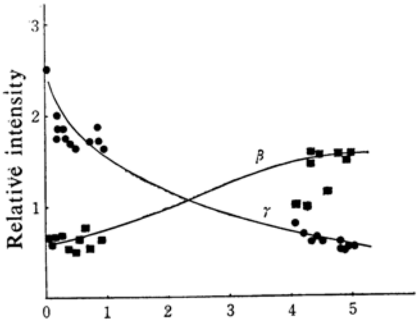

Fig. 2. The variation of the intensity of EPR absorptions in water vapor. Sample No. 5, not heat treated and evacuated, at room temperature. (The unit of the intensity is not the same in two absorptions.)

and 2 shows the decrease in this absorption in atmospheres of dry air and water vapor at room temperature. It may be seen that water vapor is 10 times as effective in causing this decrease as dry air.

Dry Air and Water Vapor.—Figure 3 shows the variation in the intensity of EPR absorption in a vacuum, in dry air and in water vapor at three different temperatures. The sample is No. 5, i. e., the sample with a commercial silica-alumina base, in Table I, and

TABLE I. THE SAMPLES USED IN THE EXPERIMENTS

Sample No.	Base material*	Cr cont. %
1	Silica gel (635)	4.88
2	Silica : alumina 4 : 1 (279)	4.27
3	Silica : alumina 1 : 1 (306)	5.40
4	Gamma alumina (233)	5.45
5	Silica : alumina 10 : 1**	2.36

* Figures indicate BET surface area in m²/g.
** Commercial silica-alumina.

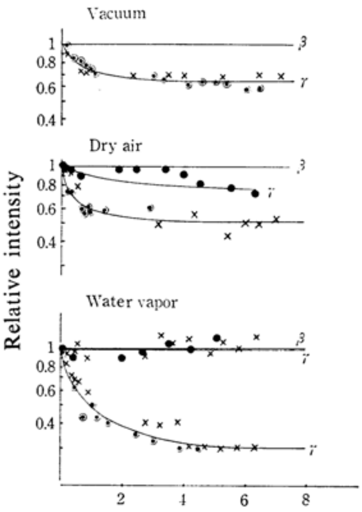

Fig. 3. The variation of the intensity of EPR absorptions.
Sample No. 5 ; ● 50°C, ◉ 80°C, × 120°C

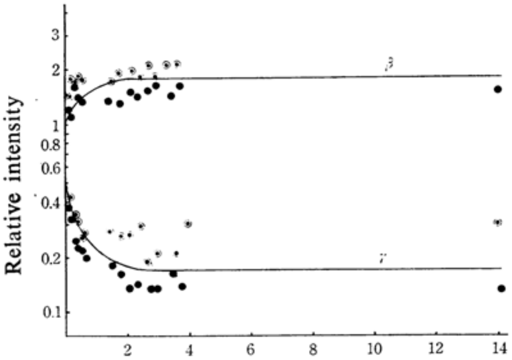

Fig. 4(a). The variation of the intensity of EPR absorptions in cyclohexane at 70°C.
Sample No. 5 ; ● 50°C, ◉ 80°C

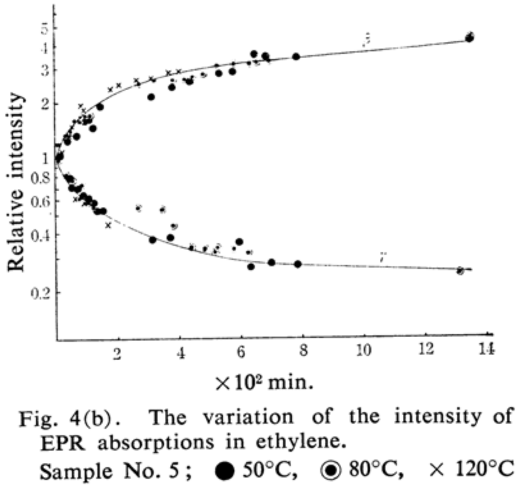

Fig. 4(b). The variation of the intensity of EPR absorptions in ethylene.
Sample No. 5 ; ● 50°C, ◉ 80°C, × 120°C

it is calcined at 500°C for 17 hr. Concerning the β-absorption, no marked increase is seen. The decrease in the intensity of the γ-absorption is accelerated by water vapor and temperature, but the acceleration does not linearly correlate with the temperature.

Cyclohexane and Ethylene.—The same material was treated with cyclohexane and ethylene; the results are shown in Fig. 4. Another series of experiments was carried out in order to compare the samples with different supporting materials. Figure 5 shows the intensity variation in each sample at 70°C in an atmosphere of ethylene. Figure 6 shows the line shapes of the EPR of samples which were picked out in the course of the polymerization experiment to be described below.

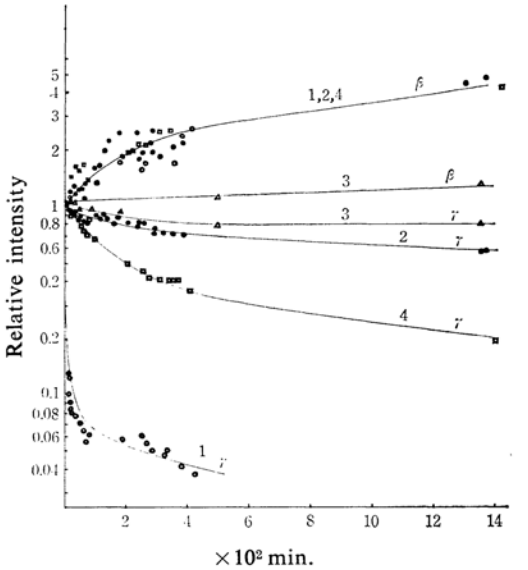

Fig. 5. The variation of the intensity of EPR absorptions by the contact of ethylene in the samples with different supporting materials at 70°C. Figures indicate sample numbers.

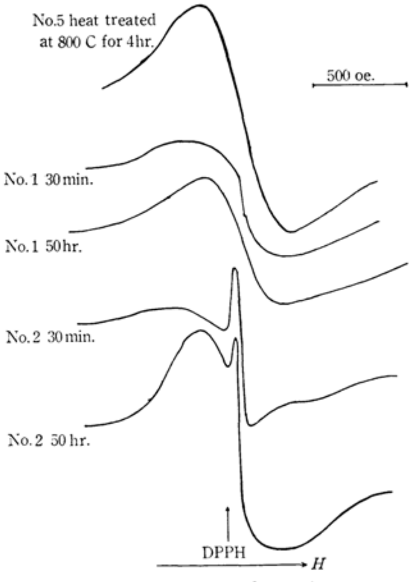

Fig. 6(a). EPR spectra after the treatment with ethylene at 1 atm. The first indicates the spectrum of the sample No. 5 heat treated in air at 800°C for 4 hr.

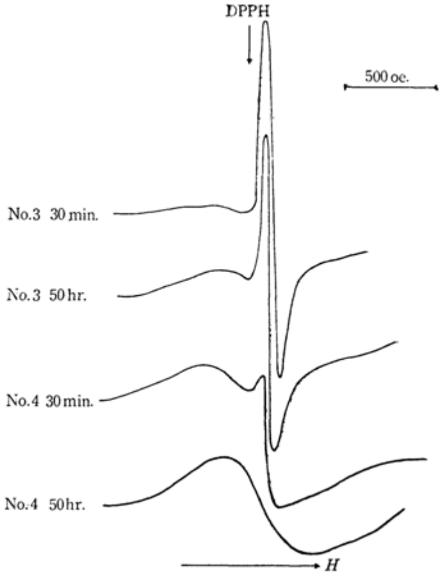

Fig. 6(b). EPR spectra after the treatment with ethylene at 1 atm.

It may be seen that in these atmospheres the β-absorption grows rapidly and that the decrease in γ-absorption is also remarkable. The variation does not depend on temperatue very much, from 50°C to 120°C, in the atmosphere of ethylene. The supporting material markedly affects the behavior of the γ-absorption. As may be seen in Figs. 5 and 6, the

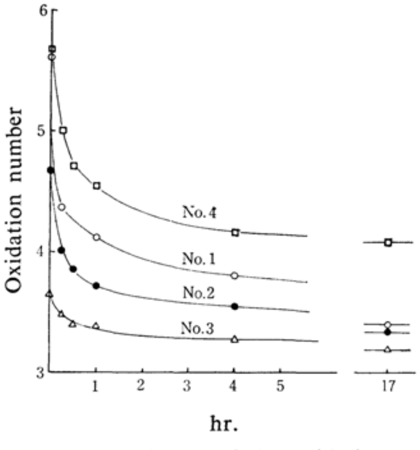

Fig. 7. The variation of the oxidation number by the treatment with cyclohexane at 60°C.

sample with a silica gel base loses the γ-absorption quite rapidly, with the sample with a gamma-alumina base next. In the sample with a silica-alumina I (silica : alumina = 4 : 1) base, the γ-absorption is rather stable, and in the sample of silica-aluminaII (silica : alumina = 1 : 1) the γ-absorption hardly changes at all during the measurement.

Figure 7 indicates the variation in the oxidation number of the four kinds of samples by the treatment with cyclohexane at 60°C. The oxidation number of the silica-gel-base sample also decreases quickly. The sample with a silica-alumina II base keeps a low oxidation number from the beginning. It may be noticed that the sample with a gamma-alumina base keeps a relatively high oxidation number, even after long treatment.

The Polmerization of Ethylene. — When the samples calcined at 500°C for 4 hr. were brought into contact with ethylene of 1 atm. at 135°C, a decrease in the pressure was observed in the cases of the samples with a silica gel base and with a silica-alumina I base, as is shown in Fig. 8. The polymers which melted during the reaction, including the particles of the samples, formed a plate. The reproducibility of the experiment was not very good, but the relative inclination was always similar. Figure 8 indicates the average curves of several runs. In all cases a short period of induction was observed. This period was shorter in the silica-gel-base sample than in the silica-gel-alumina I base sample, and the initial rate of the reaction was faster in the former. After about an hour of the rapid decrease in the pressure, a gradual drop continued for a long time.

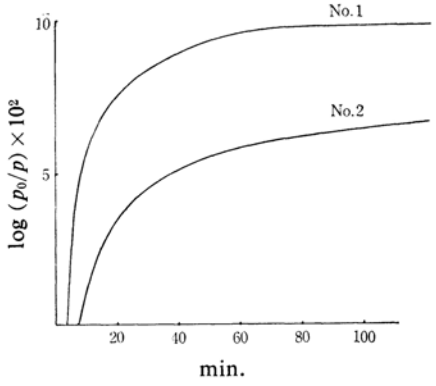

Fig. 8. The pressure decrease of the ethylene with the contact of the samples (at 135°C, from 1 atm.).

For the samples with a silica-alumina II base and with a gamma-alumina base, no decrease in the pressure could be observed. The color of the samples turned green from the initial orange or orange yellow for the samples with a silica gel base and with a silica-alumina I base, but for the sample with a silica-alumina II base the color changed little remaining brown.

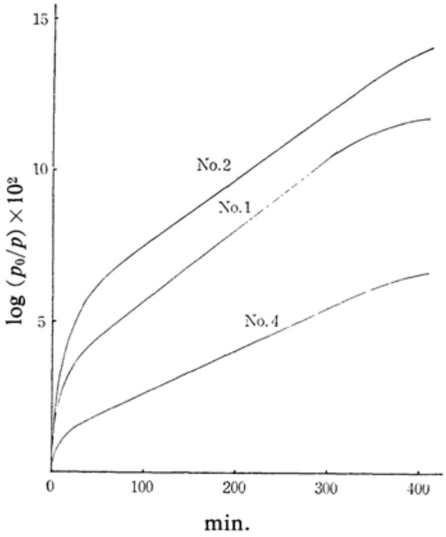

Fig. 9. The pressure drop of the ethylene with the contact of the samples (at 135°C, from 40 kg./cm^2).

Figure 9 shows the results of the experiments with an autoclave. In this case decrease in the pressure was observed even with the sample with a gamma-alumina base, but the rate was slower than with the samples with a silica gel base and with a silica-alumina I base. The difference between the latter two samples was not as clear as in the experiment started from 1 atm. The polymer produced after 20 hr. was 4—5 g. per 1 g. of the sample in the cases of silica gel and silica-alumina I, and about 1.5 g. per 1 g. of the sample in the case of a gamma-alumina base. However, as the polymerization proceeds, the samples are covered with the molten polymer and the diffusion of ethylene into the polymer becomes important in the reaction. Also, the heat of the reaction necessarily elevates the temperature at the surface of the sample, so it is difficult to decide the activity directly on the basis of these values. The sample with a silica-alumina II base did not bring about the pressure drop at 40 kg./cm^2 either.

The Decomposition of Hydrogen Peroxide.— In Table II the amount of oxygen liberated in one minute per gram of chromium in the sample and that oxidation number are shown for the four kinds of samples, each of which was measured before and after treatment with cyclohexane. This treatment was the same as that for the determination of the variation in the oxidation number, and the duration was fixed at thirty minutes.

The activities per chromium differ, but if the activity is expressed by the value per oxidation number, they are not very different. Even after the reduction, these values remain constant, except for the sample with a silica gel base, where the activity per oxidation number becomes more than two times as large.

TABLE II. THE CATALYTIC ACTIVITY IN THE DECOMPOSITION OF H_2O_2

Sample	Before reduction	After reduction*
Liberated O_2 cc./min./g. of Cr		
1	9.79×10^{12}	7.98×10^{12}
2	9.00	5.02
3	3.14	1.57
4	1.47	1.04
Liberated O_2 cc./min./g. of Cr^{6+} **		
1	11.9×10^{12}	25.8×10^{12}
2	16.8	17.1
3	13.3	10.7
4	16.8	18.7

* Treated in cyclohexane for 30 min. at 60°C.

** Determined by the method of the analysis of oxidation number.

Discussion

The Stability of γ-Absorption Sites Against Chemical Reagents. — The authors showed in Part I of this series that thermal stability of γ-absorption sites in the dispersed chromia was affected by the chemical composition of the supporting material. The sample with a silica gel base held a high mean oxidation state and showed the γ-absorption up to a higher temperature of the heat treatment. The addition of alumina to the base material lowered the thermal stability of the high oxidation state and γ-absorption sites. Pure gamma-alumina had a somewhat different inclination as a supporting material.

On the contrary, the reduction with chemical reagents proceeds most easily in the sample with a silica gel base, and the disappearance of the γ-absorption upon contact with ethylene occurs most rapidly in this sample. The sample with a silica-alumina II base, which has a relatively low oxidation number from the beginning and which shows a strong γ-abserption, is quite inert; the γ-absorption is hardly changed at all by the treatment with ethylene, as is shown in Figs. 5 and 6. The absorption of the sample with a gamma-alumina base behaved in an intermediate manner under this treatment.

As was mentioned in Part I, the γ-absorption site of the pure silica-gel-base sample must be present in the cluster of chromia, possibly at the surface. Its concentration is low, and the coordination field around the Cr^{5+} ions is a symmetric. It may be considered that under such conditions chromium ions react easily with chemical reagents.

When alumina is added to the supporting material, isolated chromium ions appear. The concentration of Cr^{5+} ions increases, and the coordination field around them becomes more symmetric. The chemical stability of these sites increases, though they are not very stable against heat treatment. It is natural to think that this effect is caused by aluminum ions or by the defects made by aluminum ions. It is, however, not clear at present whether the γ-absorption sites are present at the isolated chromium or in the clusters of chromia, but at least there are several γ-absorption sites which are different in the chemical stability, and the addition of alumina to the supporting material makes for an increase in the number of chemically-stable sites or for an increase in the general stability of the sites against chemical reagents.

Gamma-alumina acts as an intermediate supporting material. The line shape of the γ-absorption is most symmetric in the sample with this base and the coordination is most regular. Unlike silica-alumina, gamma-alumina is rather a regular substance, so the dispersion of chromia on this material is more regular, though the interaction between chromia and alumina is strong. The fact that the oxidation number does not go below four upon treatment with cyclohexane indicates the different state of the chromium ions on this material.

Kazanskii et al.⁵⁾ reported similar findings concerning variation in the line shape of the EPR in different supporting materials, though they thought mainly in terms of a substitution of the chromium atom for the silicon atom. The interaction of chromium with silica-alumina has also been discussed by a few investigators.⁹⁻¹¹⁾ Topchiev et al.⁹,¹⁰⁾ considered the formation of aluminum chromate, with reference to the work of Pode et al.,¹²⁾ and concluded that the stability of the high oxidation state of chromium is determined by the form of the chromates.

As has been seen earlier, the evacuation of a sample not calcined produces γ-absorption

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9) A. V. Topchiev, B. A. Krentsel, A. I. Perel'man and K. G. Miesserov, *J. Polymer Sci.*, **34**, 129 (1959).

10) A. V. Topchiev, ibid., **53**, 195 (1961).

11) K. G. Miesserov, *Neftekhimiya*, **2**, 681 (1962); *Chem. Abstr.*, **58**, 8042e.

12) T. V. Rode, V. B. Kazanskii and Yu. I. Pecherskaya, *J. Phys. Chem. SSSR*, **35**, 2370 (1961).

sites which easily disappear upon contact with air, even, at room temperature. Perhaps the nature of these sites is similar to that on silica gel. The EPR spectra of the samples calcined do not change very much in a vacuum or in dry air. Particularly the β-absorption does not increase. This means that the ionic state of chromium in the dispersed clusters of chromia does not essentially change. On the contrary, in the samples not calcined, a rise in the β-absorption is seen in response to a fall in the γ-absorption. The effect of water vapor is more rapid and clear, and the β-absorption appears gradually, even in the calcined sample. These phenomena correlate with the process of stabilization, indicating the formation of certain coordination states.

The Activity in the Polymerization of Ethylene.—The initial reaction rate of ethylene at 1 atm. is the fastest with a silica gel base, but the chromium ions on the same base are most easily reduced. This may correlate with the fact that when used as the supporting material the pure silica gel makes the catalyst most easily deactivated.[13] The addition of alumina produces the more stable active sites. However, addition in excess increases the number of inactive chromium ions.

The nature of the active sites in these substances in the polymerization of ethylene is not yet clear. It is, however, possible to consider that such sites exist in the dispersed clusters of chromia, where chromium ions are placed in a field of distorted octahedron. In the course of the present experiment, it was established that the samples become yellow or orange yellow when subjected to heat treatment in dry air. If the activation was carried out in wet air, the samples turned green. After the polymerization, the color generally turned green. The green samples played no part in the polymerization, as is well known. The teatment of the activated samples by cyclohexane caused a color change to brown and not to green.

Van Reijen et al.[7] also paid attention to the color change of chromia-alumina and chromia-silica. They measured the EPR and the magnetic susceptibility and concluded that, in a light blue sample, chromium ions become Cr^{2+} and active in the dehydrogenation of cyclohexane, while in a green sample chromium ions are Cr^{3+} and inactive.

These colors reflect the electronic state of the active chromium ions. From the facts that the oxidation state of chromium easily changed by the treatment with cyclohexane and that, in general, the catalyst is dispersed in some hydrocarbon before coming in contact with the solution of ethylene, the valence state of chromium has to be below 5^+ at the moment of reaction. Accordingly, the existence of chromium ions which are easily reduced to a low valence state, but yet keep some coordination condition, may be essential for the polymerization.

The life of the active site is decided by the ease of the transfer from an active to an inactive coordination state. The effect of the addition of alumina can be understood from the increase in the symmetry of the coordination field and from the subsequent increase in the stability of the state, which is reflected by the increase in the symmetry and width of the γ-absorption.

About the poisoning of the activity by water, Kazanskii and Pecherskaya[4] proposed a mechanism of the strong attaching of water to Cr^{5+} sites, which they considered to be the active sites in the polymerization reaction. This is a possibility, but at the same time it is possible to consider that water accelerates the transfer of chromium ions into an inactive state. This is because, if the air of the heat treatment is wet, the color of the sample becomes green, the presence of water produces a green sample both in a reductive atmosphere and in an oxidative.

There are a few articles about the mechanism of the polymerization of ethylene with this sort of catalyst.[10,14-19] Clark et al.[20] reported that the treatment of the catalyst by carbon monoxide above 250°C or by ethylene above 15°C produces a complex of the carboxylate type on the surface, and that only the catalyst accompanying this complex is active in the polymerization of ethylene at low temperature. The role of this complex has not yet been made clear.

Before the catalyst is introduced into the reactor, it is dispersed and held in the solvent. This procedure may, like the penetration of the solvent, be useful in making the complex. As may be seen in Fig. 8, the polymerization at 1 atm. shows an induction period, which may correspond to the complex formation. Topchiev et al.[21] have shown that the pretreatment of the catalyst by ethylene or isooctane reduces this induction period.

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[13] Phillips Petro. Co., Belg. Pat. 530617, July 23 (1954); 535082, Jan. 22 (1955); 551826, Oct. 16 (1956).

[14] F. Eirich and H. Mark, *J. Colloid Sci.*, **11**, 748 (1956).

[15] E. C. Curphey, *Brit. Plastic*, **31**, 63 (1958).

[16] T. Tsuruta, *Kagaku*, **13**, 614 (1958).

[17] A. Takahashi, *Yuki Gosei Kagaku*, **18**, 624 (1960).

[18] Stanislaw Benbenek, *Przemysl Chem.*, **41**, 719 (1962); *Chem. Abstr.*, **58**, 12677h; *Przemysl Chem.*, **43**, 28 (1964); *Chem. Abstr.*, **60**, 13320d.

[19] A. Clark and G. C. Bailey, *J. Cat.*, **2**, 230 (1963).

[20] A. Clark, J. N. Finck and B. H. Ashe, 3rd International Congress on Catalysis (Amsterdam), 1964.

[21] K. V. Topchieva, O. K. Sharaev, A. I. Perel'man and A. V. Topchiev, *Neftekhimiya*, **1**, 780 (1961); *Chem. Abstr.*, **57**, 6111c, *Neftekhimiya*, **2**, 187 (1962); *Chem. Abstr.*, **58**, 4649f.

The dispersion of chromia in the form of thin-layer clusters is convenient for the multi-point adsorption; also, if this assembly of chromia has the character of an *n*-type semiconductor in the reducing atmosphere, the d^1 or d^2 state of chromium is conductive to the adsorption from the point of view of the ligand field stabilization energy. The adsorption is also possible in a Zeise-type π-complex, such as Cossee suggested in the case of the Zieglar-type catalyst.(23) In any case, ethylene monomers are adsorbed on the surface of the cluster of chromia collectively. If the carboxylate ions cited above serve to initiate the process, the polymerization proceeds in a manner like that proposed by Duck(23) in a Ziegler-type catalyst or by Friedlander(24,25) in a standard-type catalyst. It is interesting that Eishens observed the same type of carboxylate ions on the Ni–NiO treated with CO.(26)

The Decomposition of Hydrogen Peroxide.—There have been several reports concerning the activity of chromia dispersed on the supporting materials in the decomposition of hydrogen peroxide. Voltz and Weller(27) and Matsunaga(28) have shown that the activity of the chromia-alumina system depends on the excess oxygen over a wide range of the chromium concentration; the activity per excess of oxygen is constant. Tarama et al.(29) have reported that the Cr^{6+} site and the Cr^{5+} site both have catalytic activity. On the other hand, Deren et al.(8,30) showed that the aggregative state of Cr^{6+} affects the activation energy in the decomposition reaction. From the low concentration range of chromium where an atomic dispersion occurred, to the higher concentration which resulted in the clusters, the activation energy gradually lowered and the activity increased as a whole.

In the present experiment, the decomposition activity is related to the excess oxygen of the samples in many cases. The difference in the supporting material does not produce a great difference in the specific activity. The reduction by cyclohexane lowers the total activity, but the activity per excess unit of oxygen remains constant. Only in the case of the sample with a silica gel base is the activity per excess unit of oxygen about two times larger after the reduction; the lowering of the activity is not so great as that of the oxidation number.

This phenomenon may be correlated with the coordination state of the chromium ion. If the decomposition of hydrogen peroxide by these materials proceeds via the cycle of oxidation-reduction mentioned in the case of MnO_2,(31) the quantity of the excess oxygen is only a measure of the sites in the oxidation state. In general, the rate-determining step of the reaction involves only the acceptor site. There are two possibilities in the case of the sample with a silica gel base. First, the reduction does not destroy the active site, though its oxidation state is changed. Second, both the acceptor site and the donor site contribute to the rate determination step in some coordination state. The former enlarges the finding of Tarama et al. that Cr^{4+} is also a reactive site. The results of Deren et al. are also useful in understanding special features of the chromia cluster. It would be expected that the assembly would produce an lowering of the activation energy. This must be a characteristic of this dispersion.

Summary

The dispersed state of chromium and the effect of heat treatment have been compared in Part I in chromium dispersed on different supporting materials. The behavior of the EPR absorption of the same materials in the reaction of several chemical reagents have been observed in the present work. The catalytic activities of these samples in the polymerization of ethylene and in the decomposition of hydrogen peroxide have also been measured.

The γ-absorption sites of the samples had different stabilities. In the sample with a silica gel base, this absorption disappeared quite easily in a reductive atmosphere, but that of the sample with a silica : alumina 1 : 1 base was stable in the same atmosphere. The former showed the greatest initial reaction rate in the polymerization of ethylene at 1 atm., while the latter had no catalytic activity in the polymerization, even at 40 kg./cm^2. The sample with a gamma-alumina base showed an intermediate character in many respects. The activity in the decomposition of hydrogen peroxide generally corresponded to the oxidation number of the samples, even after reduction with cyclohexane, but in the case of the silica gel base different behavior was observed.

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22) P. Cossee, *J. Cat.*, **3**, 80 (1964).

23) E. W. Duck, *J. Polymer Sci.*, **24**, 86 (1958).

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Taking the present and the preceding results into account, the character of this type of catalyst has been discussed. Its nature must essentially be due to the cluster-form dispersion of chromia; the addition of alumina to the supporting material gives an effect of stabilization to the active site, which extends the life of the catalyst, though an excess in the addition results in an inactive material. The $3d^3$ state of the chromium ions is inactive in the polymerization of ethylene, probably because of the lack of a beneficial adsorptive property to the monomer. The ease in the transfer among d^0, d^1 and d^2 states of chromium ions may decide the activity, while the transfer into the d^3 state may decide tha life of the catalyst. Water accelerates the latter and deactivates the catalyst.

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