Electron Paramagnetic Resonance Absorption of Chromium Ions Dispersed on Silica-alumina. I. The Influence of Chemical Constitution of the Supporting Materials on the Dispersed State

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The electron paramagnetic resonance (EPR) absorption of chromium ions dispersed on supporting materials, principally silica, silica-alumina and gamma alumina, has been examined by several investigators for the purpose of clarifying their catalytic active sites in some chemical reactions.[1-11] Three types of resonance absorption have been confirmed. The first of these appears in the vicinity of 1500 oe. in the X-band and has been referred to as the δ-line. This absorption has been interpreted as due to Cr^{3+} ions well dispersed and electronically isolated.[4] The second resonance,

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

[2] Yu. I. Pecherskaya, V. B. Kazansky and V. V. Voevodsky, ibid., paper no. 108.

[3] D. E. O'Reilly, *Advances in Catalysis*, 12, 99 (1960).

[4] D. E. O'Reilly and D. S. MacIver, *J. Phys. Chem.*, **66**, 276 (1962).

[5] C. P. Poole, Jr., W. L. Kehl and D. S. MacIver, *J. Cat.*, **1**, 407 (1962).

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

[7] V. V. Antuf'ev, M. P. Votinov, A. G. Sazhin, A. C. Cemenova and M. N. Peitman, ibid., 3, 353 (1962).

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

[9] A. A. Spinskin, E. A. Fedorovskaya and A. M. Rubinshtejn, ibid., **4**, 230 (1963).

[10] K. Tarama, S. Teranishi and K. Yoshida, *Shokubai* **4**, 341 (1962).

[11] D. G. Howard and R. H. Lindquist, *J. Chem. Phys.*, **38**, 573 (1963).

referred to as the β-line, is broad and centered at about 3400 oe. in the X-band. MacIver et al.[5] distinguished two kinds of β-lines, using coprecipitated chromia-alumina, and attributed them to Cr^{3+} in small clusters of chromia in the amorphous phase and in the solid solution phase. The last resonance, whose g value is almost the same as that of the β-line but whose width is narrower, has been referred to as the γ-line. This absorption has been generally attributed to Cr^{5+}.

The character of these absorptions varies with the supporting materials and the oxidation-reduction conditions and, though the various general explanations of their origin agree with each other fairly well, some uncertainty remains about the configurational state of the ions. In the present investigation, we intend to examine the structural change of chromium ions with the variation in the chemical constitution of the supporting material under the heat treatment, pursuing principally the behavior of the γ-lines and comparing their shapes with those of some chromium compounds.

Experimental

Materials and Treatment. — As supporting materials pure silica gel, silica-alumina and gamma alumina were prepared by the hydrolysis of ethylorthosilicate, aluminum isopropoxide and their mixtures in order to avoid their containing impurities of transition elements. Aluminum isopropoxide was made from highly pure metallic aluminum. After having been crushed down to 30 mesh pass, they were heat-treated at 500°C for 17 hr. in a stream of dry air. Figure 1 shows their thermal variation, while Table I indicates the chemical composition, the surface area, and the results of qualitative analysis by the emission spectroscopy of the materials heat-treated. In some cases a commercial silica-alumina cracking catalyst (Davison Co.) was employed; the official specifications are also shown in Table I.

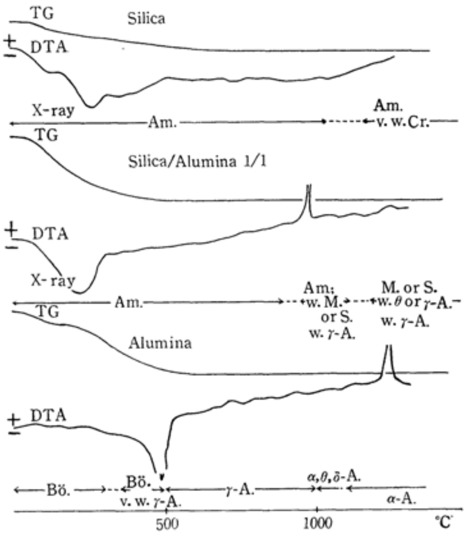

Fig. 1. Thermal transition of the supporting materials.
TG: thermogravimetry, DTA: differential thermal analysis, Am.: amorphous, Cr.: cristobalite, Bö.: boemite, A.: alumina, M.: mullite, S.: sillimanite, w.: weak, v. w.: very weak.
X-ray diffraction was measured after holding at each temperature for 4 hr.

The impregnation of chromia was carried out with an aqueous solution of chromic anhydride of a special grade (Kanto Kagaku Co.). The supporting materials were immersed in the solution and strirred at 50°C for 2 hr. The excess solution was then filtered out, and the impregnated materials were dried for 24 hr. in an air bath at 120°C. The quantity of chromium was controlled by changing the concentration of the solution and the ratio of the supporting material to the solution. Table II indicates the impregnated samples used in the experiment. The heat treatment of the impregnated materials was carried out in a stream of dry air for 4 hr. at definite temperatures.

Chromic anhydride was also heat-treated without supporting material. This compound melts at a relatively low temperature, i. e., at 196°C, and it is changed into alpha chromia at about 400°C through a few intermediates. Various intermediate chromium oxides between CrO and CrO_3 have been

TABLE I. SUPPORTING MATERIALS USED IN THE EXPERIMENT

No.	Material	SiO_2/Al_2O_3 mol.	BET surface area m²/g.	Purity*
1	Silica gel	—	634.6	Al : N.D.
2	Silica-alumina I	1 : 4	279.1	Cu : ±
3	Silica-alumina II	1 : 1	308.5	
4	Gamma alumina	—	233.4	Si : +
5	Commercial silica alumina	1 : 10	>400	

* By emission spectroscopy, No. 1—4: Ca ±, Mg, Na, Fe, Ti, Cu, Mn, Cr N. D.

TABLE II. IMPREGNATED SAMPLES USED IN THE EXPERIMENT

Sample No.	Base material*	Cr cont., wt.%
1	1	2.43
2	2	2.73
3	3	4.83
4	4	4.93
5-1	5	0.65
5-2	5	2.11
5-3	5	3.0
5-4	5	5.8
5-5	5	16.7

* Corresponds to the numbers indicated in Table I.

reported; however, their crystal structures are unknown except in a few cases. For the present work the chemical formulas of the thermal decomposition products were determined from the X-ray powder patterns obtained by Schwartz et al.[12]

The alkaline peroxychromates (K_3CrO_8, Na_3CrO_8 and $(NH_4)_3CrO_8$) were prepared using the method of Riesenfeld.[13] In one case they were prepared in the presence of supporting material.

The Measurement of EPR Spectra. — The EPR measurements were performed with a superheterodyne-type spectrometer, constructed by the Applied Electric Laboratory Co., which operated in the K-band (24 kMc./s.) using two klystrons (24 VIO) and 45 Mc./s. as I. M. F. The first derivatives of resonance spectra were recorded on a chart, using modulation amplitudes from 2 to 50 oe. The peak-to-peak width and the position of the spectra were measured with a proton magnetic resonance recorded on the same chart and corrected by the spectra of DPPH.

The relative intensity of the spectra was determined by comparing it with a resonance absorption of a piece of synthetic ruby fixed in the cavity. The absolute number of unpaired electrons in the sample was estimated from a comparison of this standard resonance with that of DPPH.

Most of the measurements were made at room temperature and in open air. It has been recognized that the width of the resonance in the X-band was affected by the partial pressure of oxygen over the sample.[2] We could not observe this effect when the sample sealed off with nitrogen after the heat treatment was exposed to air. Samples were put into quartz tubes 3 mm. in o. d. directly after the treatment and measured.

Chemical Analysis. — The portion of the chromium which dissolved out into distilled water was determined with several samples. About 100 mg. of the sample was boiled in 50 cc. of distilled water for 10 min. and then filtered. The chromium in the filtrate was determined colorimetrically.

The total chromium content was measured after the heat treatment using flux agents to make them all water soluble. In the course of this analysis, it was recognized that potassium-sodium carbonate and potassium sulfate were sufficient as the flux in most cases, but the silica-alumina II indicated in Table I fixed chromium strongly and it became difficult to make all chromium water soluble with this flux. For these exceptional cases sodium peroxide was used as the flux.

The oxidation number was also determined in some cases. About 100 mg. of the sample was immersed in 60 cc. of distilled water; 10 cc. of 1 : 4 hydrochloric acid and 1 g. of potassium iodide were added, and then the mixtures were kept still for 1 hr., after which time iodometry was carried out.

Results

The γ-Absorption of Dispersed Samples. — *The Variation in γ-Line Shape with the Supporting Materials.*

— The general features of the spectra obtained in the experiment agree with the results given in the preceding reports. The factor which has the greatest effect on the spectral shape is the constitution of the supporting material. The spectra of chromium

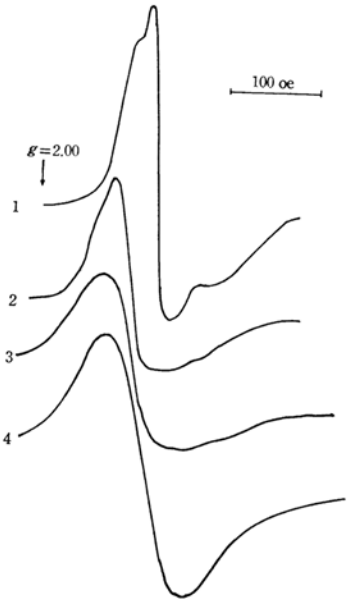

Fig. 2. Derivative of γ-absorption of chromium ions dispersed on different supporting materials (heat treated at 700°C for 4 hr.). Numbers indicate sample number in Table II.

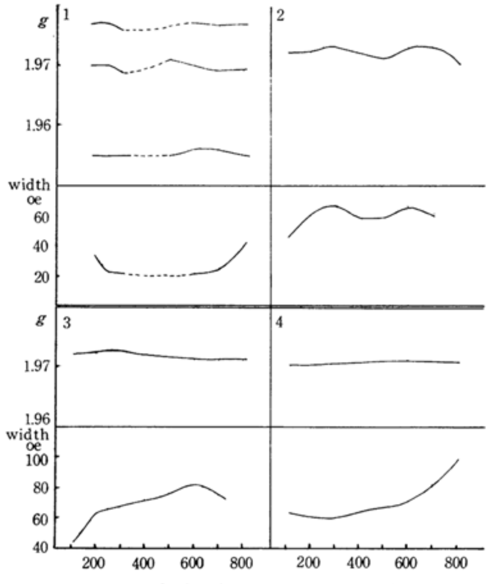

Fig. 3. The variation of g value and width of the γ-absorption with the heat treatment. Base 1: silica-gel, 2: silica/alumina 4/1, 3: silica/alumina 1/1, 4: gamma alumina

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[12] P. S. Schwartz, I. Fankuchen and R. Ward, *J. Am. Chem. Soc.*, **74**, 1676 (1952).

[13] E. H. Riesenfeld, H. E. Wohlars and W. A. Kutsch, *Ber.*, **38**, 1885 (1905).

ions on pure silica gel show typical asymmetric features; the three components of the g tensor are distinct (Fig. 2). The addition of alumina to the base material makes the separation of the peak indistinct, and only the difference between $g_{//}$ and $g_{\perp}$ can be recognized. When the content of alumina reaches 50 mol.%, it becomes more difficult to see the separated peaks and the apparent symmetry of the spectra increases. Chromium ions on gamma alumina are similar. When the measurement is performed at the temperature of liquid nitrogen, the intensity of the absorption increases but the line shape hardly changes at all.

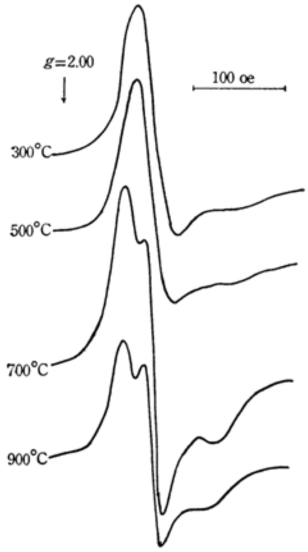

Fig. 4 (a). Variation of γ-absorption shape with heat treatment (Sample No. 5-2 in Table II).

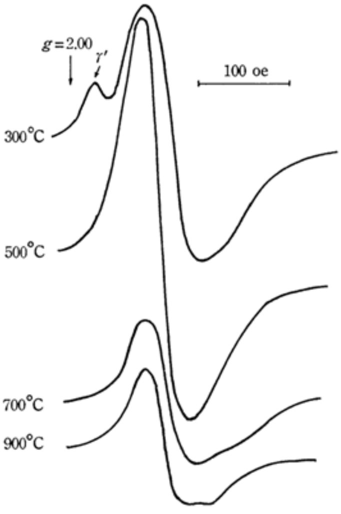

Fig. 4 (b). Variation of γ-absorption shape with heat treatment (Sample No. 5-1 in Table II).

The g values and the width of the γ-line vary slightly with the temperature of the heat treatment (Fig. 3). The chromium content in the sample also affects the line shape (Fig. 4). When commercial silica-alumina is used as the supporting material and when the chromium concentration is low, a new resonance appears at a lower magnetic field, between 250 and 300°C, of the heat treatment. This resonance, indicated in Fig. 4b as the γ'-line, does not appear in other cases; here we will only note its appearance.

The Variation in Intensity with Heat Treatment.—The intensity of the γ-line varies with the temperature of heat treatment and shows a maximum value between 400 and 700°C (Figs. 5 and 6). If one compares the relative intensities of the different samples, two main inclinations may be recognized: first, the increase in chromium content decreases the portion of chromium which contributes to the γ-absorption (Fig. 6), and second, the chromium dispersed on the supporting material which contains more alumina makes many more sites of γ-absorption, though it remains difficult to compare the relative intensities of samples with different supporting materials because of the differences in spectral shape.

As is shown in Fig. 5, the sample of pure silica gel does not show a sharp maximum of intensity during the heat treatment, but it

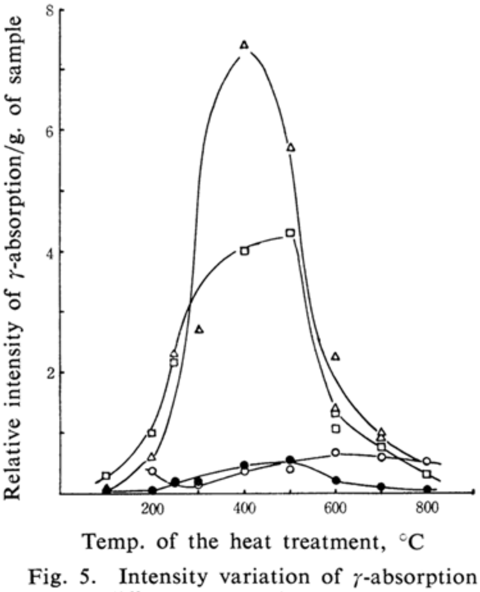

Fig. 5. Intensity variation of γ-absorption with different supporting materials.
○ 1: Base silica gel
● 2: Base silica/alumina 4/1
△ 3: Base silica/alumina 1/1
□ 4: Base gamma alumina

keeps the γ-line until a high temperature. On the contrary, the samples with gamma alumina and with silica-alumina II show sharp maxima at relatively low temperatures of heat treatment and then the intensities decrease rapidly.

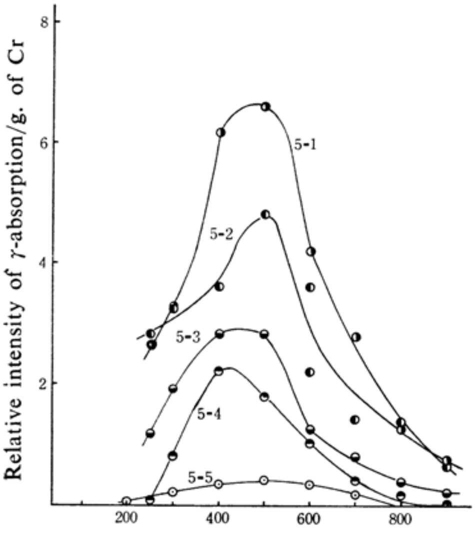

Fig. 6. Intensity variation of γ-absorption with the concentration of chromium (Base: commercial silica alumina).
5-1: Cr 0.65 wt.% 5-2: Cr 2.11 wt.%
5-3: Cr 3.0 wt.% 5-4: Cr 5.8 wt.%
5-5: Cr 16.7 wt.%
1 unit of relative intensity: ~10^{20} spins

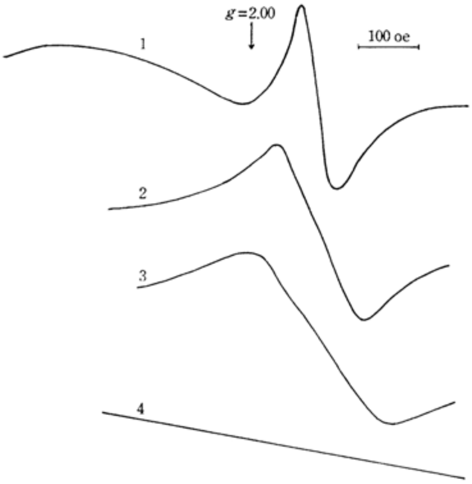

Fig. 7. EPR absorptions of the thermal decomposition products of chromium anhydride.
1: CrO_3 dispersed on silica-alumina and calcined at 500°C
2: The decomposition product of pure CrO_3 at 250°C
3: At 370°C
4: Above 500°C

As has been mentioned earlier, pure chromic anhydride turns to alpha chromia above 400°C in air. Figure 7 and Table III give the features and the variation in intensity of the thermal decomposition products of chromic anhydride. It should be noted that the dispersion on the base materials, especially on silica gel, delays the thermal rearrangement of chromia.

TABLE III. PRODUCTS OF THERMAL DECOMPOSITION OF CHROMIUM ANHYDRIDE

Temp. °C	Composition by X-rays	EPR at room temp.		
		g	Width msl oe.	rel. intensity
250	CrO_3, Cr_3O_8	1.97	140±5	1.0
290	Cr_3O_8	1.97	165±5	1.4
330	Cr_3O_8, Cr_2O_5	1.97	165±5	1.0
370	Cr_2O_5	1.97	220±5	0.6
430	Cr_2O_3	—	500	—
470	Cr_2O_3	—	1000	—

The Relation among Water-soluble Chromium, the Oxidation Number and the γ-Absorption. — The variation in the water-soluble part of chromium correlates with that in the EPR spectrum. Figure 8 indicates that the chromium on silica gel can be mostly soluble into water until a higher temperature of heat treatment than those on other materials. Silica-alumina II holds chromium so strongly that, as has been described before, it becomes difficult to

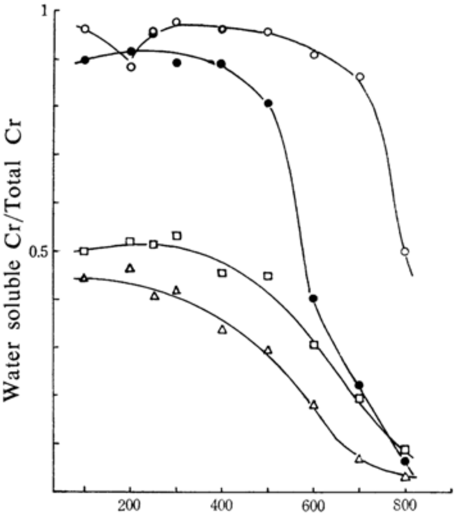

Fig. 8. Decrease of the content of water soluble chromium with heat treatment.
○ 1 Base silica gel
● 2 Base silica/alumina 4/1
△ 3 Base silica/alumina 1/1
□ 4 Base gamma alumina

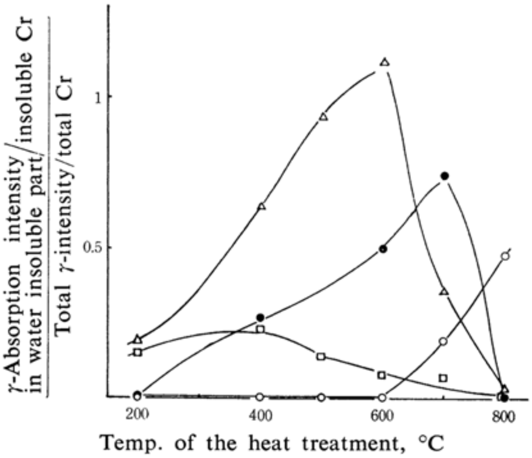

Fig. 9. γ-Absorption after dissolving out water soluble chromium.
○ 1: Base silica gel
● 2: Base silica/alumina 4/1
△ 3: Base silica/alumina 1/1
□ 4: Base gamma alumina

make the total chromium soluble using the flux which is effective in other cases.

In order to make it clear whether it is the water-soluble part of chromium or the insoluble part which contains the sites which give the γ-absorption, EPR measurements were also carried out of the residues of filtration in the analysis of water-soluble chromium. The results shown in Fig. 9 indicate that silica-alumina, particularly silica-alumina II, retains more sites of the resonance per chromium; i. e., the chromium ions which give the γ-line exist mainly in the water-insoluble part in these supporting materials. However, there remains some uncertainty whether the sites of the γ-absorption regenerate or disappear in the course of dissolving and drying.

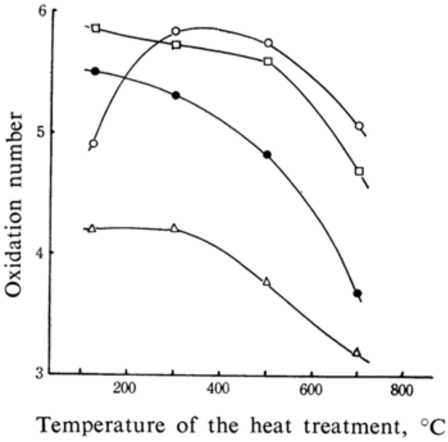

Fig. 10. Variation of the oxidation number with heat treatment.
○ 1: Base silica gel
● 2: Base silica/alumina 4/1
△ 3: Base silica/alumina 1/1
□ 4: Base gamma alumina

The variation in oxidation number is shown in Fig. 10. On the silica-alumina II, the oxidation number is already low in the original impregnated sample. It is noticiable that

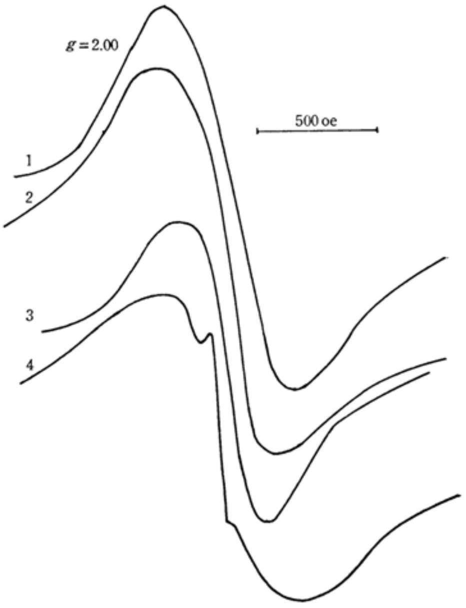

Fig. 11 (a). Derivative of EPR absorption of several chromium compounds.
1: Cr(OH)$_3$
2: Cr(OH)$_3$ on the silica gel
3: Cr$_2$(SO$_4$)$_3$ on the silica gel
4: (NH$_4$)$_3$CrO$_8$ (at room temp.)

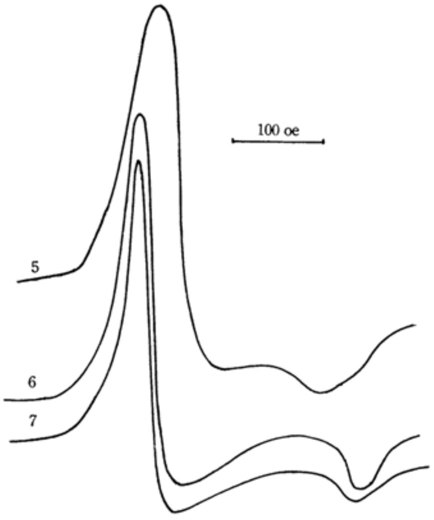

Fig. 11 (b). Derivative of EPR absorption of several chromium compounds.
5: Na$_3$CrO$_8$
6: K$_3$CrO$_8$ on the silica gel
7: K$_3$CrO$_8$ on the silica/alumina 1/1

gamma alumina gives rather a high oxidation number, though the water-soluble chromium is poorest on this material.

The EPR of Some Chromium Compounds. — For the purpose of comparison, EPR measurements were made of some chromium compounds. The results are shown in Fig. 11 and Table IV. Alkaline peroxychromates give absorptions similar to the γ-line. These materials are unstable at room temperature, and $(NH_4)_3CrO_8$ shows a spectrum which is similar to a superposition of the β-line and the γ-line. These peroxychromates contain Cr^{5+} ions; recently Swalen and Ibers[14] and McGarvey[15] discussed their electronic level scheme on the basis of the optical absorption and the EPR absorption. $Cr(OH)_3$ and $Cr_2(SO_4)_3$ dispersed on the supporting material give a resonance absorption like the β-line.

TABLE IV. EPR ABSORPTION OF SEVERAL CHROMIUM COMPOUNDS MEASURED AT ROOM TEMPERATURE

			g	Width, oe.
$Cr(OH)_3$	Powder		1.98	350
$Cr_2(SO_4)_3$	Dispersed on silica gel		1.97	170
$Ba_3(CrO_4)_2$	Polycrystal		undetectable	
K_3CrO_8	Dispersed on silica gel	$g_\perp$	1.983	(33.5)
		$g_{//}$	1.942	
Na_3CrO_8	Powder	$g_\perp$	1.978	
		$g_{//}$	1.949	

Discussion

An Analysis of the Line Shape. — Cossee and VanReijen[1] first pointed out that the chemical composition of the supporting material affected the line shape of the γ-line. We intend here to consider the differences in the dispersed state of chromium ions on different supporting materials, working through a consideration of the variation in EPR spectral shape.

As is shown in Fig. 2, chromium ions on silica gel give an asymmetrical γ-line in which three peaks in the first derivative can be distinguished. The addition of alumina makes the separation of peaks obscure. On gamma alumina the ions give an apparently symmetrical γ-line, and the apparent width increases.

The origin of the γ-absorption has been ascribed to Cr^{5+} ions, as has been cited. Indeed, alkaline peroxychromates containing Cr^{5+} ions give a quite similar absorption line (Fig. 11). Garif'yanov,[16] however, using borosilica glass, observed a similar absorption which might contain dispersed Cr^{5+} ions. The g values of these lines agree well with each other.

The shoulder of the absorption in the low magnetic field in the case of silica gel had not previously been recognized. We think that the variation in the line shape, this shoulder, depends mainly on the g anisotropy and the line width: the three principal values of g tensor can be observed with Cr^{5+} ions on silica gel, but the increase in the content of alumina in the supporting material makes it obscure and increases the apparent symmetry as a results of the increase in the width or the variation in g anisotropy.

First, we will consider the variation in the line shape from this point of view, using a simple approximation. There have been several works[17-19] about the line shape, which must be given an assembly of crystallites randomly oriented but with a g anisotropy. These works have used a δ-function approximation or a Lorentzian line shape for the absorption of each crystallite. Here we employ the method of Kneubühl.[18] The assumptions in this calculation are as follows:

(a) Each chromium ion has an anisotropy of the g tensor;

(b) The resonance absorption line of each crystallite is Lorentzian;

(c) The width is constant and independent of the orientation of the orientation of the crystallites;

(d) The orientations of the crystallites are at random;

(e) The spin Hamiltonian consists of the Zeeman, dipolar and exchange terms only.

The results of the calculation are shown in Fig. 12, where the parameter, b, is the half-width at the half-power of absorption which must be given by each individual crystallite. It must be noted that, as the three principal values of g tensor, the values observed in the silica gel sample, which was heat-treated at 700°C, are used. Figure 13 shows how the half-width, maximum slope width and asymmetry, expressed by (half-width of low field side)/(half-width of high field side), change with b.

Figure 12 shows that the three components of the g tensor are distinct until b becomes 15 oe. When b is over 20 oe., the existence of g anisotropy can be recognized only from the asymmetric figures. From Fig. 12, it can also be seen that the position of the maximum of

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[14] J. D. Swalen and J. A. Ibers, *J. Chem. Phys.*, **37**, 17 (1962).

[15] B. R. McGarvey, ibid., **37**, 2001 (1962).

[16] N. S. Garif'yanov, *Solid State Phys. (SSSR)*, **4**, 2450 (1962).

[17] J. A. Ibers and J. D. Swalen, *Phys. Rev.*, **127**, 1914 (1962).

[18] F. K. Kneubühl, *J. Chem. Phys.*, **33**, 1074 (1960).

[19] R. H. Sands, *Phys. Rev.*, **99**, 1222 (1955).

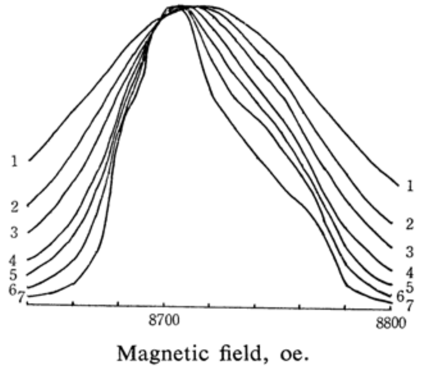

Fig. 12. Calculated absorption line shape. The maximum values of the curves are set at unity.
The half-width at half power of each crystallite, b, is taken as a parameter.
1 : $b=60$ oe. 2 : $b=40$ oe. 3 : $b=30$ oe.
4 : $b=20$ oe. 5 : $b=15$ oe. 6 : $b=10$ oe.
7 : $b=5$ oe.

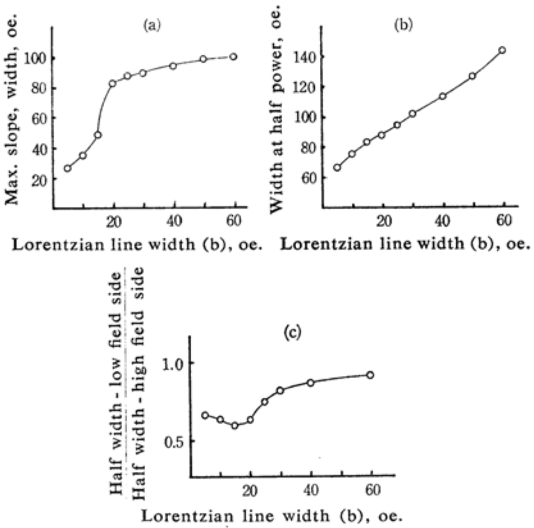

Fig. 13. Variation of line width and asymmetry as a function of Lorentzian line width, b (from the calculated curves in Fig. 12).

the absorption line goes up to a higher magnetic field with the increase in b. This inclination contradicts the experimental results shown in Fig. 3. If samples with the same supporting material are compared, the apparent g value slightly decreases or is constant when the temperature of the heat treatment rises and the apparent width of the maximum slope increases. However, if samples with different supporting materials are compared, it is noticed that gamma alumina gives lines with somewhat larger apparent g values than the g_2 values of those with silica gel. In the above calculations the definite g components given in the silica gel sample are used, but it is doubtful that the principal values of the g tensor remain constant among the different supporting materials. It is rather more probable that g anisotropy decreases with the increase in the alumina content of the supporting materials.

Keeping this precaution in mind, we will try a rough comparison of the observed results shown in Fig. 3 with those of Fig. 13. The γ-line of samples with silica gel gives spectra which show the three components of g distinctly and which have a maximum slope width of 30 oe. This corresponds to the calculated curves with $b < 10$ oe. The samples with silica/alumina 4 : 1 give γ-lines with maximum slope widths of 40—60 oe., indicating a still considerable asymmetry; they corresponds to the calculated curves with $b=15$—20 oe. Silica-alumina II produces samples which give γ-lines corresponding to those of $b=20$ oe. When gamma alumina is used as the supporting material, the width is about 60 oe. when the temperature of the heat treatment is low, but if the temperature of the heat treatment is over 700°C, the width increases up to about 100 oe.; this corresponds to the curves calculated with $b=50$—60 oe.

The Dispersed State of Chromium Ions on the Different Supporting Materials. — As has been described, three kinds of absorption, δ, β and γ, are observed with chromia dispersed on silica-alumina; the δ-absorption has been attributed to Cr^{3+} ions well dispersed and isolated. Howard[11] indicated that this δ-absorption was not observed with chromia dispersed on silica gel. This means that there are few isolated chromia on silica gel. On the other hand, the decrease in γ-absorption and the increase in β-absorption occur with the same inclination during heat treatment, though the quantitative correspondence does not exist. This indicates that the sites of both absorptions may be in the same region on the sample. Eischens and Selwood[20] concluded from their susceptibility measurements that chromic anhydride dispersed on gamma alumina is deposited mainly three oxide layers thick.

The chromia dispersed on silica gel is almost entirely water-soluble, and the solubility is not affected by the heat treatment of a higher temperature. On the contrary, gamma alumina and silica-alumina II make insoluble chromium which increases remarkably in amount with the heat treatment. As is well known, alumina easily makes a solid solution with chromia; also, alumina crystallizes from hydroxide at about 500°C. On the other hand, the

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[20] R. P. Eischens and P. W. Selwood, *J. Am. Chem. Soc.*, **69**, 1590, 2698 (1947).

silica gel used in the present experiment does not produce a solid solution with chromia, at least below 1000°C, and it does not crystallize before 1000°C, according to the X-ray diffraction analysis. Chromic anhydride changes into alpha chromia at about 400°C, as has been mentioned before.

From these facts it may be considered that on silica gel chromia exists mainly in the form of clusters, probably several atomic layers thick. If 5 wt.% of chromium are dispersed homogeneously on the material with a surface area of 500 m^2/g., the distance between chromium atoms becomes about 10 Å. This means that, though the dispersed chromia exists in the form of clusters, their thickness may be rather thin if the affinity of chromia to the supporting material does not greatly differ from the affinity between them.

On gamma alumina and on silica-alumina II, the isolated dispersion of chromium occurs simultaneously and the interaction between the base materials and chromium is stronger. It is not clear at present whether Cr^{5+} ions isolate from other chromium ions, but at least the variation in the γ-line shape with the variation in supporting materials indicates that the base materials can influence the electronic condition of chromium ions. Dereń et al.(21) reported that chromia gel also gave a variation of the water-soluble part under heat treatment similar to the present results obtained by dispersed chromia. However, in their experiment pure chromia gel showed a maximum value of water-soluble chromia at a lower temperature of heat treatment. One can consider pure chromia gel to be chromia dispersed on chromia.

As is shown in Figs. 5 and 6, the concentration of Cr^{5+} ions in the samples is at most several percent of the total chromium content, and in the case of silica gel this concentration is particularly low. From this fact, it is natural to consider that Cr^{5+} ions are separated from each other. If chromia exists almost entirely in the form of small clusters on the silica gel, the mean distance among Cr^{5+} ions becomes small and their coordination is decided principally by the superficial condition of chromia. As is well known, gamma alumina has a spinel-like structure and it contains many lattice defects of a symmetrical coordination. If these defects take part in the fixation of chromium ions or if chromium ions replace aluminum ions because of compatibility between their oxides, they bring about a more stable fixation of the chromium and give them a more symmetrical crystal field. This will cause a reduction of the g anisotropy. If the coordination becomes perfectly octahedral or tetrahedral, it is difficult to observe the EPR absorption at room temperature, as will be described below.

A Further Consideration of the Line Width.—The apparent width of γ-lines obtained in the present work by using the K-band wave is somewhat larger than those in the X-band reported by others. O'Reilly also pointed out this fact(3) in the case of gamma alumina. It shows that one of the causes of the line width is probably g anisotropy.

At the same time another cause of the increase in line width must be considered: spin-lattice relaxation. Many investigations have been made of the electronic structure of the ion which has a $3d^1$ electron in various crystal fields. When the symmetry of the field is high, the first excited level is so close to the ground level that it is generally impossible to observe the EPR absorption at room temperature. Concerning the Cr^{5+} ion, Carrington et al.(22) and Van Reijen et al.(23) showed that EPR observation of $(CrO_4)^{3-}$ and $Ba_3(CrO_4)_2$ respectively was not possible at room temperature. However, when Cr^{5+} ions are placed in a field of tetrahedrally-distorted octahedron, as in the case of $(NH_4)_2CrCl_5$,(23) or in a field of dodecahedron, as in the cases of the above-mentioned alkaline peroxychromates, a narrow absorption can be observed, even at room temperature.

In the peroxychromates, Cr^{5+} ions are situated in a field with an axial symmetry: $g_1=g_2$. Swalen and Ibers,(17) using 25 oe. as the half width, b, showed that the observed line agrees with the calculated curve. As compared with the value of b which was estimated in the preceding section for the samples dispersed on silica gel, this value is fairly large. It may arise from the dipole interaction. Indeed, McGarvey(15) indicated that the dilution of peroxychromate with peroxyniobate markedly reduced the apparent line width. In connection with this width, it is necessary to consider the possibility of motional narrowing in the dispersed samples.

At present it is impossible to evaluate the relative contribution of these effects to the line width. It will be useful to examine the variation in optical absorption, electrical conductivity, etc. in these materials.

Concerning the variation in γ-line with dissolution, some uncertainty remains, as has been mentioned before. There have been

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21) J. Dereń, J. Haber, A. Podgórecka and J. Burzyk, *J. Cat.*, **2**, 161 (1963).

22) A. Carrington, D. J. E. Ingram, D. Scholand and M. C. R. Symons, *J. Chem. Soc.*, **1956**, 4710; **1957**, 203, 659.

23) L. L. Van Reijen, P. Cossee and H. J. VanHaren, *J. Chem. Phys.*, **38**, 572 (1963).

attempts to distinguish Cr^{5+} from Cr^{6+} by using the difference between them in the solubility in water, but when the base material changes, this method can not be applied, even for relative measurements. We will discuss the variation in γ-absorption sites under several chemical treatments in our next paper.

Summary

Chromic anhydride has been dispersed on several supporting materials of silica-alumina of different compositions, and the so-called γ-line in the EPR of these samples has been observed. When the temperature of heat treatment rises, the intensity of this absorption becomes strong, but after reaching a maximum value it decreases again. The chemical composition of the base materials remarkably influences the behavior of the absorption. The variations in water soluble chromium and oxidation number show corresponding results. However, γ-absorption sites may be distributed in the water-insoluble part of chromium as well as in the water-soluble part. The ratio between them depends on the base materials.

Under the assumption of g anisotropy, the observed absorption lines have been compared with the calculated curves and the half-width at the half power of the absorption with the crystallite in these samples. From these results and from the differences in behavior, the states of chromium ions in various samples have been compared. By comparing the present results with those of other investigators, it has been concluded that, on pure silica gel, chromia is dispersed mainly in the form of thin-layer clusters and that this dispersion gives the characteristic of this matter. On the contrary, an alumina-rich base produces a more dispersive state of chromium and the fixation of chromium rapidly becomes stronger with the heat treatment. The influence of the supporting material on dispersed chromium becomes great and the characteristics are affected by this fact. These differences may be caused principally by the differences among these materials in thermal stability and in the compatibility with chromia.

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