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Supported Chromium Oxide Catalysts for Olefin Polymerization

VIII. A New Model for the Active Centers

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A new model for active center is proposed. It involves a set of chromium atoms with different valence states and located at the border of the chromium oxide domains spread over the surface of the support. This model is valid chiefly for catalyst with relatively high chromium contents and explains well a number of observations presented in previous papers.

INTRODUCTION

The true nature of the active site for olefin polymerization on supported chromium oxide catalysts (Phillips catalysts) remains a matter of discussion after 20 yr of research. The main questions which have to be answered concern (a) The number of chromium atoms in one site, their oxidation degree before and after contacting with the monomer, the location of these sites onto the surface of the supporting material, their number, and their dispersion state, and (b) The mechanism of their action, their lifetime, and the mechanism of their deactivation.

Most of the published data have been reviewed recently by Clark (*1*). It is generally accepted that only a small proportion of the chromium atoms is involved in the activity; although the maximum activity occurs for catalyst with 2–3% Cr, the proportion of active chromium increases when the chromium content decreases. At very low values a maximum is observed by Hogan (*2*), who concludes with many other authors that the sites are isolated chromium atoms dispersed onto the surface, the decrease at the lower values being explained by poisoning. Many discussions have been concerned with the oxidation degree of the atoms and the values of II, III, IV, V, and VI have been proposed (*1*). It is accepted, however, that the monomer actually undergoes the last activation step by reducing the chromium atoms of the sites to the proper oxidation degree but the question remains about the oxidation state before and after contact with the monomer. Some studies (*2*, *3*) support the view that the active sites involve a chromate where the chromium is initially hexavalent and is reduced to the tri- or divalent state by the monomer. Concerning the location of the sites, the reduction profiles of Holm and Clark (*4*) suggest that, on a silica–alumina carrier, they are on the silica part.

In the present paper we propose a new model of active sites which defines the location of the sites on the surface of the catalyst, the oxidation state (before contact with the monomer) of the chromium atoms belonging to the site, and the number of atoms of this kind of site. Such a model was chiefly derived to explain the kinetics results already obtained in this laboratory (*5*, *6*), but it also takes into account previous results on the dispersion state of the chromium oxide (*7*). Moreover, it is supported by new data reported here and in further papers of this series; for instance, it will be shown that it may explain the comparison between the activity and the intensity of the ESR signal of the γ-phase (*8*) and also the results obtained for propylene polymerization (*9*). It is to be noted that this model is valid chiefly for silica–alumina based catalyst, which has been studied extensively in our laboratory.

THE NEW MODEL

The major arguments to support the previous model of isolated chromium atoms come from studies at low chromium contents of the catalyst (*1–3*, *10*). The results obtained at higher chromium contents, and chiefly those corresponding to the maximum of activity, are not well explained.

In our opinion, the following facts need another explanation.

(a) The maximum of activity is observed after a limited reduction treatment; the catalyst is inactive either after total (e.g., with H_2 at 500°C) or too much limited reduction [e.g., polymerization at low temperature without reducing treatment (*11*)].

(b) The activity is well stabilized (for instance versus poisoning by water and oxygenated compounds, or versus destruction by propylene) after a proper reduction by a convenient reducing agent (*9*, *11*).

(c) The activity reached after pretreatment with hydrogen shows a very sharp maximum upon varying the conditions (temperature, duration) of the pretreatment.

Our new model assumes at first that the site involves a set of chromium atoms which are not all at the same oxidation degree. Such a hypothesis has already been advanced by Miesserov (*12*). This may explain the fact that the proper activation requires partial reduction, as well as the model of one chromium atom at an intermediate oxidation degree. The probability of formation of such sets lies parallel with the number of active sites and is dependent upon the average oxidation degree of the active part of the catalyst (which is supposed to be homogeneous). If the activation pretreatment involves a powerful reducing agent, i.e., a rapid reduction, that probability may reach a sharp maximum upon varying the pretreatment conditions. It may be expected that a cooperative effect of the chromium atoms belonging to the sites stabilizes the latter against various chemical attacks (poisoning, etc).

Concerning their location, the active sites cannot be found in the agglomerated chromium oxide because pure chromium oxide (even with a large surface area) is totally inactive and the catalysts with high chromium contents show only a moderate activity. As a first hypothesis we suppose that the active sites might be in monolayer chromium. Although there is no direct measurement of the chromium present as a monolayer, it may be estimated from the dispersion state data of Charcosset *et al.* (*7*) by extrapolation from the low concentration range. We assume that at very low concentration the whole of the chromium is present in one or two layers only. The values obtained are reported in Table 1 and compared there with our activity data.

It may be seen that there exists some correlation between the activity and the estimate of the area covered with a monolayer of chromium oxide; both have a maximum at around 2% Cr. However, at low contents the correlation becomes poor,

TABLE 1
PERCENTAGE CHROMIUM IN MONOLAYER AND ACTIVITY FOR CATALYSTS AT DIFFERENT Cr CONTENTS

% Cr	Average number of chromium layers	Relative % of Cr in monolayer	Absolute % Cr in monolayer	Activity *k*
0.15	1.3	60	0.09	4
0.5	1.5	50	0.25	6.6
1	1.54	46	0.46	11.1
2	1.76	27	0.54	12.9
3.6	2.5	13	0.47	9.3
5	2.56	5	0.27	

so a restricting hypothesis must be added, namely, that the sites are located only on the border of the chromium oxide domains. The active sites have both vicinal chromium atoms and bonds with the support useful for stabilization versus reduction. They correspond to a limited proportion of the Cr atoms and this proportion may increase when the size of the individual domains covered with chromium oxide decreases. At the limit, for very low chromium contents, the number of active sites per chromium atom may reach a maximum, as observed by Hogan (*2*), because the possibility of forming sets of chromium atoms finally decreases.

LOCATION OF THE SITES

This proposed location, mainly valid for chromium contents higher than 1%, may be supported on the basis of three kinds of arguments: It allows a better understanding of the dispersion state of the chromium, it may explain the effect of the chromium contents on the development of the activity, it may rationalize the data about the adsorption of the monomer and the covering of the surface with the polymer formed.

Finally, some arguments are given to show that the sites are directly bound to the silica part of the silica–alumina support.

Dispersion State of the Chromium

The activity should be dependent on two factors, namely, the average oxidation degree of the chromium located at the boundary and the whole length L of the perimeter of the chromium domains. It is believed that, for catalysts with different chromium contents, the average oxidation degree of the chromium located at the boundary would be the same when the optimum activation treatment (proper reduction) has been carried out. In these conditions, the activity k would be proportional to the perimeter of the domains covered with chromium oxide:

$$k = \alpha L.$$

Although there are some indications that, at least for moderately high chromium contents, these domains are anisotropic (*13*), the simplest hypothesis which allows calculation is to assume that they are circular in shape. Assuming further that they are homogeneously disposed on the catalyst and not dispersed in size, then if N is the number of chromium domains and r their radius, the surface covered with chromium is

$$S_{\mathrm{Cr}} = \Pi r^2 N.$$

The whole perimeter is

$$L = 2\Pi r N.$$

Thus

$$r = 2\alpha \frac{S_{\mathrm{Cr}}}{k}.$$

Using previous data for S_{Cr} (reproducibility: 5% (*7*)) and k (reproducibility: 2% (*5*)), one may derive for r the relative results plotted in Fig. 1 versus the chromium content.

It may be seen that the size of the domains grows regularly with increasing chromium contents and tends to reach a first plateau according to a roughly parabolic law (which is expected for flat circular domains) up to 2%, which corresponds to the maximum of activity. After that, between 2.5 and 5%, the size of the domains increases more rapidly and finally reaches a second plateau value. The second step of increase corresponds probably to the merging of domains because at this point the average number of chromium oxide layers begins to increase. Beyond 5% the maximum value of the area covered with chromium (about 25 m^2 of the 400

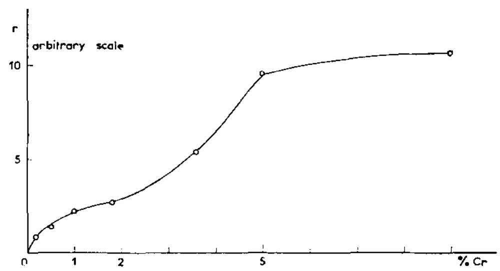

FIG. 1. Variation of the size of the chromium oxide domains versus the chromium content.

m²/g of the catalyst) is reached and one observes only an increase of the thickness of the domains.

The fact that the area of the carrier which may be covered with chromium oxide remains limited requires that the chromium covers only specific parts of the catalyst and forms domains distant enough from each other to avoid gathering. As pointed out previously (*12*) these parts correspond to the co-oxide zones of the silica–alumina carriers which are attacked preferentially by chromic acid during the impregnation step of the preparation of the catalyst. The same conclusion has been derived by Clark (*4*) from the study of the hydrogen reduction profiles.

It is possible also to estimate the relative average distance d between the active domains, using the surface area data of the whole catalyst from BET measurements (accuracy 5%), because the ratio d/r is proportional to $(S_{\mathrm{BET}}/S_{\mathrm{Cr}})^{1/2}$. The values of d obtained using the estimated values of r are plotted in Fig. 2 versus the chromium contents. This average distance which is rather large for very low chromium contents decreases very much to a flat minimum between 0 and 2% chromium, and then increases up to a flat maximum beyond 5% chromium, during the merging process. In our opinion, the different steps of the coverage of the silica–alumina carrier may be represented schematically as in Fig. 3. Silica–alumina is best described as a mixture of alumina spherical particles surrounded by a co-oxide zone and distributed in pure silica (Fig. 3, I). During the polycondensation process, the alumina particles are formed first while the formation of the co-oxide zone and of the silica

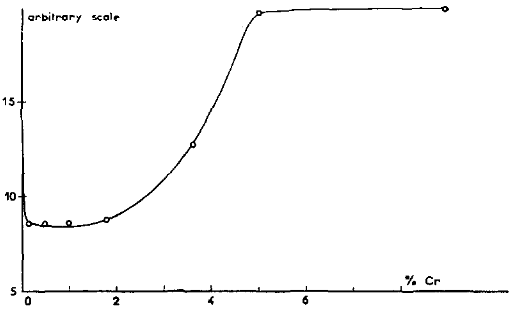

FIG. 2. Variation of the average distance between chromium oxide domains versus the chromium content.

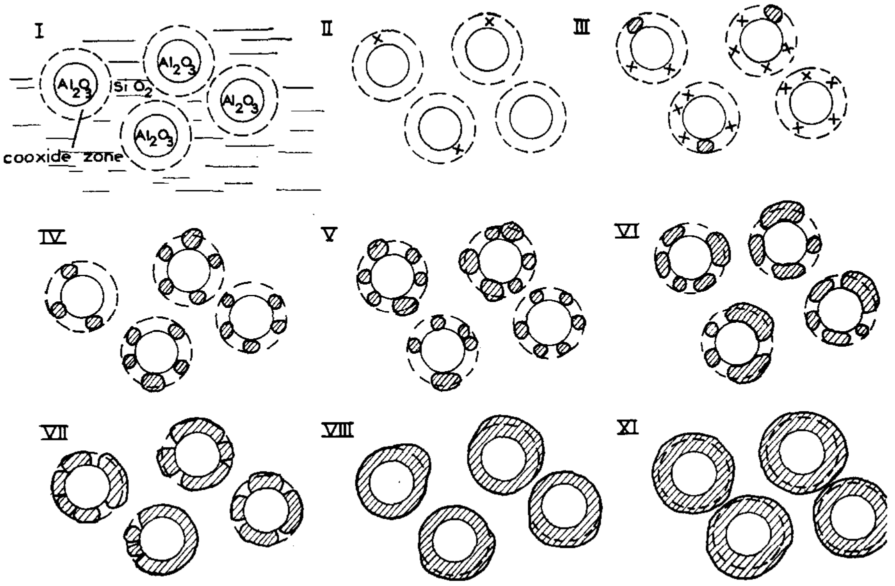

FIG. 3. Schematic changes in the surface of the carrier with increasing chromium contents.

involves more time. Then the co-oxide zones of the surface of the material are most probably elongated domains (*14*) of very small size because even upon heat treatment alumina particles cannot be identified by X-ray analysis (*15*). When the solid is impregnated with a very dilute solution of chromic acid, the chromium is fixed at specific positions of these zones distributed randomly (Fig. 3, II). As soon as the chromium content is large enough for all the co-oxide zones to be involved, the average distance between the chromium oxide domains corresponds to the distance between two domains in the same zone (III). When the chromium content increases, there is a tendency for the chromium to agglomerate around the initial positions so that the size of the domain grows regularly and the distance between two domains in the same zone decreases slowly (IV). The perimeter of each individual domain increases and also the catalytic activity. For increasing chromium contents, some domains begin to merge (V), giving rise to a discrete increase of the size of the domains, a decrease of the number of domains in the same zone, and a decrease of the perimeter of the domains. The two preceding processes counteract each other and the activity goes through a maximum (VI). More and more the domains cover the whole co-oxide zone, their size increases up to the size of the zone, their number decreases down to the number of the zones (VII, VIII), and their average distance becomes at first an average of the distance between the domains in the zone and the distance between the zones, and finally tends to correspond to the latter. Beyond 5% chromium, the evolutions of the size r and of the distance d cease (VIII–IX). The activity continues to decrease slowly because the optimum oxidation conditions of the chromium cannot be maintained, owing to the rapid reduction of clusters with large number of chromium oxide layers.

Such a picture shows that the assumption made to estimate the relative values of r and d is valid only for low chromium contents (up to step IV in Fig. 3), before the merging process occurs. After that, the domains are no longer isotropic; however, the conclusions remain qualitatively valid.

In the isolated chromium atom model for the site, as well as in our proposed model of active sites located at the boundary of the chromium oxide domains, the active chromium atoms are directly bound to the support. The main difference is in the presence of adjacent chromium atoms close to the active chromium atom in our model. Thus, it may be expected that the chromium content and the dispersion state of the chromium influence the activation conditions necessary to achieve the optimum activity. Such conditions, for instance, involve a pretreatment with hydrogen which has been shown to be very definite (*11*). The time of hydrogen treatment at 295°C which corresponds to the optimum activity is plotted in Fig. 4 versus the chromium content. The curve obtained is strikingly similar to that of Fig. 1, and suggests a direct correlation between the properties of the active sites and the average size of the chromium domains. In fact, the similarity implies that the amount of hydrogen necessary to reach the optimum activation is a direct function of the surface area covered by the chromium. Thus the reduction by hydrogen should be homogeneous for all the exposed chromium atoms and achieved progressively; however, the process is rather rapid around 300°C, so

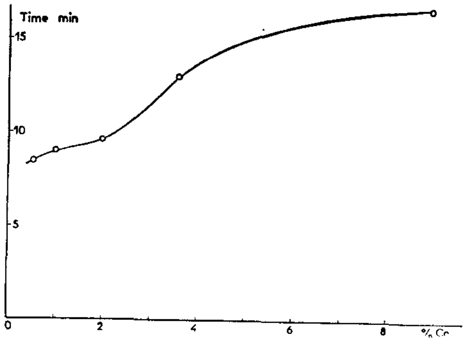

FIG. 4. Time (min) of hydrogen pretreatment at 295°C necessary to reach the maximum activity, versus chromium content (%).

that the sets of chromium atoms which, in our opinion, constitute the active sites at the boundary of the chromium domains are rapidly destroyed (reduced) if the activation pretreatment is continued beyond the optimum time. Conversely, before this optimum time, the probability of formation of these sets is at first rather low and increases suddenly when the average reduction approaches the optimum level, because the reduction process is homogeneous over the surface of the chromium domains.

Adsorption Measurements

A simple method described in a previous paper (*5*) allows the measurement of the reaction order versus the monomer concentration at every temperature where the activity is stable enough. It was first applied to catalysts after treatment leading to the maximum activity, the fixed temperature being 0°C, and the reaction was found to follow a Langmuir–Hinshelwood mechanism. For a chosen catalyst, the reaction order decreases to zero when the activity is destroyed. The decrease in activity may be controlled, for instance, by H_2 reduction of the catalyst. It suggests a saturation of the polymerization reaction when the activity decreases; this implies that the adsorption and polymerization centers are not the same and supports the idea that the active sites involve more than one chromium atom.

This method has been applied to identify the part of the catalyst which contributes to each phenomenon. In order to know whether the adsorption takes place on the chromium oxide surface or on the carrier surface, we have used two catalysts with very similar activities, namely, 1 and 3.6% Cr on silica–alumina. They are defined in Table 2 and they differ chiefly by their total Cr area. The reaction orders α at 0°C after adequate ethylene pretreatment at 145°C are 1 and 0.63, respectively. This difference can only be related to the difference in the free chromium areas since, for both catalysts, the chromium-in-monolayer areas and carrier areas are the same; that means that most of the surface chromium contributes to the monomer adsorption. So the ethylene adsorption appears not to be limited to the vicinity of the active centers and ethylene is transferred through the adsorbed layer in the direction of the active centers. This shows that the active centers are probably not isolated from the other chromium.

Some refinement can be brought to this, in order to show that the active centers effectively lie on the peripheries of the chromium domains. During the polymerization, the surface area of the catalyst has been found to decrease (*6*) to very low values together with the activity. As shown in the Appendix, the activity of the catalyst decreases according to an exponential law. This means that, if the activity is destroyed by a covering of the sites by the polymer, the sites are deactivated by their own production and not by that of their neighbors. It has been observed now that the reaction order decreases to zero during the polymerization. This fact suggests that when the active sites become progressively blocked, the adsorption area remains mostly uncovered.

The better explanation for all these results is that the active centers lie on the boundaries of the flat chromium domains where the ethylene is preferentially adsorbed, and that the polymer grows outside of these domains and hence covers mostly the area of the support uncovered

TABLE 2
PROPERTIES OF THE CATALYSTS WITH 1 AND 3.6% Cr

% Cr	S_{BET} (m^2g^{-1})	% Cr in monolayer	S_{Cr} (m^2g^{-1})	*k* activity at 145°C	α order at 0°C
1	515	0.46	8.3	11.1	1
3.6	430	0.47	20	11.1	0.63

with chromium oxide. Unfortunately, it is not possible to have a direct verification of this assumption because the measurement of the chromium area which involves severe thermal desorption treatment alters the polymer on the surface.

Location of the Sites on the Silica

According to the scheme presented in Fig. 3, the support is viewed as alumina spheres embedded in a silica matrix, which corresponds, owing to the composition of the solid, to the major part of the surface area. Because the polymer finally covers most of the surface area but leaves free the area covered by the chromium, we think that the active sites, located at the boundary of the chromium domains, are on the silica side of these domains. Such a view is in agreement with the conclusions drawn by Clark (*4*) from his hydrogen reduction profiles. These profiles show a tail at high temperatures for the catalysts with the maximum activity (2–3% Cr), which suggests that the active sites may correspond to Cr very difficult to reduce. In a previous paper of this series (*11*), it has been shown that, for catalyst supported on silica, the induction period observed in the absence of proper pretreatment and the time of hydrogen pretreatment necessary to reach the maximum activity are longer than for catalyst supported on silica–alumina. These results suggest that the chromium atoms corresponding to the sites bonded to silica are more difficult to reduce. Similarly, in the case of silica–alumina, the induction period and the pretreatment time both increase with chromium contents, and this suggests that, with increasing chromium contents, the chromium is spread preferentially on the silica part of the support.

OXIDATION DEGREE OF THE ACTIVE CENTERS

In the previous section, we mentioned that the active centers involve a set of chromium atoms with probably different oxidation degrees. In a previous paper (*5*), it has been shown that the optimum pretreatment with hydrogen leads to an average oxidation degree of 4 for the whole chromium. This suggests that, after the activation treatment but before contact with the monomer, the active center might involve a set of three chromium atoms, Cr^{3+}, Cr^{6+}, Cr^{3+}. Such a picture is favored versus another one consisting of an isolated atom in an intermediate valence state of 4 [as suggested by Eden *et al.* (*16*)] or 5 [as suggested by Kazanski and Turkevich (*10*)] because, as previously shown (*17*), there is no ferromagnetism which would correspond to Cr^{4+} atoms, and there is no direct correlation between the activity and the amount of chromium atoms responsible for the ESR signal of the γ-phase attributed to Cr^{5+}. This last point will be discussed more deeply in the following paper (*8*).

The last step of the activation of the site is done by the monomer and corresponds probably to a further reduction of the central Cr^{6+} atom of the site. Depending upon the temperature, this last step involves a relatively long time, which corresponds to the residual induction period necessary to reach the maximum activity, observed even after the optimum pretreatment by hydrogen (*5*). This time is shorter when the temperature is higher. In the absence of an optimum pretreatment, the induction period increases because the monomer has to reduce the chromium oxide to give birth to the active site. Because the reduction is homogeneous, the initial average oxidation degree reached after the activation treatment under air or nitrogen is not critical when it is higher than 4; this fact explains why the activity is not dependent on the atmosphere used for the activation treatment (nitrogen or air). The necessity for the monomer to make the last reduction step and to desorb the oxidized organic products of this reduction may also explain the fact reported previously (*6*), but not explained until now, that in the absence of pretreatment the reaction obeys at 145°C a second-order law versus the monomer pressure p if p is lower than 0.1 atm while in the same pressure range and at the same temperature the order becomes unity if the catalyst has been previously used at higher pressure.

It remains to know what is the final oxidation degree of the central atom of the site. There are a number of studies which advocate that the active sites correspond to Cr^{2+} atoms. Thus Krauss (*18*) has shown that, for low chromium contents, an activation treatment with CO leads to Cr^{2+} atoms, the number of which lies parallel with the polymerization activity. Other work (*19*, *20*) shows that Cr^{2+} organochromium compounds in a homogeneous medium are active catalysts for polymerization. Finally, the catalysts studied by the Union Carbide group (*21*, *22*) also involve supported organochromium Cr^{2+} compounds as active.

It may be suggested that a site formed by a Cr^{3+}, Cr^{6+}, Cr^{3+} set has an electronic configuration such as to allow the monomer to reduce the central Cr^{6+} atom directly to the Cr^{2+} state which is active, while the same Cr atom in the same position on the surface of the catalyst may be reduced to the Cr^{3+} inactive state if it is reduced through an incorrect activation treatment. Such a picture may explain well the sensitivity of the activity level to the exact conditions of the activation treatment.

Finally, it is to be noted that our new model of a set of chromium atoms for the active site is supported by a recent statement from Henrici-Olivé and Olivé (*20*), comparing the behavior of the Phillips catalyst and homogeneous chromium based catalyst for ethylene polymerization versus the transfer reaction on the monomer for the limitation of the molecular weight. They suggest that the high activity of the Phillips catalyst versus the transfer reaction might be explained only on the basis of a cooperative action of the chromium atoms adjacent to the site.

APPENDIX

Covering Process of the Surface by the Polymer

Two kinds of mathematical law are generally proposed to describe the covering process. They are said to be exponential and hyperbolic, respectively, in the simpler cases. With the integral reactor used for our experiments, the expressions are more complex.

Assuming that the blocking of the surface is only a local phenomenon, i.e., that each active center is blocked only by its own polymer, the instantaneous deactivation of sites is proportional to the amount of polymer. Denoting by d_0 and D the carrier gas and ethylene flows, respectively, k the activity, r the instantaneous conversion ratio (proportion of ethylene flowing through the reactor which is polymerized), and m the mass of catalyst, we obtain.

$$dk/dt = -\beta rD/m,$$

where β is characteristic for the blocking.

On the other hand, if the polymer formed by one center can cover the neighbors, the blocking is further proportional to the activity so that a square term appears:

$$dk/dt = -\beta'(rD/m)^2,$$

where β' replaces β.

The calculations which can be made from these two hypotheses depend on the conditions of the measurements, and we have to consider two main cases.

CASE 1: Experiments at 1 atm Pressure without Diluting Gas

There is no pressure gradient, and classical expressions (*17*, *18*) are found: exponential law for the local mechanism,

$$r = r_0 \exp(-\beta t);$$

hyperbolic law for the total mechanism,

$$1/r = 1/r_0 + \beta' Dt/m.$$

An experiment carried out in these conditions shows that the exponential law gives the best agreement (Fig. 5) but the difference is not conclusive and it is not evident that the mechanism is the same at lower pressure.

CASE 2: Experiments at 0.1 atm Pressure

In these conditions, the following system has to be solved for the exponential law:

$$dk/dt = -\beta rD/m,$$
$$km = rD - d_0 \ln(1 - r),$$

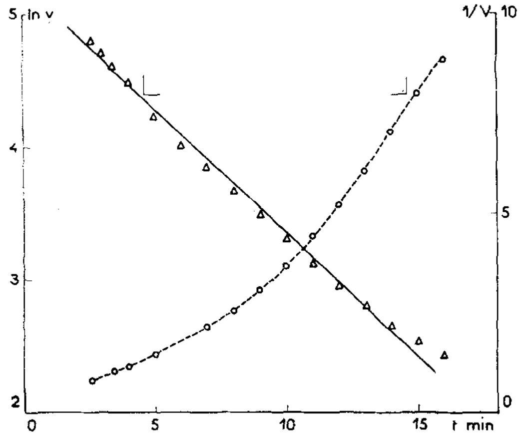

FIG. 5. Decrease of the activity according to exponential (△) and hyperbolic (○) laws at 1 atm pressure C_2H_4.

which gives, by eliminating, the differential equation

$$[D + d_0/(1 - r)]dr/dt = -\beta rD.$$

The solution is

$$(D + d_0) \ln r - d_0 \ln(1 - r) = -\beta Dt + \gamma,$$

where γ is a constant.

This law is well verified for conversion ratios varying from 0.7 to 0.05 as shown in Fig. 6. With the hyperbolic law, a simliar calculation leads to

$$-(D + d_0)/r + d_0 \ln(r/(1 - r)) = \beta' D^2 t/m + \gamma',$$

which is not in such good agreement with the experiment.

With the exponential law, the decreasing part of the kinetic curve would be linear in a large domain of conversion ratios (0.7–0.3). If rD is small compared with $d_0 \ln(1 - r)$, because $D/d_0 = 0.1$, we obtain

$$dr/dt = \beta r (1 - r) D/d_0,$$

which corresponds to an inflexion point at $r = 0.5$ and a linear part around this value. The kinetic curves allow that linear part to appear when the starting r is great enough. For a hyperbolic law, the linear part would be narrower and around the value $r = 0.65$.

It may be concluded that the deactivation process obeys an exponential law and then the active centers are not close together. But, since the size of the polymer molecules is rather large ($\bar{M}_n = 2000$ at 0.1 atm), the average distance between the sites is surprisingly large. A better explanation of these findings is to assume that the polymer chain is growing from the boundary of the chromium domains and spreads over the uncovered part of the carrier and not over the adjacent sites.

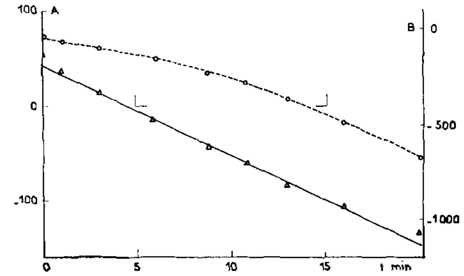

FIG. 6. Decrease of the activity according to exponential (△) and hyperbolic (○) laws at 0.1 atm pressure C_2H_4. $A = (D + d_0) \ln r - d_0 \ln(1 - r)$; $B = -(D + d_0)/r + d_0 \ln(r/1 - r)$.

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