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Polymerization of Ethylene over Supported Chromium Oxide Catalysts

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The polymerization of ethylene to polyethylene over chromium oxide supported on silica-alumina has been studied at low pressures with ethylene in the gas phase and in the absence of a solvent. The kinetics of the polymerization between −40° and 0°C follows a zero order law, which allows an estimate of the number of active sites. This can be compared with the number of Cr^{5+} ions present as determined by ESR measurements. The activity of the catalyst depends strongly on the temperature of its first exposure to ethylene. When ethylene is chemisorbed on the catalyst, decreases and increases of the signal strength of the ESR signal are observed depending on catalyst preparation. After ethylene chemisorption exposure to water vapor results in an increase of the signal. No direct correlation between signal strength and activity could be established, but a nearly linear relation was found between the activity and difference in signal strength of ethylene-treated catalysts before and after exposure to water vapor. The bearing of these results on the mechanism of the polymerization reaction is discussed.

INTRODUCTION

The polymerization of ethylene to polyethylene using chromium oxide supported on silica-alumina as catalyst has been the subject of a number of investigations (*1*) since its discovery several years ago. Many of these investigations were concerned with the nature and identification of the catalytically active species and for this purpose electron spin resonance methods proved particularly useful (*2*).

Catalysts of partially oxidized chromia deposited on either silica-alumina or on alumina show three significant ESR absorption peaks, two very broad ones, generally attributed to Cr^{3+} ions in different degrees of dispersion, and a much narrower one (width 50 gauss, $g = 1.97$) which has been assigned with a considerable degree of certainty to Cr^{5+}. It was suggested at an early stage of these investigations that the Cr^{5+} ion is the catalytically active species or at least is intimately connected with the catalytic activity. This agrees with many general observations such as, for instance, the presence of activity in a partially reduced chromium oxide catalyst, and the absence in a completely reduced one. However, for this conclusion to be established with certainty a clear relation between the Cr^{5+} content, i.e. the intensity of the ESR signal and the activity for polymerization must be established.

The best evidence is that of Bukanaeva, Pecherskaja, Kazanskii, and Dzisko (*3*), who showed that the signal strength before polymerization of catalysts with different chromium content and the catalytic activity vary in a parallel manner. However,

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the same authors showed that the signal strength declines appreciably during the polymerization at a temperature and over a period where the activity, as indicated by all previous experience, should be constant, a result which contradicts the one just mentioned.

The experiments reported here show 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. A simple relation between activity and signal strength is therefore not generally to be expected.

A good correlation which seems to hold widely was, however, found in the following way. It is known that water vapor displaces chemisorbed hydrocarbons including ethylene and polyethylene from the catalytically active surface. We have found that this displacement is accompanied by a considerable increase in the strength of the ESR signal. Quantitative determination of the signal strength before and after this displacement process by water vapor shows that there is a significant parallelism between the catalytic activity and the increase in signal strength.

EXPERIMENTAL

In most previous investigations the technique used to determine the rate of polymerization was similar to that of the industrial process; reaction was carried out with the solid catalyst present as a slurry in a solvent in which ethylene was dissolved under a pressure of 30–40 atm. While it is essential to use these conditions in the industrial process in order to remove the polymer continuously from the catalyst, polymerization proceeds readily on the solid catalyst in the absence of a solvent and with ethylene in the gas phase at atmospheric and lower pressure.*

The polymer formed envelops the catalyst powder, but the polymerization is slowed down only after 2–2.5 g polymer/g catalyst have accumulated, diffusion of ethylene to the catalytic surface being sufficiently rapid at this stage. These conditions made it possible to perform kinetic measurements and to test various modes of catalyst activation at low pressure and without a solvent.

A simple high-vacuum system was used which consisted of the usual pumping train, McLeod gauge, purification and storage vessels for ethylene, a reaction vessel (volume 2 cc) connected to a supply vessel of ethylene of 500 cc. Mercury manometers, and a small McLeod gauge were used to follow pressure changes in the region 0–100 mm Hg. A modified Sprengel pump was incorporated to circulate gases over the catalyst and to remove continuously gases evolved from the catalyst. A furnace, the temperature of which could be kept to within ±1°C, was used to heat the reaction vessel to various temperatures up to 500°C. For each series of experiments 0.5–1.5 g of catalyst were transferred through a ground joint in a stream of dry nitrogen from the storage to the reaction vessel. The catalyst was outgassed to 10^{-5} mm Hg and could be subjected to various treatments before a polymerization experiment was carried out. The polymerization itself was followed by the decrease in pressure. At temperatures above 0°C temperature control was difficult because of insufficient dissipation of the heat of polymerization; below 0°C this effect was absent. The activity of the catalyst was checked frequently and in general remained constant until the critical quantity of 2.5 g polymer/g catalyst had accumulated. Within the range of 0.2–1.5 g of catalyst, employed in the present experiments, the polymerization rate was proportional to the amount of catalyst used.

Catalyst preparation. Davison low-density grade 960 silica-alumina was used as support (Al_2O_3 content 12%, BET surface 415–515 m^2/g, pore volume 0.70–0.86 cc/g, bulk density 0.475 g/cc). This support was digested with an amount of chromic acid solution (Analar grade CrO_3) just sufficient to be completely absorbed by the solid. In general catalysts contained from 0.5 to 3.0 wt % Cr calculated as CrO_3.

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* We are much indebted to Dr. T. Hill for drawing our attention to this technique which he has developed.

After evaporation and drying at 110°C, the catalyst was heated in a quartz tube to 550°C in a stream of dry air, under flow conditions which dispersed the solid as a "fluidized" bed. The oxidized catalyst was transferred while still hot in a rapid stream of dry air through a ground joint to a storage vessel. As has been mentioned the activity of a given catalyst preparation was very stable, but there were considerable differences in activity between one catalyst preparation and another, which may have been caused by hydrocarbons chemisorbed in the course of the catalyst preparation.

Ethylene. Philips Petroleum Co. Research Grade Ethylene was used. The purity was above 99%, the only detectable impurity being ethane. The gas was introduced into the apparatus from a cylinder, liquefied in a cold trap, outgassed, and distilled under heavy reflux, the first and last third of each sample being discarded.

Electron spin resonance measurements. A Varian V-4500 EPR spectrometer, with a Mullard 10-inch electromagnet was used at an operating frequency of 9.30 kMc sec^{-1}. The modulation frequency was 100 kc sec^{-1} and the spectra were recorded as the first derivative of the absorption curve. The treatment and conditioning of all catalyst samples was done either in the reaction vessel or directly in the quartz sample tubes used in the ESR measurements. If the reaction vessel was used, a number of sample tubes were sealed to the system through graded seals. After conditioning of the catalyst, the reaction vessel and the sample tubes were removed from the rest of the system and the catalyst transferred from the reaction into the sample tubes by tilting and shaking. After filling, the tubes were sealed off. The sample volume was approximately 0.2 ml; all measurements were made at room temperature. The total intensity of absorption was obtained by double integration of the derivative peak. An accuracy of 10% is estimated for this operation. Relative concentrations were obtained by comparing these integrated areas under standard experimental conditions; the absolute value of the unpaired spin concentration was obtained by comparison with a standard solution of diphenylpicrylhydrazil (DPPH) in benzene, observed under conditions such that the microwave power saturation was negligible (*5*).

RESULTS

An active catalyst can be obtained by heating the oxidized preparation *in vacuo* to 400°C. It was thought that under these conditions reduction of Cr^{6+} to lower valent chromium ions takes place by simple decomposition of CrO_3 with the elimination of oxygen. However, when the gas given off was collected quantitatively, with or without pumping from the catalyst, it was found to consist almost entirely of carbon dioxide, only minor quantities of other gases being present, as is seen in Table 1.

In Expt. 4 a catalyst was used which had

TABLE 1
GASES EVOLVED ON HEATING THE CATALYST TO 400°C *in vacuo*

Expt. no.	Treatment	$\%CrO_3$ on catalyst	Moles gas evolved $\times 10^6$	$\% CO_2$	$\frac{\text{Mole } CO_2 \times 10^6}{\text{mole } CrO_3}$	Components of gas other than CO_2[a] (%)
1	Without pumping, final pressure 2.3 mm Hg	2.01	85	93	19.1	2 air
2	Continuous pumping on Sprengel pump		104	98	26.2	2 air
3	To a final pressure of 10^{-4} mm Hg	1.82	100	89	23.0	6.6 N_2, 2.5 H_2 1.6 CH_4, 0.3 O_2
4	Prepared in greaseless system and protected from tap grease Sprengel pumping to 10^{-4} mm Hg	0.63	4.5	44	2.3	35.1 N_2, 6.7 H_2, 3.7 O_2, 0.4 CH_4

[a] Mass spectrographic analysis.

been prepared in an entirely greaseless system and during decomposition *in vacuo* had been protected from grease vapors by a trap cooled by solid CO_2. The amount of gas evolved (4.5×10^{-6} mole) was too small to be measured accurately in the system used, but was clearly only about one-tenth of the amount evolved in the previous experiments. The color of this catalyst after vacuum treatment remained yellow with a few small green spots where some reduction had occurred, whereas Preparations 1–3 were uniformly green after evacuation treatment, indicating a more general reduction to Cr^{3+}.

These experiments show that unless precautions are taken to avoid contamination of the catalyst surface, reduction occurs either through organic vapors adsorbed on the catalyst during its preparation or through grease vapors in the course of the vacuum treatment. It is also remarkable that in the absence of organic vapors supported CrO_3 is stable up to temperatures of 400°C, whereas in bulk it decomposes at 200°C.

Rate Measurements

The polymerization rate at various temperatures as expressed by the zero order rate constant

$$k = \frac{\text{mg } C_2H_4 \text{ polymerized}}{\text{minute} \times \text{g catalyst}}$$

is shown in Fig. 1. In these experiments a first polymerization experiment was carried out at 100°C in order to stabilize the activity of the catalyst. (This stabilization will be discussed below.) It is seen that the rate of polymerization reaches a maximum around 20°C. The rate figures at and above that temperature must be taken as semiquantitative only because of the exothermic heating effects. At these temperatures a very rapid reaction takes place at first but a steady rate is attained soon. The results plotted in Fig. 1 refer to the region of steady reaction rates.

Below 0°C the rate is practically of zero order, as shown in Fig. 2. Above this temperature it changes to first and later to an even higher order. The last observation may be unreliable because of the heating effects, but it seems that the high-temperature behavior above 20°C is consistent with a gradual depopulation of the catalytic surface. This is in contrast to the conditions of the industrial process where much higher temperatures are used, but in this case the reaction is carried out under pressure, which counteracts the depletion of the surface population.

The zero order of the reaction below 0°C is demonstrated in Fig. 2. Four consecutive runs at a temperature of —22°C and at varying pressures of ethylene show that the rate is independent of time and independent

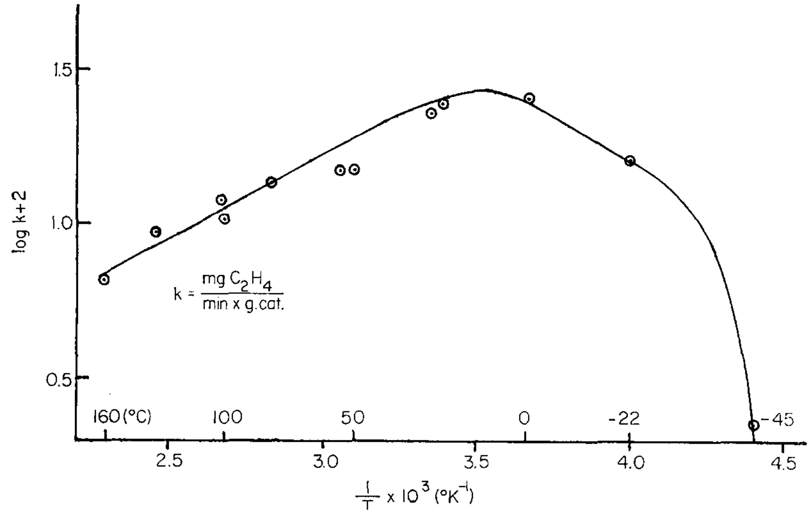

FIG. 1. Polymerization rate at various temperatures.

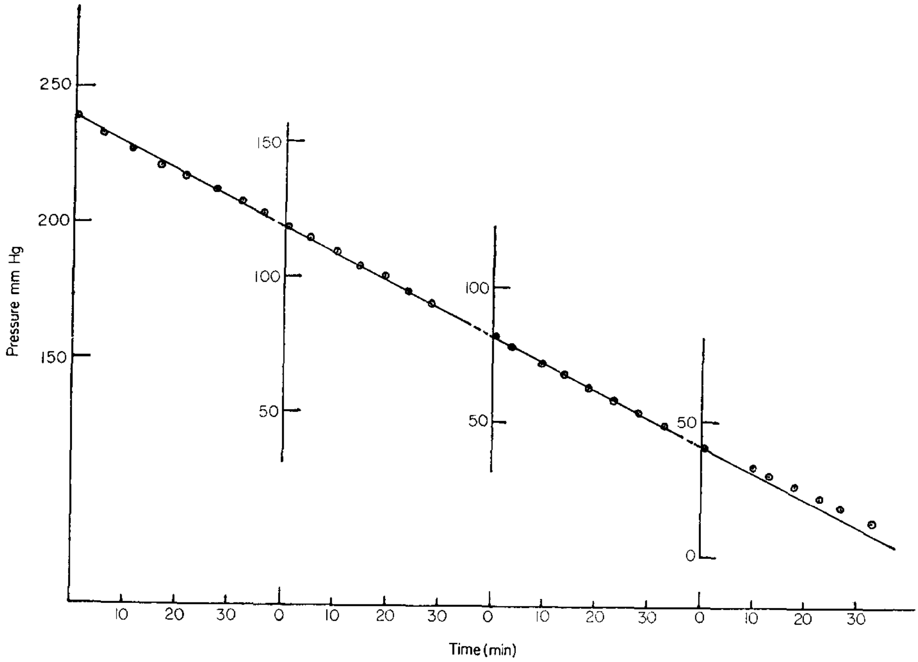

FIG. 2. Polymerization rate at —22°C and at various pressures.

of the pressure of ethylene. At the same time the experiment demonstrates that the rate of polymerization is constant and reproducible over the series of these four experiments. Below —30°C the rate becomes inconveniently slow for rate measurements and there are indications of diffusion processes influencing the rate. Over the range —30°C to 0°C a good Arrhenius plot is obtained (Fig. 3) which leads to an apparent activation energy of 14.1 kcal/mole. Since the reaction in this temperature range is of zero order this should be the true activation energy, and under these conditions it is possible to apply the following formula of the transition state theory

$$[k] = (kT/h) \times S \times (f'/f)e^{-E/RT}$$

in order to obtain an estimate of the number of active sites per gram of catalyst (*6*). Here $[k]$ is the zero order rate constant, S the number of active sites per gram of catalyst, f and f' are the partition functions of the adsorbed, and of the adsorbed activated species, respectively. To a first approximation the latter two factors cancel. For the most active catalyst, obtained by activation with ethylene at 130°C (see next section), $[k]$ at —22°C was 5.95×10^{-7} mole C_2H_4/sec $\times$ g catalyst. This leads to $S = 1.4 \times 10^{17}$ sites/g catalyst equivalent to 2.3×10^{-7} mole sites/g catalyst. This sample contained 2.3% by weight of chromium calculated as CrO_3, equivalent to 2.5×10^{-4} mole Cr/g catalyst. The fraction of active sites therefore is of the order of 0.2–0.3% of the total chromium content.

A quantity of 10^{-5} mole of reducible chromium is below the detection limit of the ferrous phenanthroline test. Assuming the catalytic species to consist of a reducible chromium ion this agrees with the observation that the activity of the catalyst persists when no reducible chromium can be detected chemically.

Activation of Catalyst by Pretreatment with Ethylene

It has been mentioned that reproducible polymerization rates are obtained only after a first contact of the catalyst with ethylene at a temperature higher than that of the subsequent polymerization. If after this first contact of the catalyst with ethyl-

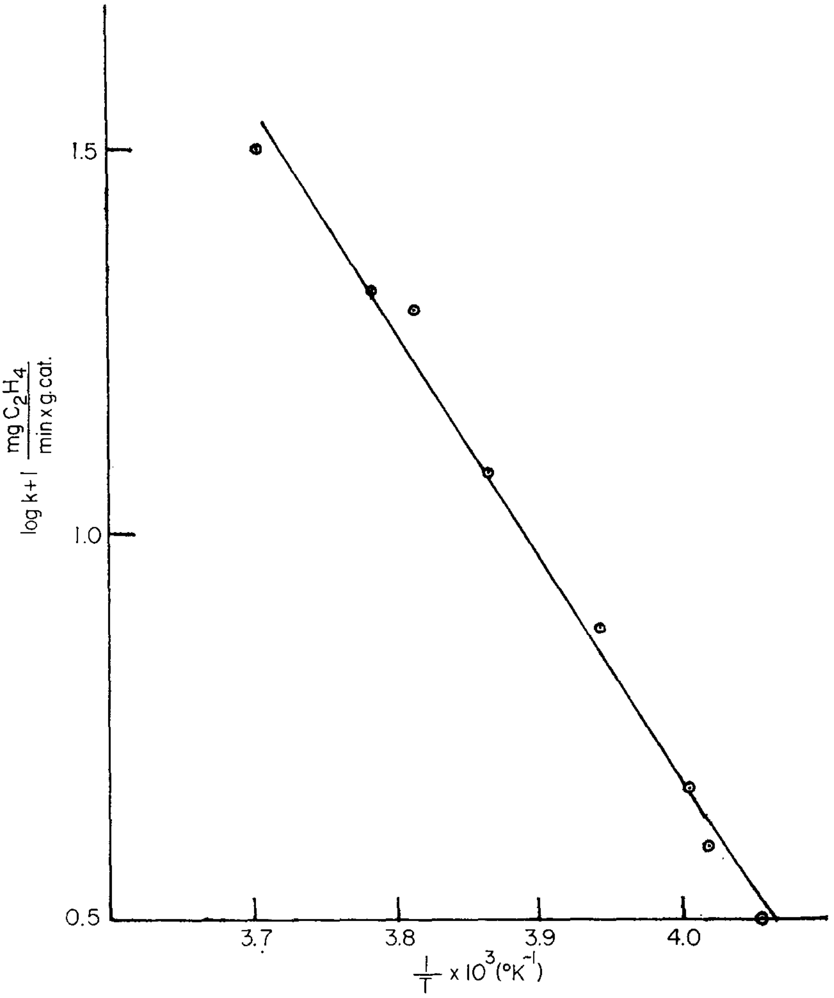

FIG. 3. Polymerization rate between —30°C and 0°C.

ene all subsequent experiments are carried out at lower temperatures the activity remains constant and reproducible until blocking through accumulation of polymer occurs. The following series of experiments shows that this activation pretreatment is strongly dependent on temperature (Fig. 6, curves A and B). In this series a first ethylene polymerization was carried out at a given temperature and subsequently the activity was tested at the arbitrarily chosen standard temperature of —22°C (freezing CCl_4 used as cryostat). The results indicate that there is a sharp increase in activity with increasing activation temperature with a maximum of the activation at 130–140°C, the exact temperature of the maximum being difficult to locate because of the heating effects. Activation above these temperatures leads to progressively less active catalysts. Since the activity tests were done at a temperature (—22°C) where the active surface is fully saturated the increased rates after activation must mean that new active sites are formed. The increase may be due in part to the formation by reduction of new Cr^{5+} sites from Cr^{6+} sites but, as later experiments will show, an activated adsorption of ethylene on the existing Cr^{5+} sites is also necessary before polymerization can occur. The decline in polymerization rate after the maximum in the activation temperature has been passed must then be due either to desorption of chemisorbed ethylene molecules, or to a reduction of active Cr^{5+} sites to inactive Cr^{3+} sites, or to both effects occurring simultaneously.

Electron Spin Resonance Measurements

In general we are concerned here with the relatively narrow peak (50 gauss) corresponding to $g = 1.97$ which is found in partially oxidized supported chromium oxide catalysts, and which has been discussed by a number of authors. It is accepted that this peak is due to Cr^{5+} ions present on the catalyst (*2*d). We found that this peak can be observed already after the oxidation treatment of the catalyst, i.e. before any reduction or vacuum treatment has been applied. The signal persists after exposure to water vapor at room temperature, while treatment with water vapor at 100°C for 2 hr reduces it to half its size. Ethylene affects the signal permanently* above 150°C and hydrogen above 250°C. Exposure to hydrogen at 350°C for 3 hr reduced all chemically detectable higher valent Cr ions to Cr^{3+}, while the Cr^{5+} signal was reduced to half its strength. However, it is necessary to take into account the sensitivity of the chemical test for reducible Cr ions which, as mentioned previously, is of the order of 10^{-5} moles while the ESR signal strength is equivalent to 10^{18} spins or approximately 10^{-6} moles. It is therefore possible that Cr^{6+} ions survive in quantities comparable to the Cr^{5+} ions but escape detection because of the limited sensitivity of the chemical tests. As mentioned previously the signal strength was calibrated against the signal of a known quantity of DPPH. For the most active catalyst used in this investigation (Fig. 6, Catalyst I, CrO_3 content 2.5 wt %) the signal before contact with ethylene corresponds to 3.2×10^{18} spins/g catalyst. This has to be compared with the figure of 10^{19} spins/g catalyst obtained by Kazanskii and Pecherskaya (*2*d). Their catalyst, however, contained double the amount of chromium; if, therefore, for an approximate comparison our figure is doubled the two results compare well, particularly if probable minor differences in the technique of preparation of these catalysts are taken into account.

Relation between ESR Signal Strength and the Catalytic Activity

Qualitatively the relationship between the ESR signal strength and the catalytic activity of the catalyst is shown by reduction of the catalyst with hydrogen at temperatures of 400°C. This treatment destroys the catalytic activity completely and at the same time the ESR signal vanishes. This is further support for the view that Cr^{5+} ions are the active species, since such ions should be reduced quantitatively to Cr^{3+} by this drastic treatment.

In order to establish a quantitative relationship between activity and signal strength we exposed the catalyst at 360°C to hydrogen contained in a constant volume which was filled to various initial pressures. In all experiments the hydrogen was used up completely. The initial pressure therefore is a measure of the amount of reduction. After reduction the activity at a temperature of 22°C and the strength of the ESR signal (after polymerization) was measured. The results, given in Fig. 4, show that here again the behavior of the ESR signal and the catalytic activity run parallel. However, this conclusion applies only in a qualitative sense, as shown by a direct plot of activity against intensity of ESR signal (Fig. 5).

The relation between catalytic activity and signal strength is obviously complex. The signal strength declining long before the catalytic activity falls off, the latter decreasing very suddenly (point B of the graph) to a small proportion of its original value.

Assuming that a direct relation between signal strength and activity exists, one must conclude from this graph that only a part of all the Cr^{5+} sites form active centers and that this part comprises the sites most resistant to reduction. It may be significant

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* A temporary effect of ethylene on the signal is observed at lower temperatures, as discussed later.

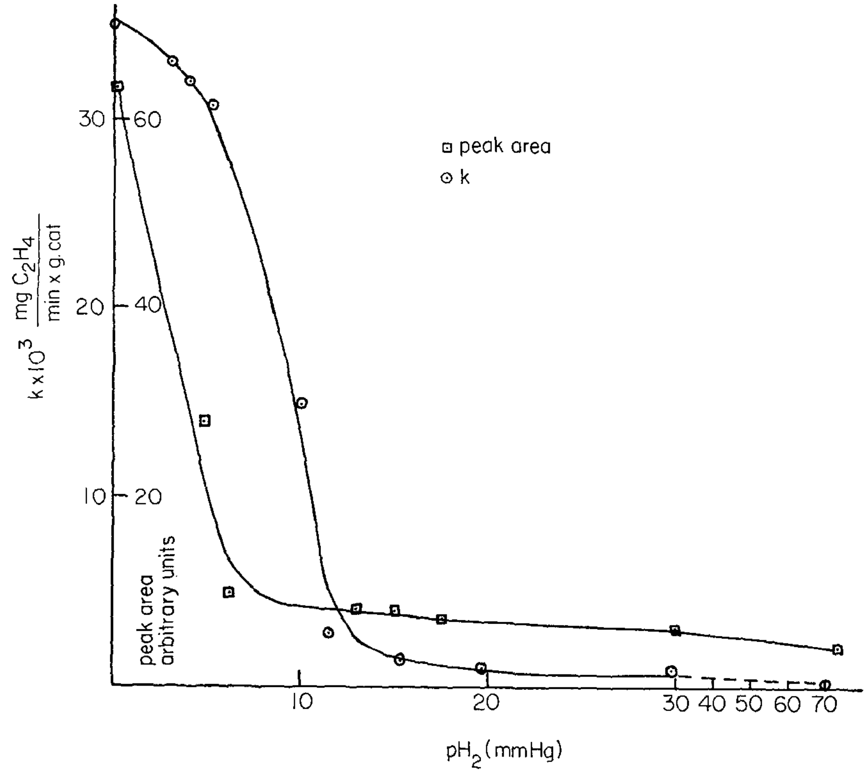

FIG. 4. Polymerization rate and signal peak area against initial pressure of hydrogen.

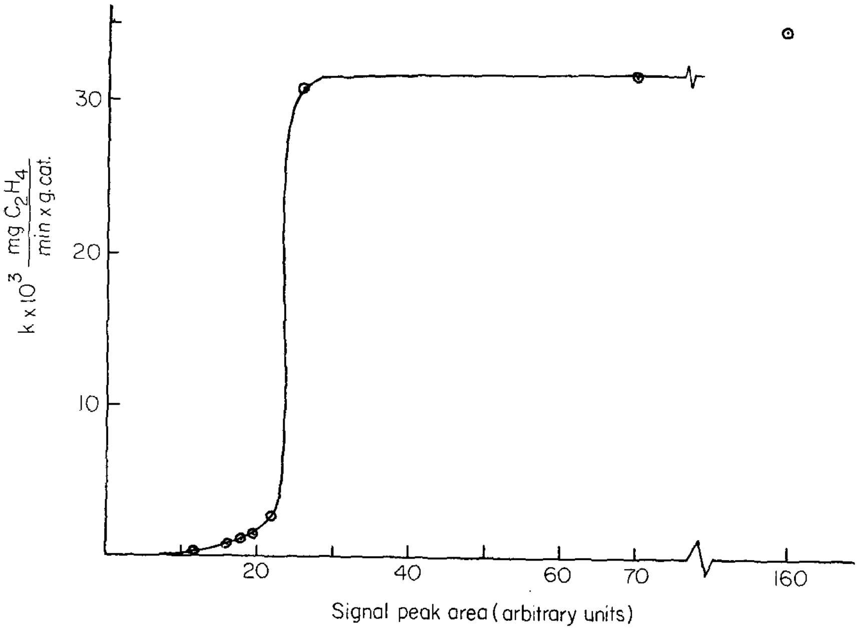

FIG. 5. Polymerization rate against signal peak area.

that point B coincides with the stage of reduction where reducible chromium ions are no longer detectable in the Ferroin test. It is likely that the disappearance of Cr^{6+} ions below the detection limit is observed here because the ESR evidence indicates that at this stage Cr^{5+} ions are removed to below this limit. The simultaneous and abrupt fall of catalytic activity may indicate therefore a participation of Cr^{6+} ions, in addition to Cr^{5+} ions, in the formation of active sites.

Influence of Ethylene on ESR Signal and Polymerization Rate

The first contact of the catalyst with ethylene strongly influences the peak area of the ESR signal and here again the temperature at which the contact is made is of particular importance. After this first contact the peak area is not affected further by the subsequent polymerization reaction itself. Results of experiments with two catalysts are shown in Fig. 6 where the peak area after contact with ethylene is plotted against the temperature at which contact was made. The original peak area before contact with ethylene is also indicated. In the case of Catalyst I (open circles), which was a very active catalyst, the signal area decreases on exposure to ethylene, the decrease being a minimum in the temperature range where activation by ethylene leads to a maximum of the polymerization rate. In the case of Catalyst II, which was only of moderate activity (full circles), the peak area of the signal increases after activation at all temperatures except the highest.

The polymerization activities follow a similar pattern in both cases, showing a maximum after activation in the temperature range of 120–150°C, as previously demonstrated. There appears, however, only a weak correlation between the peak area curve and the activity curve of Catalyst I and no correlation between the two curves in the case of Catalyst II.

These last results appear to be very complex and at first sight there seems little point in further analysis. However, the following series of experiments lead to a considerably better understanding of the situation. In these experiments the influence of water vapor on the strength of the ESR

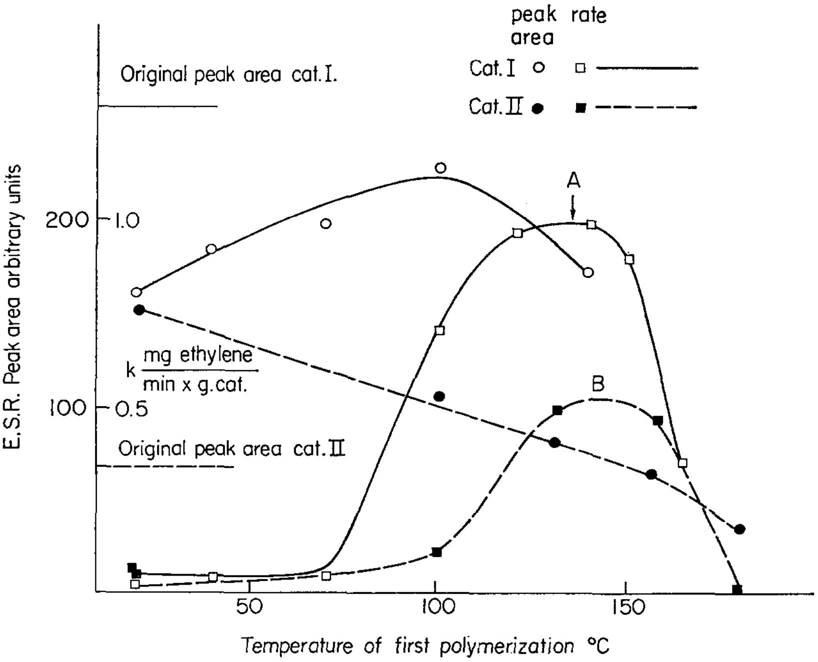

FIG. 6. ESR peak area and rate against temperature of first polymerization.

signal before and after contact with ethylene and polymerization was investigated.

As has been shown by Kazanskii and Pecherskaya (*2*d) water vapor added to the catalyst, before contact with ethylene, sharpens the ESR signal without altering the peak area; thus there is no change in the number of free spins involved. We have fully confirmed this observation. However, the behavior is quite different if the catalyst is exposed to water vapor after it has been in contact with ethylene. In this case considerable increases in the peak area are noted. Addition of up to 6% of water vapor, based on the chromium oxide present, roughly doubles the peak area; larger amounts do not bring about further increases.*

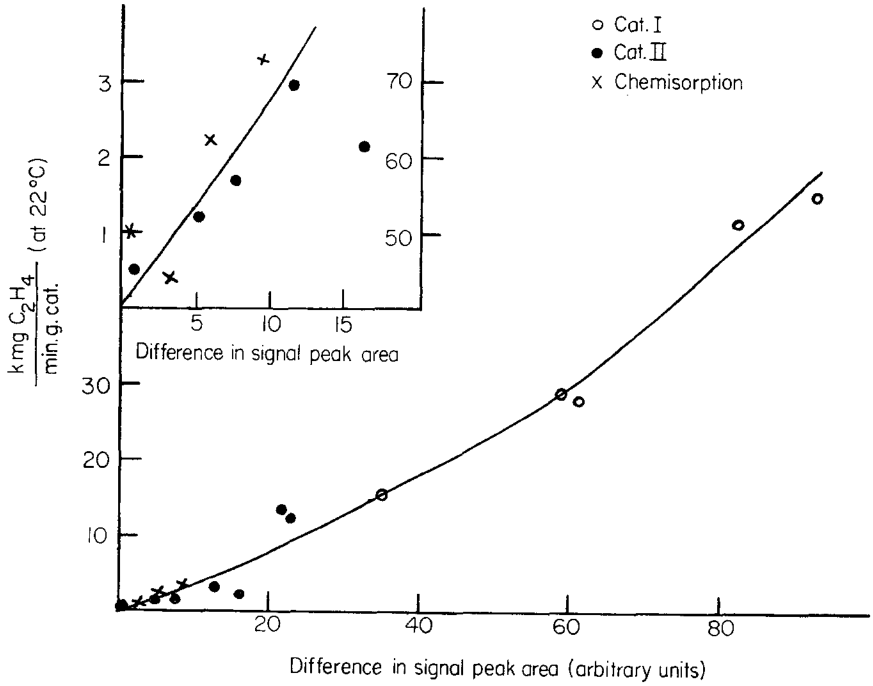

FIG. 7. Rate and difference in signal peak area before and after water treatment.

Similarly, exposure of the catalyst to water vapor after polymerization brings about considerable increases in the peak area of the signal. Moreover, these increases are greater the greater the activity of the catalyst. This is illustrated in Fig. 7 where the differences in the peak area of the signal taken (1) after polymerization and (2) after subsequent treatment with water vapor are plotted against the activity of the respective catalysts. The data refer again to samples of the active (open circles) and of the less active catalyst preparation (solid circles) of Fig. 6. In order to cover as wide a range of activities as possible catalysts of very low activity were included in these experiments. This made it necessary to carry out the polymerization tests at +22°C, where even with the low-activity catalysts reasonable reaction rates could be obtained. Both catalysts had received various pretreatments by initial contact with ethylene at different temperatures. It is seen that a clear and nearly linear relation exists between activity and the difference in peak area of the signal before and after treatment with water.

These observations, as also the previous

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* There should be no direct relation of this figure to the number of active polymerization sites since the catalyst support will also chemisorb water.

ones on the change in signal strength on first exposure of the catalyst to ethylene, can be explained by assuming the formation of electron pair bonds between the substrate ethylene and the chromium ions (Cr^{5+}) of the catalyst. On formation of these bonds the signal decreases. However, since ethylene also contributes to the reduction of the catalyst and thus turns Cr^{6+} ions into active Cr^{5+} ions, there is in addition a factor leading to an increase in the signal. Finally, particularly at somewhat higher temperatures, ethylene also reduces Cr^{5+} ions to Cr^{3+} ions. Thus there is a further factor diminishing the signal strength. The resultant changes therefore must be expected to be complex, as has been observed.

If it is assumed that on treatment with water vapor the electron pair bonds between ethylene or ethylene polymer and the catalyst are broken by water molecules displacing the ethylene from the catalytic surface, this process would explain the increase in signal strength. If the polymerization rate is approximately proportional to the number of electron pair bonds formed by chemisorption of ethylene on the catalyst the nearly linear relation between activity and the increase in signal strength after water treatment is explained. This interpretation is supported by the well-known poisoning action of traces of water on the polymerization activity of the catalyst.

Comparison of Number of Spins and Active Sites

The most active catalyst (Fig. 7, Catalyst I, activated by a first polymerization at 130°) gave a figure of 1.4×10^{17} sites/gm catalyst (see page 282), which has to be compared with the number of spins of 3.2×10^{18} spins/gm for the same sample. The latter number therefore is greater by a factor of 20. This is in accordance with the last results which show that only those spins which can be regenerated after polymerization by the water displacement treatment, are associated with active sites. In general these recoverable spins are only a fraction of the total spins and in the case of the catalyst under consideration these numbers amounted to one-third of the number of total spins. This would reduce the ratio of these spins to the number of active sites to a factor of 7. This factor should be near unity. The deviation seems too large to be accounted for by an accumulation of experimental errors only. It may be that the assumption of near equality of the partition functions of the chemisorbed reactants and of the transition configuration is not justified in this case. The formation of a transition configuration, which involves the combination of a chemisorbed ethylene molecule and of the chemisorbed polymer chain, may well entail a loss of entropy. A loss of 4 e.u. would account for the discrepancy observed.

ESR Signal and Polymerization Rate after High-Temperature Chemisorption

Further experiments were carried out using the property of ethylene to chemisorb on the catalyst at temperatures of 250°C without initiating a subsequent polymerization.*

If this chemisorption is interrupted by pumping the ethylene from the catalyst after about 10 min contact the catalyst shows nearly its full activity in a subsequent polymerization experiment at room temperature. If the catalyst after treatment at 250°C is heated to 400° and evacuated at that temperature for an hour it also remains active though the activity is considerably decreased. If, however, the catalyst is left under ethylene at 250°C for about 60 min without pumping, followed by evacuation of the ethylene for 5 min, the polymerization activity is lost. The greater part of the activity can be regained by evacuation for an hour at 400°C subsequent to the treatment at 250°C. In experiments of this type the ESR signals were observed in parallel with the activity tests, and in addition the signal after water treatment was also measured. The results are given in Table 2.

Once again it is clear from the results of Table 2 that a good correlation exists be-

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* Private communication by Dr. T. Hill (see ref. *4*).

TABLE 2
ACTIVITY AND ESR SIGNAL OF CATALYST AFTER CHEMISORPTION OF ETHYLENE AT 250°C

	Ethylene exposure		Evacuation		Signal strength[a] after			
Expt. no.	Time (min)	Temp (°C)	Time (min)	Temp (°C)	Ethylene treatment	Water treatment	Gain after water treatment	$[k]$ $\frac{\text{mg ethylene}}{\text{min g/cat}}$
1	5	250	5	250	0.236	0.317	0.081	3.30
2	5	250	60	400	0.032	0.062	0.030	0.40
3	60	250	5	250	0.20	0.20	0.00	0.00
4	60	250	60	400	0.036	0.087	0.051	2.24

[a] In arbitrary units.

tween the catalytic activity and the increase in the signal after water treatment while there is no correlation between the catalytic activity and the signal strength after ethylene but before the water treatment. This is further confirmed in Fig. 7 where the points marked by crosses, which refer to the results of Table 2, are seen to agree with the previously established correlation between catalytic activity and the increase in signal strength after water treatment.

These last experiments also show that the increases and decreases of the ESR signal on exposure to ethylene and on water treatment are connected with the chemisorption of ethylene and do not depend on the subsequent polymerization reaction. On the other hand in conjunction with the previous evidence, one can conclude that ethylene chemisorption through formation of electron pair bonds is a necessary first step in the polymerization reaction.

From the present results some further general conclusion about the possible mechanism of the polymerization reaction can be drawn.

The experiments fully confirm the conclusions of Clark and Bailey on the propagation mechanism of the polymer chain (*7*). A mechanism involving direct addition of a gaseous ethylene molecule to a chemisorbed polymer chain was rejected in favor of one where a chemisorbed ethylene molecule combines with the chemisorbed chain. The zero order of the polymerization reaction as observed in the present work clearly is only compatible with the latter mechanism.

As regards the structure of the catalytic centers, an important result is the persistence of a great part of the Cr^{5+} signal after exposure to ethylene, even at comparatively high temperatures. This indicates that not every Cr^{5+} ion is capable of chemisorbing ethylene and could be explained by postulating a two-point attachment of chemisorbed ethylene to two neighboring Cr ions, as has been often proposed for olefins (*8*). Since the concentration of Cr^{5+} sites is very small, the probability of two Cr^{5+} ions occupying neighboring sites will be extremely small. However, Cr^{3+} which is present in greater concentration on the catalyst, may act as the second center.*

The formation of clusters of chromium oxide on the support, as demonstrated by Eischens and Selwood (*9*), also increases the probability of neighboring Cr ion pairs. A two-center attachment, moreover, would provide a simple picture of the chemisorption of ethylene through electron pairing, both electrons being involved in the formation of bonds. If only one Cr^{5+} center were involved it is difficult to visualize complete pairing, and some fine structure of the signal rather than a reduction in intensity should be observed. This picture does not exclude an additional one-point attachment of an alkyl radical, which acts as the growth center of the polymer chain, and to which chemisorbed ethylene is fed in the growth reaction.

A final observation is worth recording. On some catalysts which were not rigorously protected from contamination by

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* We have observed recently effects on the ESR signal of Cr^{3+} ions when chemisorbing ethylene, similar to those described here for Cr^{5+} ions.

tap grease similar increases in signal strength were noted when a catalyst, which had been reduced partially by hydrogen, was subsequently treated with water vapor, i.e. without even coming into contact with ethylene. However, when such catalysts were again oxidized and reduced under strict protection from tap grease contamination this effect disappeared. It must be concluded therefore that organic materials, such as tap grease vapor, or their oxidation or decomposition products are also chemisorbed through the formation of electron pair bonds with the catalyst. This mode of adsorption, however, does not take place in the case of hydrogen.

ACKNOWLEDGMENT

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