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A Comparison of Cr/SiO$_2$ and Cr/AlPO$_4$ Polymerization Catalysts

I. Kinetics

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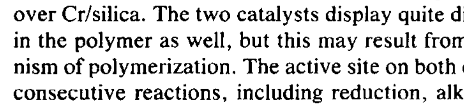
Ethylene polymerization over Cr/aluminophosphate has been examined and compared to that over Cr/silica. The two catalysts display quite different kinetics and produce important differences in the polymer as well, but this may result from slight variations in a common underlying mechanism of polymerization. The active site on both catalysts is seen as a transient species in a series of consecutive reactions, including reduction, alkylation, and decay. This model has been used to analyze and interpret the development and decline of activity under various polymerization conditions.

INTRODUCTION

The Phillips polymerization catalyst is made by depositing a chromium compound onto a wide pore silica and then calcining in oxygen to activate the catalyst. This leaves the chromium as a hexavalent oxide, monodispersed on the silica surface (*1*), probably as a surface chromate or dichromate ester.



When the catalyst is exposed to ethylene a series of reactions, shown in Fig. 1, take place. First the chromium is reduced, we believe to Cr(II) (*2*), although some workers argue for Cr(III) (*3–6*). Formaldehyde has been identified as one of the products (*7*). It probably coordinates to the chromium until displaced by ethylene. Next an initiation reaction alkylates the chromium and starts the first chain. Little is known about this step. The formation of an allyl species, as proposed by Krauss (*8*), is one of many possibilities. The new chain might start from either the H or the allyl. Then propagation occurs in which the chain grows as ethylene is added. Some think this happens through a carbene intermediate (*9–11*). Finally a chain transfer reaction terminates the chain and allows a new one to begin on the same active center. The transfer occurs through a beta hydride elimination.[1] Each chain, whose life is probably less than a second (*6, 12*), then has a methyl on one end and a vinyl on the other. The chain length is determined by the rate of propagation relative to chain transfer.

Each of these steps can be accelerated or retarded by the particular environment surrounding the active site. This gives the Phillips catalyst a remarkable sensitivity to even minor variations in catalyst purity, porosity, or calcining history (*13, 14*). Manufacturers of polyethylene sometimes consider it a nuisance, but this sensitivity also permits fine control of numerous polymer properties.

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[1] For clarity Fig. 1 shows the transfer reaction in two steps, where the H goes first to Cr, then to incoming monomer. However, several facts suggest that the process is concerted, or even that H is shifted directly to monomer. For example, increasing monomer concentration increases the propagation rate, but the increase in MW is not proportional, indicating that the transfer rate also varies with monomer concentration.

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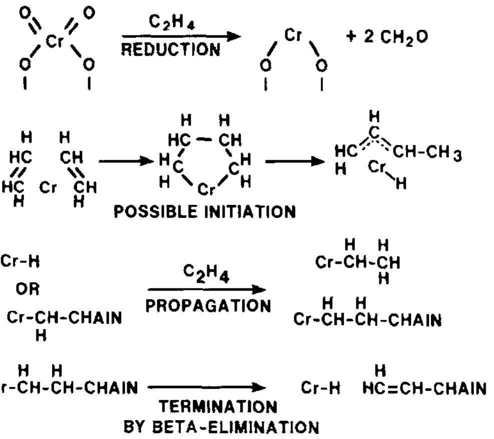

FIG. 1. Possible steps of polymerization over chromium oxide based catalysts.

The silica can also be replaced by a porous aluminum phosphate, which is isoelectronic and has nearly the same structure (*15*, *16*). Again hexavalent chromium is stabilized on the surface at high temperatures, and reduces on contact with ethylene to initiate polymerization. But on the surface these two supports exhibit quite different chemistry (*17*, *18*). Hydroxyls on AlPO$_4$ are more varied (P—OH and Al—OH) and more acidic, and the P=O species has no equivalent on silica. So the support becomes very influential, and many differences are seen between chromium oxide bound to silica versus AlPO$_4$, most notably the kinetics of polymerization.

We have found only two references describing Cr/AlPO$_4$ as a polymerization catalyst. In 1960 Kerber and Platz (*19*) at BASF noted that AlPO$_4$ could be used as a support for Cr to provide a polymerization catalyst. But the reported activity was extremely low (<10 g/g) and little other information is contained in the brief patent. In a more recent patent, Hill *et al.* (*20*) reported better activity (<1000 g/g-h). Their work was not confined to stoichiometric AlPO$_4$ but also extended to aluminophosphates having less phosphate.[2] They noted that unlike Cr/SiO$_2$, Cr/AlPO$_4$ had no induction time, but polymerized ethylene immediately after being introduced into the reactor. We too have confirmed this finding (*21*) and in this report we examine in further detail some of the differences between the two catalysts.

EXPERIMENTAL

Activity tests were conducted under slurry conditions at 95°C (unless otherwise stated) in a 2-liter stirred autoclave. A pressurized jacket filled with boiling alcohol held the internal temperature of the reactor constant to within 0.5°C. First, about 0.05 g of the catalyst was charged under dry nitrogen, then 1 liter of liquid isobutane diluent sometimes containing triethylborane, and finally ethylene was supplied on demand at 550 psig unless otherwise stated, until about 200–250 g of solid polyethylene had been made. Under these conditions the polymer does not go into solution but remains as a slurry. The rate of polymerization was followed by monitoring the flow of ethylene into the reactor through a calibrated dp cell. Isobutane and ethylene stock were Phillips polymerization grade, further purified through activated alumina and, in the case of isobutane, through a CO-reduced Cr/SiO$_2$ column.

Aluminophosphate catalysts were made for this study by quickly neutralizing a concentrated solution of aluminum nitrate and ammonium phosphate, usually in a ratio of P/Al = 0.8. For convenience we refer to this material as AlPO$_4$ in this report. After washing and drying, the support was then impregnated with an alcoholic chromium acetate solution to equal 1 wt% Cr.

To activate the catalyst, about 10 g was fluidized in a dry air stream for 3 h at 300–850°C, as specified in each experiment. A quartz tube was used with sintered glass disk to support the sample, which was raised to temperature at 400°C/h with the flow rate through the bed at 1 cm/sec. Gasses were predried through activated alumina or, where possible, through CO-re-

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[2] For convenience we will refer to aluminophosphates in general as AlPO$_4$.

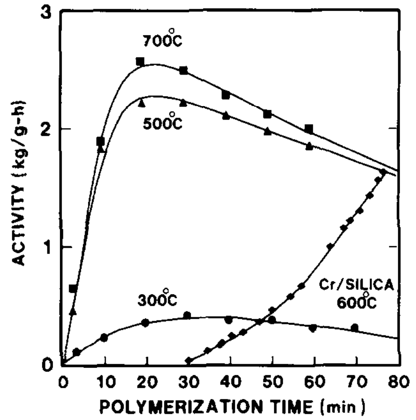

FIG. 2. Aluminophosphate was impregnated with Cr, calcined at 300, 500, 700°C, and charged to an autoclave where ethylene was supplied on demand. The rate of polymer formation is plotted against time. Cr/SiO_2 is also shown for comparison.

duced Cr/SiO_2. Surface areas after activation were as follows: 200°C, 370; 400°C, 335; 600°C, 315; 800°C, 300; 900°C, 260 m^2/g. More information concerning the structure of these catalysts can be found in Ref. (*22*). The silica used in this study was Davison Grade 952, having a surface area of about 280 m^2/g after activation at 600°C.

RESULTS AND DISCUSSION

Kinetic profile. The kinetics of ethylene polymerization over $Cr/AlPO_4$ are quite unlike that of Cr/SiO_2, as shown in Fig. 2. Here the rate of polymer formation is plotted against time for both catalysts where ethylene was supplied on demand to maintain a constant pressure. Typically, hexavalent Cr/SiO_2 does not immediately polymerize ethylene but first has an induction time which can last from a few minutes to over an hour, depending on conditions. This corresponds to the reduction step, from Cr(VI) to Cr(II) (*2, 12*), or at least to the desorption of redox by-products. Prereducing the catalyst to the divalent state by carbon monoxide at 350°C, eliminates the induction time but the gradual rise in activity is still often seen. This we attribute to the initial alkylation step (see Fig. 1).

In contrast we found the aluminophosphate supported catalysts polymerize ethylene immediately on contact. Usually the activity peaks within 30 min and then declines, as shown in Fig. 2. All samples display this activity pattern whatever their activation temperature or phosphate content. Thus the lack of an induction time suggests that reduction and/or desorption occur more easily on aluminophosphate than on silica. That the rate so quickly reaches its maximum, in contrast to Cr/SiO_2, further suggests that initiation must also occur more readily on the aluminophosphate supported chromium. We find this behavior on Cr/alumina catalysts too, which suggests that it may be associated with attachment of chromium to aluminum rather than to phosphate.

Activation temperature. In Fig. 2 a catalyst was calcined at 300, 500, and 700°C, and the activity improved with temperature. On silica this well-known phenomenon has been attributed to condensation of surface hydroxyls, which are believed to interfere with polymerization (*6, 13, 14*).[3] This same explanation may also hold for the aluminophosphate supports. Notice that the kinetic profiles of all three samples in Fig. 2 are nearly identical. Thus the number of active sites probably increases with temperature, but the character is not greatly affected.

Figure 3 shows several trends on $Cr/AlPO_4$ which are also typical of Cr/SiO_2 (*13*). Activity increases up to the point of sintering, in this case about 850°C, and then declines as surface area and porosity are

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[3] Possibly by coordinating to, and thus blocking, the active center. Although the figure is difficult to estimate, it is believed that only a fraction of the chromium is active. What distinguishes active from inactive chromium is not entirely clear but probably involves the extent of coordinative unsaturation around each site. Thus the location of coordinating groups on the surface, like O and OH, becomes important. See Ref. (*6*).

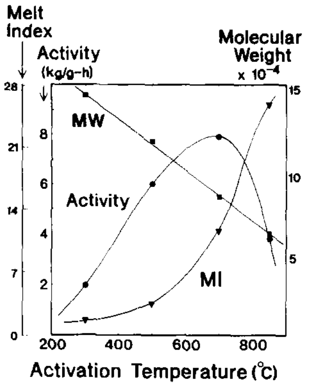
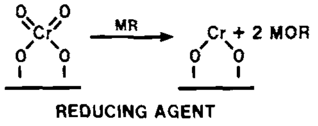
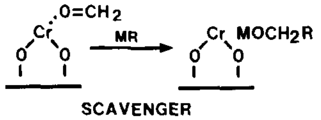


FIG. 3. The activity of Cr/AlPO$_4$ catalysts is enhanced by increasing the activation temperature, at least up to the point of sintering. This is true whether or not TEB is used as a cocatalyst. The chain transfer reaction, which determines the molecular weight of the polymer, is also accelerated, as can be seen here from the weight average molecular weight (MW) and the fluidity, or melt index (MI).

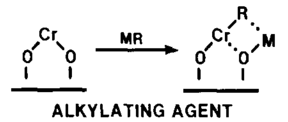
destroyed. The chain transfer rate, which determines the molecular weight of the polymer, behaves similarly, as shown in Fig. 3 by the weight average MW and the melt index, a measure of the fluidity of the molten polymer which is inversely related to the MW. These effects are thought to be a consequence of the changing hydroxyl population, which somehow interferes with the active site.

Promotion by cocatalysts. Metal alkyls have long been added to the reactor to promote the activity of Cr/SiO$_2$ catalysts (*25*). They can be strong reducing agents without forming inhibiting by-products, or they can also serve as powerful scavengers to remove the usual redox by-products. Thus the induction time of Cr(VI)/silica is usually eliminated by the addition of metal alkyl cocatalysts.





However, even prereduced Cr/SiO$_2$ catalysts are sometimes further activated by the metal alkyl, suggesting that it may also alkylate the chromium site, as happens on Ziegler polymerization catalysts.



This could explain why the increasing rate of polymerization so characteristic of Cr/SiO$_2$, and which was attributed above to alkylation, is not always found in the presence of metal alkyls. Instead the rate often tends to be more constant with time. An example of this is shown in Fig. 4, where the same Cr(VI)/silica catalyst of Fig. 2 was used in conjunction with triethylborane (TEB) cocatalyst.

The polymerization activity of Cr(VI)/AlPO$_4$ is also greatly enhanced by the addition of a small amount of metal alkyl to the reactor. A variety of agents are sometimes used, such as the alkyls of zinc, aluminum, or lithium, but those of boron are by far the most effective. In fact, the behavior of the boron alkyls is quite unique, both on the

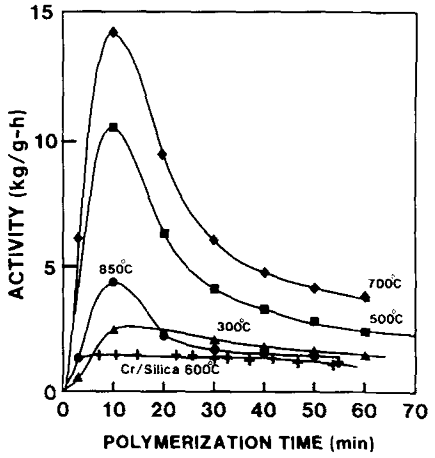


FIG. 4. Cr/aluminophosphate catalyst, calcined at 300, 500, 700, and 850°C, was charged to an autoclave containing triethylborane (TEB) in the isobutane diluent. Ethylene was supplied on demand and the rate of polymerization is plotted against time. Cr/SiO$_2$ with TEB is also shown for comparison.

activity of Cr/AlPO$_4$ catalysts, and also on chain transfer which is discussed in Part II of this series. Figure 4 plots the activity of the same catalysts used in Fig. 2, except that the isobutane diluent contained 5×10^{-5} mole per liter of triethylborane (TEB). Notice that the general pattern of activity was unchanged. A maximum is quickly reached followed by a declining rate of polymerization during the rest of the run. However, this peak activity is about five times higher in the presence of TEB, and the rise and decline sometimes occurred a little more sharply.

Usually about one mole of TEB per mole of chromium is sufficient to enhance the activity of the catalyst. However, the concentration of catalyst in the reactor (~50 mg/liter) is so dilute that an excess of TEB often further stimulates polymerization. TEB begins to inhibit polymerization when the excess increases much above fivefold.

Notice in Figs. 2 and 4 that TEB has an altogether different promotional effect on Cr/AlPO$_4$ than on Cr/SiO$_2$. The development of activity on Cr/SiO$_2$ is much accelerated by TEB, suggesting that it reduces and alkylates the usual sites, but there is rarely much change in the maximum rate of polymerization. In contrast, the kinetic profile of Cr/AlPO$_4$ is hardly affected by TEB, since reduction and alkylation already occur so rapidly. Instead the rate of polymerization is improved by about fivefold. This suggests that a vast new population of sites is created by TEB.

Notice also in Fig. 4 that the calcining temperature of the catalyst again determines the maximum activity. The highest polymerization rate is achieved in about 10 min with TEB whatever the temperature of calcining, indicating again that the sites formed at 300°C are reduced and alkylated as readily as those formed at 700°C despite the lower overall activity. The sample calcined at 850°C has a severely diminished polymerization rate, probably due to sintering.

Prereduction in CO. Cr(VI)/silica can be prereduced in carbon monoxide at 350°C to yield Cr(II), quantitatively if the support has been highly dehydroxylated (*2, 14, 26–28*), otherwise some Cr(III) is probably also produced (*26–28*). Cr(II)/silica is a pale green catalyst, highly coordinatively unsaturated, which strongly chemisorbs CO, olefins, and even nitrogen weakly. On contact with oxygen it immediately oxidizes back to the hexavalent form, producing a brilliant yellow chemiluminescence. CO-reduced Cr/SiO$_2$ polymerizes ethylene immediately, that is without the usual induction time, but otherwise the kinetic profile is not changed much. The polymerization rate still increases during the run, which we attribute to the initial alkylation of the site.

Cr(VI)/AlPO$_4$ can also be prereduced in CO at 350°C to yield a similar blue–green, presumably divalent, catalyst which flashes on contact with air. Unlike prereduced Cr/SiO$_2$, prereduced Cr/AlPO$_4$ catalysts exhibit exactly the same kinetic profile, shown in Fig. 5, as the oxidized parent. This is reasonable since, as we have already seen, reduction in the reactor is al-

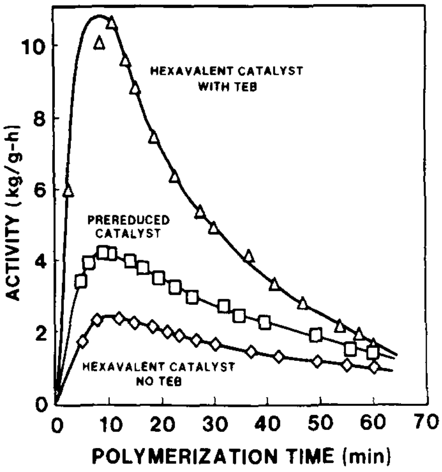


FIG. 5. Cr/aluminophosphate catalyst was calcined at 600°C in air, leaving most of the Cr in the hexavalent state. The polymerization activity of this catalyst with and without TEB additive is plotted against time. The hexavalent catalyst was then prereduced in CO at 300°C and its activity is also shown. It was not enhanced by TEB.

ready so fast. But the rate of polymerization is greatly enhanced by prereduction in CO, usually by as much as twofold. This again suggests a new population of sites which do not become active unless they receive some reducing help, probably those same sites which are also activated by TEB.

Notice in Fig. 5 that $Cr/AlPO_4$ catalysts reduced in CO are not quite as active as those reduced by TEB. Reduction in CO at 300°C may be more severe than reduction in the reactor at 95°C. Some rearrangement of the Cr at 300°C may result in a partial loss of activity (*2*). Reoxidation at 25°C is not as clean as is seen on silica (*14*). Instead of a bright orange, a brown catalyst is obtained, again suggesting some rearrangement. Some other catalysts, not shown in Fig. 5, were prereduced at 200°C, where the reduction was incomplete, and at 400°C, which again resulted in a pale blue catalyst but of greatly diminished activity. Therefore the best prereduction temperature seems to be 300–350°C, like Cr/SiO_2.

The role of TEB. The activity of CO-reduced $Cr/AlPO_4$ is not improved by the addition of triethylborane. Even the kinetic profile is little affected. This is understandable in terms of previous conclusions. These catalysts have already been reduced, so the TEB cannot enhance activity by acting as a reducing agent. Nor can it scavenge the by-products of reduction since the CO_2 was swept away at 300°C. But it could in principle still act as an alkylating agent. That the activity is not improved by TEB suggests that it normally activates the oxidized catalyst by reduction or by scavenging, but not by alkylation. Apparently alkylation is the slow step in the formation of activity whatever conditions are used.

Thus TEB probably enhances the hexavalent catalyst by creating, through reduction or possibly scavenging, a new population of sites. In one experiment the catalyst was first allowed to polymerize ethylene without TEB for 60 min. The rate peaked and then fell. Next TEB was added and during 10 min the rate soared again, this time to nearly 12 kg/g-h, about the same peak activity obtained from a virgin catalyst with TEB. Afterward the rate decayed normally as in Fig. 4. Thus the initial reduction, polymerization, and decay of activity had little effect on the later polymerization induced by TEB. TEB created new sites and might even have rejuvenated some dead sites. Once the TEB sites died, however, they could not be rejuvenated by more TEB.

The decay in activity. Two explanations for the sharp decline in activity in Fig. 4 come to mind: (1) the active sites undergo some chemical change; or (2) polymer build-up around the catalyst particle physically retards diffusion of ethylene to the active sites. The second possibility seems unlikely because otherwise all catalysts, even Cr/SiO_2 or silica supported Ziegler systems, should display similar kinetic profiles. As we have seen, they do not (*23*). Moreover, even a single aluminophosphate catalyst, like that in Fig. 4, yields grossly different amounts of polymer depending on the calcining temperature. Yet peak activity is always reached in about 10 min followed by a decline in rate, whatever the yield of polymer. If polymer build-up were responsible for the declining rate, one would expect the peak activity to occur at a constant polymer yield rather than at a constant time.

Instead the first explanation seems more probable, that the sites are chemically unstable, or become poisoned by some by-product of the polymerization. In one experiment with TEB, a second shot of TEB was added at the end of a 90-min run, when the rate had fallen to only about 15% of its previous maximum value. No rejuvenation of the catalyst occurred. At the end of another 90-min run the ethylene and isobutane diluent were bled out, leaving only the dry catalyst and accompanying polymer. These continued to be stirred in the reactor another 20 min at 100°C while hot nitrogen was flushed through to remove volatile poisons. Then the catalyst and polymer were

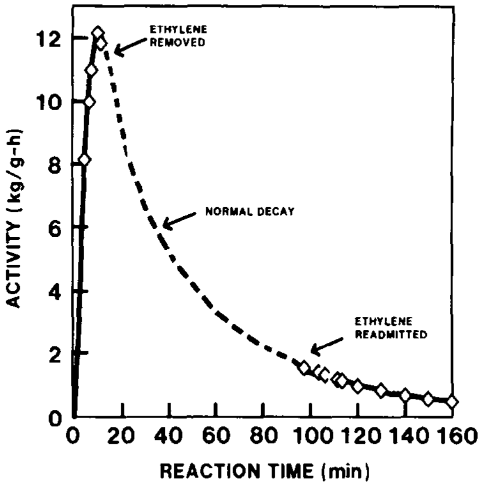


FIG. 6. Cr/aluminophosphate catalyst (600°C) was charged to an autoclave along with TEB/isobutane solution and ethylene. The ethylene was bled out after 13 min of polymerization, when the peak activity had just developed. The other ingredients remained in the autoclave at 95°C until 95 min had passed, when the ethylene was again admitted. Activity decayed normally even in the absence of polymerization.

washed several times in fresh isobutane at 95°C. Finally diluent, a fresh shot of TEB, and ethylene were readmitted, but again no resurgence of polymerization occurred. Thus whatever caused the decay in activity seems to be irreversible.

These conclusions are reinforced by a stopped flow experiment, shown in Fig. 6. Catalyst, diluent, TEB, and ethylene were charged to the reactor and polymerization started normally. However, the run was stopped 13 min later, just after peak activity had developed, by bleeding out the ethylene. Only ethylene was removed; catalyst, TEB, and diluent remained stirring in the reactor at 95°C another 82 min. Then ethylene was readmitted to the reactor after a total of 95 min. The polymerization rate did not return to the peak where it had left off, but instead continued at only about 15% of its previous activity. Thus, once formed, the active sites decayed normally even in the absence of polymerization. This confirms that the decay is not due to polymer build-up, neither is it caused by a poisonous side reaction of the polymerization itself. Instead the active sites seem to be genuinely unstable.

Apparently the site becomes unstable mainly after the initiation by ethylene. This is demonstrated by another experiment, shown in Fig. 7. The reactor was charged as usual with catalyst, diluent, and TEB, but not ethylene. It was then allowed to stir at the usual polymerization temperature (95°C) for 96 min before the ethylene was finally added. This was long enough for the usual decay to be well advanced had it occurred. Instead, we found the usual kinetics. The polymerization rate soared immediately after ethylene was admitted, the activity peaked 10 min later, and then the rate declined as usual. Thus even in the presence of a potential alkylating agent like TEB, these unstable sites were mainly formed after ethylene was admitted. However, the activity was reduced about 40% even though the kinetic profile remained unchanged.

Consecutive series reactions. Thus it seems reasonable to describe the active species as an intermediate in a series of

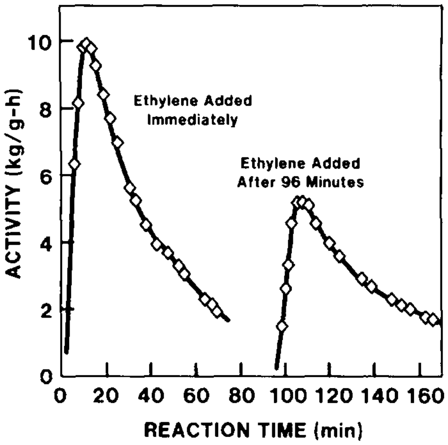
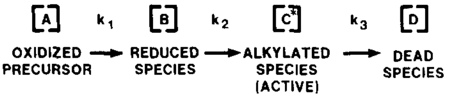


FIG. 7. Cr/aluminophosphate catalyst (600°C) was charged to an autoclave containing TEB/isobutane solution at 95°C. In separate experiments, ethylene was added either (A) immediately, or (B) after 96 min of stirring. The rate of polymerization is plotted for each case against time.

consecutive reactions, such as $A \rightarrow B \rightarrow C^* \rightarrow D$:



Applying this simple kinetic model provides the following expression for the concentration of active species C at time *t*.

$$[C] = k_1 k_2 \left[\frac{e^{-k_1 t}}{(k_2 - k_1)(k_3 - k_1)} + \frac{e^{-k_2 t}}{(k_1 - k_2)(k_3 - k_2)} + \frac{e^{-k_3 t}}{(k_1 - k_3)(k_2 - k_3)} \right]$$

Since only a portion of the chromium is potentially active, [C] is not given in absolute terms but as a fraction of this unknown population. If we then assume that the measured polymerization rate at time *t* is proportional to the concentration of active species, we have

$$\text{Activity} = R[C]$$

Where *R* is the polymerization rate expected if all of the site population were present as the active species C.

Using iterative nonlinear regression, the above expression can be fit nicely to the data described in this report. In fact, the lines drawn in Figs. 4–10 were obtained from this equation (the points are experimental), giving a numerical analysis of the rates of formation and decay of activity. The model cannot distinguish between k_1 and k_2; a similar curve is obtained if the two constants are reversed. Therefore we always took the smaller of the two calculated constants to be k_2, because as we have already seen, the reduction is rapid and it is the initiation that seems to be the slow step in the formation of activity.

Using this approach, we find the following: typically about 75–85% of the potentially active site population exists as the active species C at peak activity. The activity constant *R*, which should include the active site density, increases fivefold on addition of TEB, and twofold by prereducing the catalyst in CO. As expected, TEB increases the decay rate k_3 by 50–100%. Prereducing in CO does not appreciably change k_2. Again, only the numerical values come from the model; we reached these same qualitative conclusions by just looking at the kinetic profiles.

Validity of the model. Obviously the model above is oversimplified. For one thing, the catalyst probably contains a diversity of sites, each with its own characteristic rates of formation and decay. The model deals only with the average site. And each of these consecutive reactions may involve multiple steps. For example, the step $A \rightarrow B$ must involve both reduction and desorption, and each of these may involve still further consecutive steps.

In addition to the three-step model above, a four-step model was also explored ($A \rightarrow B \rightarrow C \rightarrow D^* \rightarrow E$), which introduces another parameter k_4. This rarely improved the fit to an appreciable extent; instead it usually reproduced the fit obtained from the three-step model by setting one of the formation constants (k_1, k_2, or k_3) much greater than the others. A two-step model was also tried ($A \rightarrow B^* \rightarrow C$) in which all of the site formation steps were lumped into one rate constant k_1. This provides a fair fit to the data in many cases, particularly where one step dominates the others, but is often clearly inferior to the three-step model.

Dependence of rate constants on ethylene. We have already observed in a qualitative way that the formation of active sites depends on the presence of ethylene, but their subsequent decay does not. This suggests a slow initial alkylation reaction in which the first ethylene is incorporated. In one experiment, four runs were made at 95°C which differed only in the ethylene pressure applied to the reactor. These are shown in Fig. 8. As the ethylene concentration increased, obviously the overall activity also increased, but in addition the rate of formation of active sites was likewise enhanced. Thus in Fig. 8 the peak activity took less time to develop as the ethylene pressure was increased.

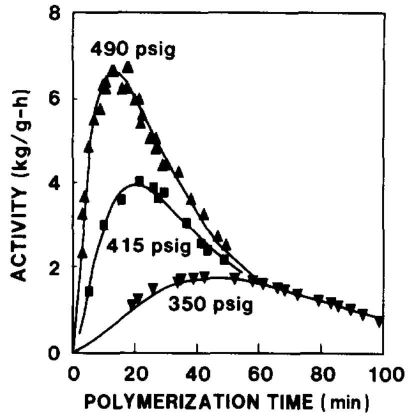


FIG. 8. Cr/aluminophosphate catalyst (600°C) was charged along with TEB/isobutane solution to an autoclave at 95°C where ethylene was supplied on demand at the pressures indicated. The lines shown were fit to the data using the model A → B → C* → D.

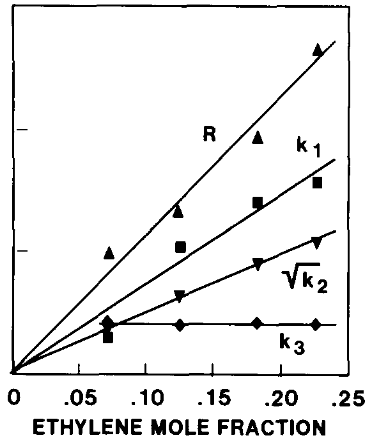


FIG. 9. The model A → B → C* → D was fit to polymerization data collected at different pressures. The linear plots suggest a second-order dependence on ethylene for k_2, the rate-limiting step in the development of sites, zero order dependence for the decay of sites (k_3), and first order for the polymerization itself (R).

Nonlinear regression was applied to the data in Fig. 8 to generate a fit to the three-step model (the equation above) and the resulting curves are plotted in Fig. 8 as solid lines through the data points. The computed rate constants, shown below in Table 1, buttress our earlier conclusions, because k_1 and k_2 increased with ethylene pressure whereas k_3 did not.

In Fig. 9 the fitted model parameters are plotted against ethylene concentration in the reaction diluent. The plot of k_1 yielded a rough line passing through the origin, suggesting first-order dependence. This could be taken as support for the reduction shown in Fig. 1, which requires one ethylene per chromium. However, we cannot identify k_1 as the reduction step with certainty. It could also be a desorption or a part of the alkylation step, with reduction occurring too rapidly to be noticed.

TABLE 1

Rate Constants Determned from Runs at Various Pressures

Ethylene pressure, psig	Ethylene mole fraction	k_1	k_2	k_3	R
550	0.2270	0.50	0.30	0.032	13.5
490	0.1825	0.45	0.21	0.033	9.9
415	0.1250	0.33	0.10	0.031	6.8
350	0.0725	0.09	0.03	0.032	5.0

Another straight line passing through the origin is also obtained from the square root of k_2. This suggests second order dependence of k_2 on ethylene. As we observed earlier, the slow step in the development of activity k_2 can be ascribed to alkylation, but the exact mechanism of initiation is unknown.

Also plotted in Fig. 9 is k_3, the rate of decay, which does not depend on ethylene, and R. If we assume in these four experiments that the number of potentially active sites is constant, because each used the same catalyst reduced by TEB at 95°C, then R might be taken as an indication of the rate of polymerization per site. Thus the linear plot of R in Fig. 9 suggests an approximate first-order dependence for the polymerization itself, which agrees with reports on Cr/SiO$_2$ catalysts (*29, 31*).

Temperature dependence. Figure 10

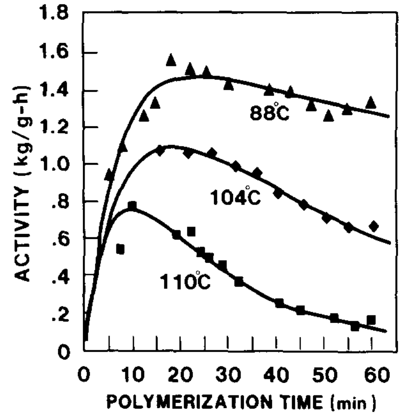


FIG. 10. Cr/aluminophosphate catalyst was allowed to polymerize ethylene at the temperatures shown. The ethylene pressure was adjusted in each run to provide the same concentration of ethylene in the isobutane solvent. The higher the temperature, the more rapidly the activity decayed.

shows three kinetic profiles typical of a $Cr/AlPO_4$ catalyst when allowed to polymerize ethylene at different reactor temperatures. In each case the ethylene pressure was adjusted to compensate for ethylene solubility in the isobutane solvent, which also changes with temperature. Thus the ethylene mole fraction remained at 0.175 for each run. Little effect is apparent on the formation of activity, but the decay is greatly accelerated by increased reactor temperature. Again the model equation above has been fit to these and other runs, and a strong trend of increasing k_3 with increasing temperature is evident. Figure 11 shows an Arrhenius plot of this dependence, giving an activation energy for the decay of active sites of about 26 kcal/mole, which is consistent with a chemical rather than physical deactivation.

Notice also in Fig. 10 that the overall activity of the catalyst declines with increasing reactor temperature. In fact, both the overall yield per hours, as well *R*, go through a maximum at about 93°C, which is shown in Fig. 12. Maxima have also been reported for Cr/SiO_2 at 80°C (*29*), for chromocene/silica at 60°C (*30, 31*), and for Ziegler systems (*32*). The cause is not understood, but is thought to indicate a complicated polymerization scheme, such as in Fig. 1.

The dead species. Having little evidence, we can only speculate about the identity of the terminal species D. Possibly the normal polymerization mechanism takes a bad turn on rare occasions, through a hydride shift or other rearrangement, yielding a crippling

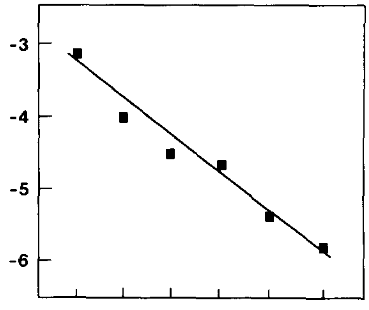


FIG. 11. Cr/aluminophosphate catalyst was allowed to polymerize ethylene at the temperatures shown, the pressure adjusted to provide a constant ethylene concentration. The log of the rate constant k_3, which measures the decay of activity, has been plotted against the reciprocal of the run temperature. The slope of the linear plot provides an activation energy for the decay of about 26 kcal/mole.

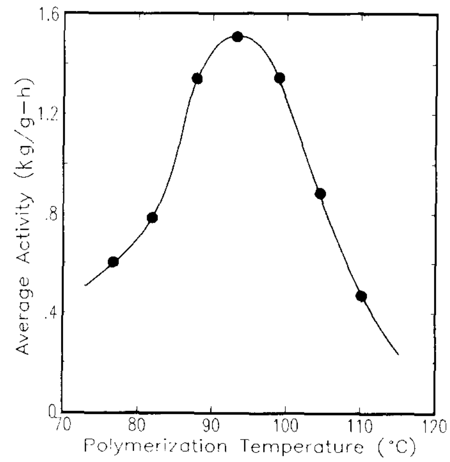


FIG. 12. Cr/aluminophosphate catalyst was allowed to polymerize ethylene at various temperatures, the ethylene concentration held constant. Plotted above is the yield of polymer obtained in 1 h.

product. We do notice that some conditions which favor chain termination also favor decay (high reactor temperature, high TEB concentration, high calcining temperature). But as we have seen in Fig. 6, the decay continues even in the absence of polymerization.

Another suggestion is that the Cr alkyl is somehow oxidized by the support. Surface hydroxyls might be involved. However, they are probably not very mobile at 95°C where polymerization is carried out, and we have seen no evidence that dehydroxylating the support retards the decay. Perhaps the phosphate groups are reactive. This would explain why Cr/$AlPO_4$ catalysts decay while Cr/SiO_2 does not. But Cr/alumina catalysts also display a kinetic profile like those reported here. For the present, the mechanism of decay remains mysterious.

Other catalysts. The model can also be used to describe the kinetic profile of other catalysts, such as Cr/SiO_2. It provides a fair fit to the data when Cr/SiO_2 has a short induction time, but it breaks down for runs such as the example in Fig. 2, where the induction time was about 30 min. Increasing the complexity of the model to four steps ($A \rightarrow B \rightarrow C \rightarrow D^* \rightarrow E$) improves the fit to Fig. 2, but it takes five steps to provide an adequate fit.

This behavior probably results from several reactions in series, each being slow enough to influence the formation of active sites, and the rate of each step varying considerably among sites. We know the initial reduction step (and/or the desorption of byproducts) is slow on Cr/SiO_2 because prereducing the catalyst in CO eliminates the induction time (*14*). Then the activity gradually rises during the next hour or two, whether or not the catalyst has been prereduced, suggesting that alkylation also governs the rate of active site generation. Although active sites are formed more slowly on Cr/SiO_2, they are apparently more stable because declining activity is rarely observed.

In Fig. 4 is an example of Cr/SiO_2 run with TEB. There is no induction time and no gradual rise in rate, only an instant generation of activity followed by a barely discernible rate of decay. This suggests that on Cr/SiO_2 the TEB can indeed act as an alkylating agent, as well as a reducing agent.

Ziegler catalysts also display this same kinetic profile, and more interesting, organochromium compounds deposited on oxide or phosphate carriers. Examples of the latter are β-stabilized alkyls of Cr(II), diarene Cr(0) compounds (*33*), or chromocene (*30, 31, 34*). Typically the maximum polymerization rate is reached quickly after the catalyst is introduced into the reactor, then the rate declines during the rest of the run. Since these compounds are already reduced, there is no induction time. It is still unclear whether these compounds can be considered as already alkylated, but even if not, they initiate extremely rapidly.

CONCLUSIONS

The unusual activity profile of Cr/$AlPO_4$ catalyst is probably due to the gradual formation and death of an unstable active species. The reduction of Cr(VI) to a lower valent species, presumably Cr(II), occurs quickly and therefore has little influence on the kinetics. Instead the rate-determining step in the development of activity is the alkylation of Cr, which is primarily affected by ethylene concentration. The death of the active species, which may result from oxidation by the support, is accelerated by higher reactor temperatures. Although reducing agents like TEB do not change the kinetics much, they are highly effective at promoting activity, probably by creating a new population of active sites. To do this TEB acts as a reducing agent or as a scavenger, but not as an alkylating agent.

These same factors probably also determine the quite different kinetic profile exhibited by Cr/SiO_2 catalysts. However, these sites are slower to form, and once formed, slower to die. Thus reduction does become a rate-determining step on Cr/SiO_2, comparable to alkylation. Metal alkyls accelerate the development of activity by accelerating the reduction and possibly also the alkylation of Cr. But unlike the Cr/$AlPO_4$ catalysts, there is no hint that a vast new population of sites is created on silica.

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