

## Kinetics and ESR Studies of Ethylene Polymerization on Chromia-Silica Catalysts

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A study has been made of the kinetics of the polymerization of ethylene on chromia-silica catalysts. ESR spectra of the catalysts were also measured before and during the process of polymerization. A mechanism for the reaction in terms of the crystal field of Cr(V) is proposed.

The polymerization of ethylene to produce polyethylene can be carried out by two major processes, the Ziegler-Natta process, using primarily titanium tetrachloride and triethylaluminum at 10 atm of ethylene, and by the Phillips process, using supported chromium oxide catalyst and low ethylene pressure. We are concerned in this investigation with the elucidation of the mechanism of the latter process and particularly with the determination of both the valence and coordination state of the chromium responsible for the catalytic activity.

An investigation of the catalytic characteristics of this system has been the subject of a number of communications (1-3). The salient features reported are that the reaction takes place at subatmospheric pressures of ethylene and at temperatures as low as  $-40^{\circ}\text{C}$ . The catalyst is prepared by soaking chromic acid on silica (and on other supports). This material is partially reduced either by evacuation at  $600^{\circ}\text{C}$  or by careful treatment at less-elevated temperatures with hydrogen, carbon monoxide, or ethylene. The reaction kinetics have been reported as those of zero order by Ayscough *et al.* (3) and first order by Clark *et al.* (2).

ESR measurements have been used in an

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attempt to determine the nature of the "active" chromium center. The ESR characteristics of chromium are complex. The chromium can exist either on the surface or in the bulk of the support, but can also have valence states of II, III, IV, V, VI, each of which can be subject to crystal fields of square planar, cubic, or octahedral symmetry, which in turn can be distorted by crystal fields of lower symmetry. Interactions of chromium atoms with themselves may give rise to exchange effects which may result in ferromagnetism or in antiferromagnetism. The literature on this subject is extensive (4-8).

For the purpose of this paper it is sufficient to note that a correlation has been proposed by one of us (VBK) between the catalytic activity and the ESR signal at  $g = 1.97$  identified with Cr(V) measured *before* the polymerization reaction (9). Another correlation has been recently proposed between catalytic activity and the increase in the signal at  $g = 1.97$  *after* an active catalyst had been treated with water vapor and its activity thereby poisoned (3).

However, the correlation between the activity of the catalyst and the ESR signal intensity at  $g = 1.97$  *during* the reaction is poor. One of the authors (VBK) has previously reported that the ESR signal declines appreciably during the polymerization process while the activity appears to be sustained

(9). Recently Ayscough, Eden, and Steiner reported that "the reduction of the catalyst and the chemisorption of ethylene appreciably influence the ESR signal, thus complicating the relation between activity and signal strength"(3).

It was therefore decided to investigate more thoroughly the relation between the catalytic activity and the details of the ESR signal at  $g = 1.97$  during the preparation, catalytic reaction, and after poisoning with water and oxygen. Particular attention was paid to the *form* of the ESR as a clue to the nature of the crystal field surrounding the active chromium center.

#### EXPERIMENTAL PROCEDURE

The kinetics of polymerization of ethylene was studied in a conventional static system which could be evacuated to  $10^{-5}$  mm Hg. All stopcocks, however, were metallic (Veeco Co., Plainview, N. Y.) and did not require stopcock grease. The latter was reported to have an influence on the rate of polymerization (3, 9).

The reaction was carried out in a 400-ml spherical vessel with a glass or quartz appendix containing the catalyst and a metal Bourdon gauge for measuring the pressure. The final value of the extent of polymerization was checked by measuring the increase in weight of the catalyst. The polymerization rate is expressed in terms of milligrams of polymer formed per minute per gram of catalyst. The reaction vessel together with its metallic valve and Bourdon gauge could be cut off from the gas handling system and introduced into the ESR apparatus since the appendix containing the catalyst was of suitable diameter for insertion into the microwave cavity. Inasmuch as the reaction was highly exothermic, the glass appendix containing the catalyst was kept in a bath in order to dissipate the heat evolved.

The ESR measurements were carried out at three frequencies: 35 kGc/sec (Varian V4561), 9 kGc/sec (Varian V4500), and at  $-300$  Mc/sec (Alpha ESR spectrometer A-340). Standard procedures of ESR measurements were followed and measurements were made at temperatures from that of liquid air to  $200^{\circ}\text{C}$ . At room temperature it

was possible to carry out at the same time both kinetic and EPR measurements.

#### MATERIALS

The Phillips Research Grade ethylene was 99.98% ethylene. The impurities were 0.01% methane and 0.01% ethane. Oxygen and water were present in less than the 20 parts per million.

The catalyst was prepared by impregnating with chromic acid Davison Silica Gel Grade 70 catalyst. The surface was 340  $\text{m}^2/\text{g}$ . The pore volume was 1.16  $\text{ml}/\text{g}$  while the diameter of the pores was 140 Å. The impurities were 0.01%  $\text{Fe}_2\text{O}_3$ , 0.06%  $\text{Na}_2\text{O}$ , 0.007%  $\text{C}_2\text{O}$ , 0.02%  $\text{TiO}_2$ , and 0.03%  $\text{ZnO}_2$ .

The amount of the chromic acid solution used for the impregnation was just sufficient to be absorbed by the silica gel and the content of the chromium on the catalyst was controlled by the amount of chromium in the solution. After impregnation, the catalyst was dried in an oven overnight at  $120^{\circ}\text{C}$ , transferred to a reactor, and evacuated at  $450^{\circ}\text{C}$  from 4 to 10 hr. The catalyst was then used for polymerization studies. The amount of catalyst used was 0.200 g.

The effect of poisons was studied both before and during the course of reaction. In the first case the poison was introduced into the catalyst chamber for a definite period of time and then the reaction vessel was evacuated. The ethylene was then introduced and the polymerization rate studied. In the second case the reaction was allowed to proceed for a short time in order to avoid excessive formation of polymer on the surface of the catalyst. The ethylene in the gas phase was then pumped off, the poison introduced, the ethylene was then reintroduced, and the measurement of the reaction rate was resumed.

#### KINETIC STUDIES

The catalyst had a high activity, facilitating the polymerization of ethylene at  $-20^{\circ}\text{C}$ . The kinetic behavior is shown in Fig. 1. A rapid reaction took place immediately after introduction of ethylene. A considerable amount of heat was evolved, particularly if the reaction was studied above

room temperature. If proper precautions of using a sufficiently low temperature were not taken the temperature of the catalyst would increase by  $50^\circ$ . Temperature was measured by a thermocouple attached to the reaction vessel. After a short time the reaction proceeded at a constant rate, particularly in the range of polymer product of 0.1 to 0.6 g polymer catalyst. It slowed down when amounts of polymer larger than 0.6

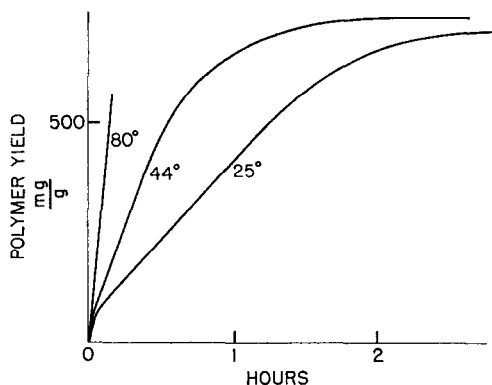


Fig. 1. Polymer yield at various temperatures (schematic).

g polymer/g catalyst were produced. This was undoubtedly caused by the blocking of the surface of the catalyst by a film of polyethylene produced by the reaction. If the degassing of the catalyst at high temperature was inadequate, an induction period of 10-15 min was observed. A shorter induction period was also observed during experiments carried out at  $100\text{--}150^\circ\text{C}$ .

The pressure dependence of the reaction rate gave 0.60 to 0.65 for the value of the reaction order in the pressure range from 40 to 760 mm.

The temperature dependence (Fig. 2) of the reaction rate showed that at temperatures below  $50^\circ\text{C}$  the Arrhenius equation was valid. The activation energy is calculated at 8 kcal/mole. The Arrhenius plot shows deviation from linearity above  $50^\circ\text{C}$ , a maximum at  $100^\circ\text{C}$ , and a linear portion with a negative slope up to  $200^\circ\text{C}$ , the highest temperature used. At  $250^\circ\text{C}$  no reaction took place in spite of rapid chemisorption of ethylene during the first few seconds after introduction of the gas into the catalyst

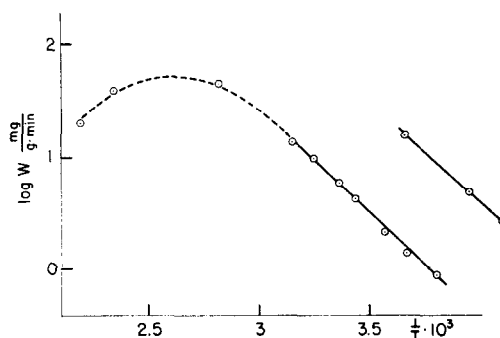


Fig. 2. Temperature dependence of the polymerization process. Dotted line represents temperature range in which catalyst became deactivated because of excess heat of reaction. Line on right represents results obtained by more active form of catalyst.

chamber. At high temperatures, the temperature control of the catalyst was difficult because of the excessive heat evolution during the course of the reaction. Consequently precise quantitative interpretation cannot be given of the rate above  $50^\circ\text{C}$ . However, the reaction rate does go through a maximum in the neighborhood of  $100^\circ\text{C}$  and does drop to zero at  $250^\circ\text{C}$ .

The dependence of the reaction velocity on chromium content of the catalyst showed that the activity of the catalyst reaches a constant value at 2-3% total chromium (Fig. 3). This result is consistent with previously reported data which indicated that there was a maximum in catalytic activity at 3-4% chromium (9).

Pretreatment of the catalyst at  $150^\circ\text{C}$  with 30 mm of ethylene (an amount cor-

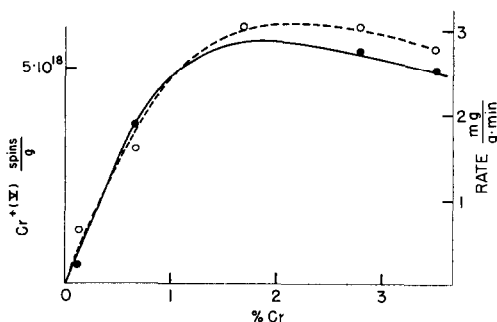


Fig. 3. Dependence of rate of polymerization (full line) and Cr(V) spin concentration (dotted line) on total chromium content.

responding to 10 moles of ethylene per gram of chromium) for 30 min caused a 10–20-fold increase in the catalytic activity at 0°C. Neither the order of the reaction nor its activation energy was changed by the treatment. However, if the pretreatment temperature with ethylene was 250°C, the catalyst was completely deactivated. These findings are similar to those reported by Clark, Finch, and Asche (2).

Oxygen and water are poisons for the polymerization process. The following yields of polymer from 700 mm of ethylene on a 0.7% chromium catalyst illustrate the poisoning effect. Under the conditions of optimum purity of the ethylene, a yield of 5 mg/g catalyst per minute was obtained at 20°C, 60–70 mg at 100°C, and 25 mg at 150°C. If the catalyst was kept for 30 min at 20°C in 20 mm of oxygen and then the catalyst was pumped off for 5 min at room temperature, the rate was zero at 20°C, and was 70 mg/g min at 100°C. This was taken to indicate slight poisoning at room temperature. If the oxygen was introduced during polymerization, the poisoning effect was more pronounced. This addition of only 0.1 mm Hg of O<sub>2</sub> to ethylene (corresponding to 0.01%) dropped the reaction rate to zero at 20°C and to 55 mg/g min at 100°C. A higher concentration of oxygen in ethylene of 1 mm Hg (corresponding to 0.1% ethylene concentration) reduced the rate to zero at 20° and at 100°C and 10 mg/g min at 150°C.

The poisoning effect of water seems to be different; it is more marked if the catalyst is treated with water before the introduction of ethylene than during reaction. Thus, if as little as 0.1 mm Hg of water vapor was introduced into the reactor before the ethylene, the rate of polymerization dropped to zero at 20°C and to 10 mg/g min at 150°C. If the same amount of water was added to the ethylene during the reaction, the poisoning effect was hardly noticeable, the rate being 3 mg/g min at 20° and 30 mg/g min at 150°C. However, if the contamination of the ethylene by water was higher, it acted as a strong poison. For instance, the addition of 1 mm Hg of water to the ethylene (0.1%) decreased the rate to zero at 20° and at 150°C.

#### ELECTRON SPIN RESONANCE STUDIES

The ESR spectra of a silica catalyst containing 0.7% chromium heated in a vacuum at 450°C and measured at room temperature at 35 kMc/sec ( $\lambda = 8$  mm), 9 kMc/sec ( $\lambda = 3$  cm), and 300 Mc/sec ( $\lambda = 1$  m) are shown in Fig. 4. The signal obtained at 9 kMc/sec had the same characteristics as observed by previous investigators.

The line was asymmetric. The  $\Delta H$  between the first maximum and the second minimum was 125 gauss. The  $g_{\perp}$  was equal to 1.978 and  $g_{\parallel}$  to 1.910 giving a  $g_{av} = \frac{1}{3}(2g_{\perp} + g_{\parallel})$  of 1.955. The observed width of the line near  $g_{\parallel}$  was 25 gauss. Measurements carried out at 35 kMc/sec also gave an asymmetric

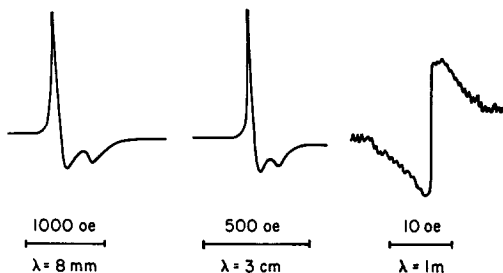


Fig. 4. Variation of the form of ESR signal with frequency of measurement.

line with a  $\Delta H$  between first maximum and second minimum of 495 gauss. The  $g_{\perp}$  has the value of 1.978 and  $g_{\parallel}$  of 1.916 gave a  $g_{av}$  of 1.957. The equality of  $g_{\perp}$  and  $g_{\parallel}$  at the two frequencies indicates that we are dealing with a true asymmetry and not a broadening due to a superposition of a number of ESR lines with slightly different values.

The ESR signal at 300 Mc/sec had a different form from that at higher frequencies. Although the noise level was quite high, a slight asymmetry in the signal could be noticed. The  $g_{av}$  value was again 1.95. The constancy of the  $g_{av}$  value over a hundredfold range of frequency indicates that the  $D$  term in the Hamiltonian expression is zero. The marked decrease in asymmetry and the narrowing of the line to 5 gauss at the lower frequency of 300 Mc/sec indicates that the width of 25 gauss observed at 9 kMc/sec is due to the inhomogeneous

broadening of a set of lines each of which must have a true width of less than 5 gauss.

The intensity of the line increases with chromium content, reaching what appears to be a constant value at 2% total chromium. One of us (VBK) has previously reported (9) that this ESR signal corresponded to  $5 \times 10^{18}$  spin and this constituted a small fraction of the chromium present in the catalyst. The correlation between the catalytic activity for ethylene polymerization and this ESR signal before reaction should be noted (Fig. 3). Similar correlation had been reported for a larger range of chromium concentration by one of us (VBK) (9). The form of the line measured at high frequency did not change with chromium content.

The ESR line at  $g = 1.97$  is more narrow if the measurements are performed at liquid nitrogen temperature. The  $g_{\perp}$  and  $g_{\parallel}$  values remain the same, indicating that individual lines which contribute to the asymmetry of observed lines sharpen with decrease in temperature.

The reversible broadening of the ESR on introduction of oxygen previously reported by one of us (VBK) (7) was confirmed. The effect of water vapor on the signal was studied in detail. Introduction of water vapor at room temperature produces an immediate increase in its amplitude due to the narrowing of the width of the signal (lowering of the anisotropy of the  $g$  tensor). This has been previously reported (12). This change was studied as a function of the amount of water adsorbed (Fig. 5). The marked increase in the signal with and without water is indicated in comparing 5(a) and 5(d), keeping in mind that the signal in 5(a) has been measured with a fourfold increase in sensitivity. The decrease in anisotropy previously reported is also evident in this comparison. The  $g_{\parallel}$  increases from 1.910 to 1.95. We were also able to observe a change in  $g_{\perp}$  from 1.980 to 1.975, which is clearly evident in Fig. 5(b) and 5(c), where one sees the two signals superimposed on each other with intensities determined by the amount of water introduced. We are therefore dealing with two distinct species of Cr(V). Since the total intensity of the signal remains unchanged and only the line shape

and positions of the  $g_{\parallel}$  and  $g_{\perp}$  change, we ascribe this change as due to a change in the crystal field acting on the Cr(V) with the incorporation of water or hydroxyl into the inner coordination sphere of the chromium central ion. A quantitative evaluation of the effect of water vapor on the ESR signal appears when the number of water molecules

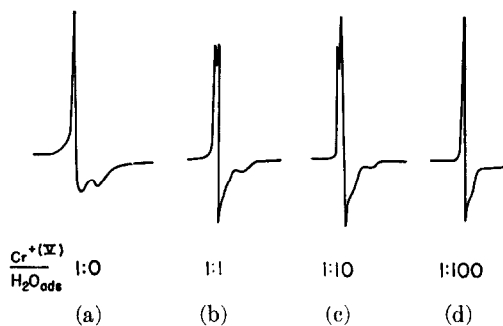


Fig. 5. Effect of water on the form of the Cr(V) signal.

introduced was equal to the number of Cr(V) species; one-third of the latter changed their state as seen in the ESR spectrum. When the number of water molecules is ten times the Cr(V), then about two-thirds of the latter changes their states. This shows the strong adsorptive power of the Cr(V) since it must compete with a large surface of silica gel for the water present in the system.

During the course of polymerization at room temperatures and lower temperatures than room temperature, the intensity of the signal does not change. However, the following small change in its form is observed. The amplitude of the signal increases slightly at the expense of the increase in the minimum. This small change in the form of the lines just noticeable at room temperature becomes more marked if the reaction is carried out at higher temperatures. This change was observed both at 50° and 100°C (Fig. 6). The signal before reaction has a double minimum [Fig. 6(a)], 2 min after the reaction the one minimum increases and the other flattens out, and after 5 min, a single asymmetric line is observed. This line is more narrow with  $\Delta H$  of 25 oersteds. The  $g$  factor of 1.97 is the same as that observed for catalysts treated with water vapor, alcohol, or aldehyde. The integrated intensity of this line is

five times less than before the reaction. Catalysts containing a high chromium content produce in addition to this narrow signal, a signal at 1600 gauss and a broad signal at 3200 gauss ( $g = 2$ ). The same effect, namely, the conversion of one line into another, was also observed after treatment of the catalyst with ethylene at 150°C. It should be recalled that such a treatment enhances the catalytic activity by an order of magnitude at room temperature.

Treatment of the catalyst with ethylene at 150°C enhanced the activity of the catalyst by an order of magnitude at room temperature and decreased the intensity of the line at  $g = 1.97$  very markedly.



FIG. 6. The change of the shape of the ESR signal of Cr(V) during course of ethylene polymerization.

The action of water and ethylene on the course of the ethylene polymerization was followed by ESR measurements. In order to avoid blocking of the surface by the polymer produced in the reaction, the inhibitor was introduced into the reaction at early stages of the polymerization process. At a definite time the reaction was interrupted by pumping out the ethylene, the inhibitor was introduced, and a new portion of ethylene was added. The results obtained in the inhibition of the reaction by oxygen at room temperature for a catalyst heated in vacuum at 400°C are shown in Fig. 7. After adding 0.1% oxygen to the system the polymerization reaction became zero. The ESR spectra after the reaction showed a weak line (whose parameters and form corresponded to the spectrum of a catalyst with adsorbed water) riding on top of the original Cr(V) line. If the oxygen was introduced to a catalyst that had been previously activated ethylene at 150°C, the signal intensity in-

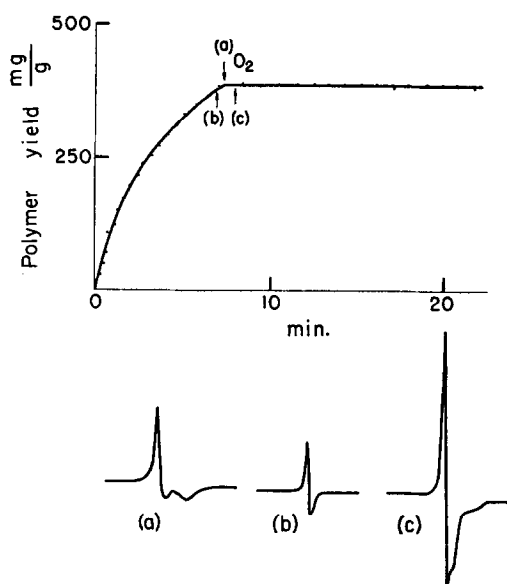


FIG. 7. The effect of oxygen on the rate of polymerization and on the ESR signal of Cr(V).

creased approximately five times and becomes comparable in intensity to the signal obtained before the reaction was carried out.

The action of water after the reaction does not change the signal intensity was reported by Ayscough, Eden, and Steiner (3), although the experiment was repeated a number of times at various depths of the polymerization.

#### DISCUSSION OF THE RESULTS

A comparison of the velocities at low depths of polymerization reaction observed in this investigation with those obtained by previous workers shows that the pretreatment of the catalyst in a vacuum leads to higher activity than activation of a catalyst in air. We were able to obtain a polymerization reaction at  $-20^{\circ}\text{C}$  while other workers found that their catalysts were active at  $+15^{\circ}\text{C}$ .

A comparison of the absolute activities of our catalysts with those used by Ayscough, Eden, and Steiner (3), who used essentially the same experimental method, shows that our catalysts were two orders of magnitude more active. Our results are in agreement with the findings of Habeshaw and Hill (10),

who reported an increase in the polymerization of ethylene on catalysts treated with oxygen and evacuated at high temperature.

The kinetic behavior of ethylene polymerization can be explained in the following way: In the initial stages the reaction takes place with the polymer very rapidly filling the pores of the catalyst and gradually blocking the active centers. Due to this the velocity of the reaction drops and diffusion of the ethylene becomes the rate-determining process. The reaction rate becomes constant. Finally, the polymer formed completely covers the surface of the catalyst and the reaction velocity drops to zero. Ayscough, Eden, and Steiner (3), using a less active catalyst, found a first order reaction with an activation energy of 14 kcal/g mole. Our kinetics are in agreement with these results since our order is 0.6 and the activation energy 8 kcal/g mole, indicating that we were working under conditions of diffusion-controlled kinetics.

As stated in the introduction, a good correlation has been found between catalytic activity and the signal at  $g = 1.97$  before the reaction and with the signal produced by poisoning the catalyst with water after the reaction.

One of us (VBK) has previously reported a decrease in signal intensity during the course of the catalytic reaction.

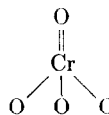
Recently Ayscough *et al.* have reported a lack of correlation between the signal strength at  $g = 1.97$  and the catalyst right after the reaction. In this paper we are reporting the virtual disappearance of the signal at  $g = 1.97$  on treatment of the catalyst with ethylene at 100°C. At the same time the catalyst activity rises by an order of magnitude. A crucial question arises: What exactly is the state of the Cr atom at the active catalytic site?

The signal observed at  $g = 1.97$  must be due to a precursor of the active site. Its disappearance is due either to a change in the valence of Cr(V) or to a change in the nature of the crystal field surrounding Cr(V). In this paper the experimental data is interpreted in terms of the change of coordination of the ligands rather than as due to a change in the valence of Cr(V). The latter approach

is being pursued at present by one of us (JT) at Princeton.

There seems to be no doubt that the ESR signal observed at  $g = 1.97$  is due to Cr(V). The lack of frequency dependence of the  $g$  value indicates that the species responsible for the ESR signal has no  $D$  term in its spin Hamiltonian and the pentavalent chromium is the only chromium species that lacks such a  $D$  term.

The asymmetric form of the ESR signal of the Cr(V) and the change of this form with frequency indicate an anisotropy of the  $g$  factor. In other words, the Cr(V) is located in a crystalline field whose symmetry is lower than octahedral or tetrahedral. It must be assumed therefore that when the Cr(V) replaces silicon in the oxygen tetrahedra of the silica gel, the ligands surrounding the Cr(V) have a symmetry of a distorted tetrahedron such as



A more precise determination of the nature of the molecular configuration of the Cr(V) must await preparation of chromium silica catalysts which are more suitable for ESR measurement. In the distorted tetrahedron (Fig. 8) the low lying doublet is split by the axial field to give an asymmetric signal with

$$g_{\perp} = 2 - (2\lambda/\Delta)$$

$$g_{\parallel} = 2 - (8\lambda/\Delta)$$

If we take  $\lambda = 220 \text{ cm}^{-1}$  and  $\Delta = 2 \times 10^4 \text{ cm}^{-1}$  (8) as values appropriate for Cr(V), we obtain 1.980 and 1.94, in good agreement with the experimentally observed values of 1.978 and 1.910. An octahedral configuration would involve six equivalent oxygens and would therefore be symmetric and consequently would not give a signal. Kinetic studies indicate that the distorted tetrahedron Cr(V) is the precursor of the active catalyst site. On mild reduction either by evacuation at high temperature or reduction under mild conditions, a small fraction of the species is converted into an active form which does not give an ESR signal. Furthermore, the amount so converted is a fixed

fraction of the total Cr(V), as indicated by the ESR signal at  $g = 1.97$ . This accounts for the proportionality between catalytic activity and the signal at  $g = 1.97$ .

The active catalytic site for ethylene polymerization is visualized as follows. The Cr(V) is in a square pyramid derived from the distorted tetrahedron. The square pyramid is lying on its side on the silica surface with three of the oxygens of the surface forming the triangular side of the pyramid.

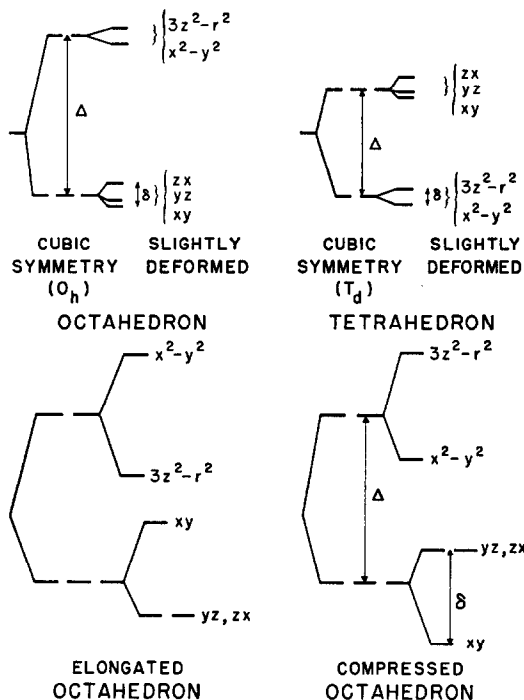


FIG. 8. Energy level diagrams for Cr(V) in different crystal field environments. [Adapted from Van Reijen (8).]

The flat square face of the pyramid is tilted to the surface. Two of its corners are occupied by the oxygen atoms of the silica surface, the third is occupied by OH and the fourth by a vinyl radical or polymerizing chain. This configuration is a distorted octahedron with the position six empty, being the "port of entry" of the reacting ethylene molecules. This active site has been obtained from the precursor, a distorted tetrahedron, by ethylene reacting with the double-bonded oxygen and converting it to an OH single-bonded to chromium and a

vinyl group ( $\text{HC}=\text{CH}_2$ ) bonded to the chromium. Whether or not this configuration gives a signal depends on whether the distance between the oxygen atoms in the apex of the square pyramid (in the plane of the silica surface) is shorter or longer than the distance of the other four ligands lying in the plane (two oxygen atoms, the silica surface, the OH, the vinyl group) to the chromium atom. If it is shorter, the signal can be observed at room temperature, if it is longer the signal is not observed. Since no signal is observed at room temperature, the active chromium atom must be in the latter elongated octahedron configuration (chromium-apex oxygen distance long).

The process of ethylene polymerization is visualized in the following way. As the ethylene approaches the square face along the axis joining the chromium and the oxygen at the apex of the pyramid, the chromium will move toward the apex stretching the chromium-carbon atom distance. This permits the ethylene molecule to be inserted between the chromium and the carbon, thus performing the polymerization step. The chromium then moves away from the apex oxygen and is in the proper configuration to receive another ethylene molecule.

This model of polymerization can be rationalized in terms of the Jahn-Teller effect. In the elongated octahedral configuration which we identify with the active catalyst site, the ground state has an orbital degeneracy which tends to be lifted by atomic motion. Thus when the ethylene molecule impinges on the active site, a distortion which lifts the degeneracy is favored: the chromium-apex oxygen distance is decreased, the chromium-carbon distance becomes stretched, and the ethylene molecule is inserted. The configuration then snaps back into the original elongated octahedron configuration.

#### Action of Water

The adsorption of water on the catalyst before the reaction causes a decrease in the anisotropy of the ESR signal without change in its intensity. This may be interpreted as a change in the symmetry of the crystal field surrounding the Cr(V). Two water molecules



are adsorbed in the distorted tetrahedron forming a distorted octahedron similar to that found in aquo complexes of the chromium in aqueous solution. Since the signal is observed it must be a compressed octahedron similar to a square plane configuration with small chromium oxygen apex distance. The expressions for  $g_{||}$  and  $g_{\perp}$  are

$$g_{||} = 2 - (8\lambda/\Delta) \text{ and } g_{\perp} = 2 - (2\lambda/\delta)$$

Using the experimental values of  $g_{||} = 1.95$  and  $g_{\perp} = 1.975$  and a value of  $\lambda$  equal to  $220 \text{ cm}^{-1}$ , we obtain for  $\Delta$  and  $\delta$  values of  $33\,600 \text{ cm}^{-1}$  and  $16\,100 \text{ cm}^{-1}$ . These values are to be compared with  $23\,500$  and  $12\,900 \text{ cm}^{-1}$  obtained by Gray and Hare (11) and  $18\,000$  and  $13\,500 \text{ cm}^{-1}$  reported by van Reijen (8).

At high temperatures the adsorption of water is accompanied by a decrease in the integral intensity of the Cr(V) signal. This is interpreted to indicate that the rather weak coordination bonding which caused the adsorption of water goes over into a stronger bond. This may cause a change in the valence state of Cr(V) or the octahedral configuration will become symmetrical causing the disappearance of the signal.

Another possibility is that the compressed octahedron that gave the signal will go over into an elongated one that does not give a signal.

#### *Action of Oxygen*

The poisoning action of oxygen is much more drastic if oxygen is present during the reaction than if the catalyst is treated with oxygen before the reaction. It is probable that the oxygen reacts during the ethylene polymerization not with the Cr(V) centers but with the organic ligand. In so reacting, it restores the signal due to Cr(V) by changing

the configuration from an elongated octahedron to a compressed octahedron (square pyramid).

There is a possibility to explain all the effects enumerated on the basis of change of Cr(V) into a lower valence state. Work on this aspect is now pursued by one of us (JT) at Princeton.

#### ACKNOWLEDGMENT

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