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Ethylene Polymerization Catalysts from Supported Organotransition Metal Complexes

III. Support Interactions

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During the polymerization of ethylene, supported chromium catalysts display a strong interaction with the carrier, which affects the molecular weight of the polyethylene produced at a site. As a consequence, size exclusion chromatography (SEC) of the polymer sometimes provides evidence for different types of sites. In this study organochromium compounds and chromium oxide were deposited onto aluminas, aluminophosphates, and silicas treated in various ways. SEC traces of the resultant polymers suggest interaction of the Cr with Al, P, Si, and Ti.

INTRODUCTION

Researchers working with the Phillips Cr/silica polymerization catalyst often speculate that it contains a wide variety of active sites due to local heterogeneity on the support. This is suggested by variations in the energies of reduction or chemisorption which have been observed between sites (*1–5*). During ethylene polymerization these sites probably also differ in their propagation and termination rate constants. Chain transfer, or termination, occurs continuously during polymerization through β-H elimination as shown by

$$\begin{aligned}&\mathrm{CH_2{=}CH_2}\\&\quad \mathrm{Cr{-}CH_2{-}CH_2{-}chain} \rightarrow\\&\qquad \mathrm{Cr{-}CH_2{-}CH_3 + CH_2{=}CH{-}chain}\end{aligned}$$

Thus each type of site produces its own characteristic molecular weight of polymer since the chain length is determined by the rate of propagation relative to termination. This would explain why the molecular weight distribution of polymer from Cr/silica is broad. The ratio of the weight average to the number average molecular weight (M_w/M_n), a common measure of the breadth of the MW distribution, ordinarily ranges from 8 to 30. In contrast, a value of approximately 2.0 is expected from a single type of site (*6, 7*).

Indeed, a large body of evidence does suggest that polymerization sites can be influenced by the local environment. When the calcining temperature of Cr/silica is increased, starting at 500°C and proceeding to 900°C, the activity increases and the average molecular weight of the resultant polymer declines (*8, 9*). This suggests that the sites somehow change as the silica becomes dehydrated. Perhaps hydroxyl groups coordinate or otherwise interfere with surface-bound chromium sites. Or the surface strain introduced by the condensation of hydroxyls may influence the chromium site.

Various modifiers can also be added to the catalyst and these have an effect on the molecular weight of the polymer or its MW distribution. Fluoride, which takes the place of hydroxyls, sometimes tends to narrow the distribution and to increase the average chain length (*10*). Titania, on the other hand, tends to shorten the chain length and broaden the distribution (*11–13*).

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Substituting another support for silica, such as alumina or aluminophosphate, also affects the polymer generated (*14–16*).

All these facts, and others, argue that the chromium polymerization site is influenced by its local environment—the metal to which it is attached and the ligands surrounding it. Indeed, earlier reports in this series (describing pentadienyl and alkyl derivatives of Cr) examined the effect of unusual organic ligands on the polymerization. But the carrier is also a ligand and can play an equally important role. In this paper we report some work with organochromium catalysts which provide more visible confirmation of the surface heterogeneity often postulated. Because different types of sites can produce different chain lengths, the MW distribution of the polymer furnishes some insight into the diversity of sites.

EXPERIMENTAL

In the preparation and handling of organochromium compounds all operations were conducted under a nitrogen atmosphere. Solvents were freshly distilled from calcium hydride or Na/benzophenone under nitrogen, or in some cases they were passed through a CO-reduced Cr/silica column. Chromocene was purchased from Strem Chemical Co. and used without further purification. The 2,4-dimethylpentadienyl derivative of chromium (II), or $Cr(DMPD)_2$, was made according to Ref. (*17*). Dicumene Cr(0) was obtained from Aldrich Chemical Co. Another compound of Cr(II), octakis (μ-trimethylsilylmethyl) tetrachromium(II), or $Cr_4(TMSM)_8$, was prepared as previously described (*18*), and $Cr(mesitylene)_2$ according to Ref. (*19*).

The catalyst supports used in this study were all of high porosity, suitable for polymerization catalysts. The preparation procedure and the physical properties of the aluminophosphate supports have already been described in some detail (*20*). Pore volumes varied around 2.0 cm^3/g depending on the P/Al ratio of the support, and surface areas around 300 m^2/g. The silica used was Davison grade 952, which has a total porosity of 1.6 cm^3/g and a surface area of about 280 m^2/g. To activate the support, 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, as previously described (*20*).

Catalysts were prepared by slurrying about 5 g of the calcined support in dry heptane. The organochromium compound was then added to make the resultant catalyst about 1% Cr by weight. Usually all of the chromium adsorbed onto the support. Any unadsorbed Cr was rinsed away by three pentane washes; then the excess pentane was evaporated at <50°C. Chromium oxide-based catalysts were prepared by impregnating the uncalcined support with an alcoholic solution of chromium (III) acetate, drying the catalyst under vacuum at 100°C, and then calcining as described above. This treatment converts the chromium, again about 1% by weight, into the hexavalent oxide.

Ethylene polymerization was conducted under slurry conditions at 95°C in a 2-liter stirred autoclave, as previously described (*15*). Unless otherwise stated, each run was made with 10 psig (69 kPa) hydrogen in the reactor. Size exclusion chromatography on the polymer was done at 140°C on a Waters Model 150 GPC equipped with infrared detector. The solution concentration, 0.25% polymer in 1,2,4-trichlorobenzene, was chosen to give reasonable elution times.

RESULTS AND DISCUSSION

Aluminophosphate Supports

Organochromium compounds such as those used here are not usually active for ethylene polymerization until they have been deposited onto an oxide carrier of high porosity and surface area. Generally it is believed that they attach to the surface by reacting with hydroxyl groups, often losing one ligand in the process (*21–25*):

$$-\mathrm{OH} + \mathrm{Cr(lig)_2} \rightarrow -\mathrm{O{-}Cr{-}lig} + \mathrm{lig{-}H}.$$

The diarene Cr(0) compounds may undergo oxidation to Cr(I) since a strong ESR signal develops and H_2 is evolved (*25*). Why the support is necessary for polymerization to occur is a mystery. Possibly it prevents the active species from reacting with each other (*26*).

One type of support which functions well as a carrier for most of these organochromium compounds is the aluminophosphates (*14–16, 20*). Under the typical slurry polymerization conditions which were used in these experiments, activity usually ranged between 1–5 × 10^5 g-polymer/g-Cr/h, or turnover frequencies often as high as 500 mol ethylene/mol Cr/s, depending on the particular chromium compound. The diarene Cr(0) complexes tended to be most active. Figure 1 shows the size exclusion chromatography (SEC) of polymers made by various organochromium compounds supported on aluminophosphate carrier. In these and other experiments, a bimodal molecular weight distribution was nearly always obtained, i.e., two peaks in the SEC. The exception was chromocene which terminates by hydrogenation rather than by the usual β-H transfer (see Ref. (*21*) for further explanation).

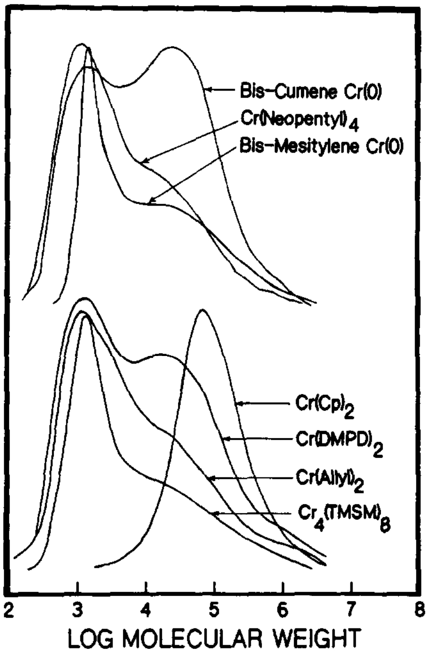
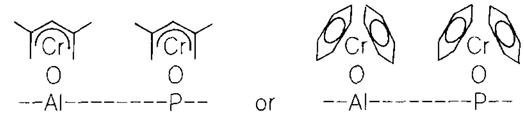


FIG. 1. Size exclusion chromatograms of polyethylene obtained from various catalysts, each made by depositing an organochromium compound onto an aluminophosphate (P/Al = 0.9) support calcined at 700°C.

Note in Fig. 1 that the type of chromium compound can vary widely. The initial oxidation states included Cr(0), Cr(II), and Cr(IV). And the organic ligand can be charged on neutral, π- or σ-bonded. Although the exact size and position of the two SEC peaks differed somewhat from one organochromium compound to another, all produced a broad bimodal MW distribution. This was not usually observed on silica or alumina, only on the aluminophosphates. Therefore the presence of two peaks seems to be connected to the choice of support.

Infrared bands from two types of surface hydroxyl groups on aluminum phosphate have been reported, one attached to phosphorous and one to aluminum (*27*). This is probably a characteristic of the aluminophosphates in general, i.e., materials other than stoichiometric $AlPO_4$ (*20*). Therefore reaction with an organochromium compound could conceivably generate two types of active sites, and these may be responsible for the two MW's of polymer generated. Thus when bis-2,4 dimethylpentadienyl Cr(II) or bis-benzene Cr(0) (*28*) reacts with an aluminophosphate support the two sites might be as shown in Scheme 1.



SCHEME 1

Whether these ligands remain attached after polymerization begins is unclear. On the bis-2,4 dimethylpentadienyl Cr catalysts, polymerization could conceivably initiate by a rearrangement of the pentadienyl group to its monohapto form, followed by insertion of ethylene into the Cr–alkyl bond (*21*). On the diarene Cr(0) catalysts, however, alkylation by ethylene must somehow take place, again possibly displacing ligands (*21*).

Since these carriers were made by coprecipitation of aluminum and phosphate ions (*20*), the amount of phosphate in the carrier can be varied over a wide range. Figure 2 shows the SEC traces of polymers made from bis-2,4-dimethylpentadienyl chromium (II), or Cr(DMPD)$_2$, deposited on aluminophosphates in which the P/Al ratio was varied from 0.0 (alumina) to 0.9 (almost AlPO$_4$). The ratio of the two SEC peaks was found to vary with the amount of phosphate in the carrier, and the alumina catalyst produced only one SEC peak. Treating the alumina carrier with a small amount of phosphoric acid and recalcining brought back the low MW peak (*25*). Thus the low MW peak seems to be associated with phosphate in the carrier and the high MW peak with aluminum.

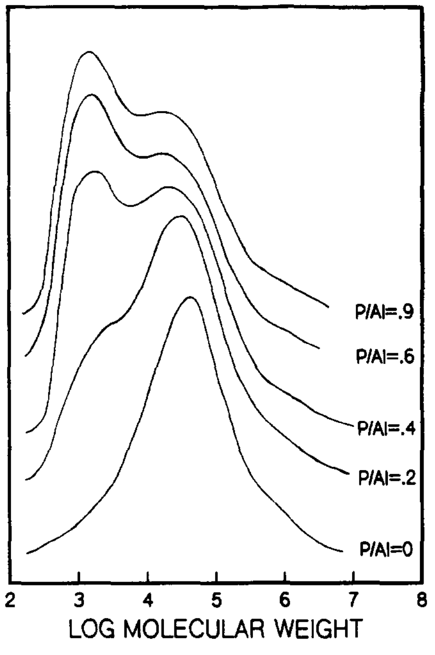
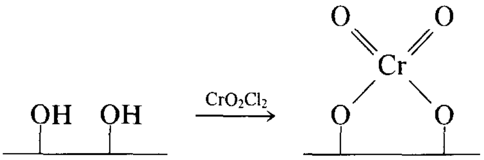


FIG. 2. Size exclusion chromatograms of polyethylene obtained from the catalyst Cr(DMPD)$_2$ on various aluminophosphates calcined at 700°C. Only the amount of phosphate in the support, i.e., the P/Al ratio, varies in each case.

Reacting these same aluminophosphate carriers with silanes provided further insight into this phenomenon. After treatment with hexamethyldisilazane two surface –Si(CH$_3$)$_3$ species could be detected by Si-29 solid state MAS–NMR. The chemical shifts corresponded to P–O–Si(CH$_3$)$_3$ and Al–O–Si(CH$_3$)$_3$, and again their intensity varied according to the P/Al ratio of the carrier. These experiments are being reported elsewhere (*29*).

The behavior of these organochromium catalysts was different from that of catalysts based on chromium oxide, which yielded only a single broad SEC peak. They are usually made by aqueously impregnating a chromium compound onto the support, then calcining at a high temperature (*30*). The chromium is thought to attach to the support through two links, rather than just one, (*31*, *32*). For example chromyl chloride vapor reacts with a fully hydrated silica to yield a chromate surface species which becomes active for ethylene polymerization (*33*). Dichromate species have also been postulated and may coexist in small quantities on some catalysts (*31*, *32*).



Thus chromium oxide on aluminophosphate should also contain different types of active species, and reaction of the support with difunctional silanes, such as Me$_2$SiCl$_2$, suggested this. Solid state NMR of such silated supports indicated silane species attached to Al/P, Al/Al, and possibly P/P (*29*). Unfortunately, SEC traces of polymers from chromium oxide catalysts were never so well resolved into individual peaks as is characteristic of the organochromium catalysts. Apparently differences between sites of a given type were greater than differences between the types (i.e., the SEC peaks overlap too much). Perhaps the strain introduced by two attachments becomes a factor, or perhaps there were just too many types of sites for resolution. Some examples are shown in Fig. 3.

One indication that the chromium oxide-based catalysts can also have different types of sites is the different response to reactor additives. For example upper Fig. 3 shows the SEC's of two polymers obtained under different conditions. One was a simple homopolymer; the other was a copolymer made in the presence of triethyl borane (TEB) and 1-hexene, both of which can act as mild chain transfer agents (*15, 16, 30*). (That is, 1-hexene and TEB tend to accelerate the termination reaction, possibly by displacing the growing chain from the site.) The carrier used in this experiment contained a low phosphate level, i.e., P/Al = 0.2. The SEC trace was shifted to slightly lower MW by the transfer agents but the basic shape of the curve was little changed. In contrast lower Fig. 3 repeated the experiment but with a high phosphate catalyst, P/Al = 0.9. Here the additives produced a much narrower molecular weight distribution, suggesting that some of the sites responded more than others. The overall shift to lower MW was also more pronounced, which we attribute to the influence of the phosphate (*16*).

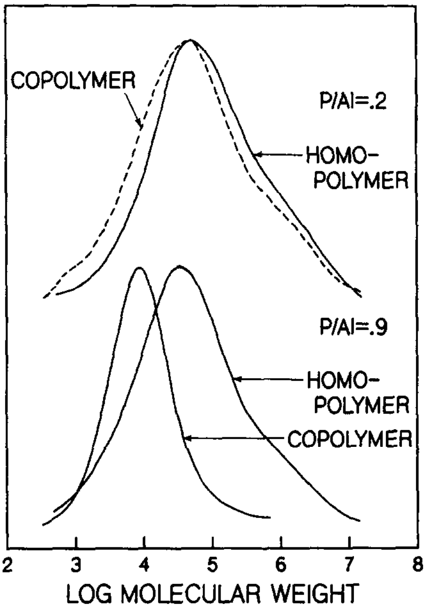


FIG. 3. Size exclusion chromatograms of polyethylene obtained from chromium oxide on aluminophosphate carriers calcined at 600°C. Two carriers are represented, containing high and low phosphate, and two reactor conditions. Homopolymer: no additives. Copolymer: 8 ppm triethylborane and 20 ml hexene added to reactor.

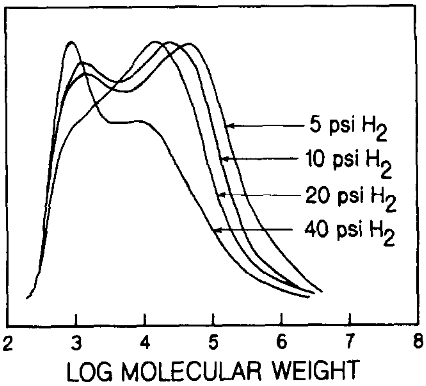


FIG. 4. Size exclusion chromatograms of polyethylene obtained from $Cr(DMPD)_2$ on calcined aluminophosphate (0.9 P/Al, 600°C). The amount of hydrogen in the reactor during polymerization was varied.

The two types of sites on the organochromium catalysts also displayed different sensitivities to additives. Hydrogen, for example, another common transfer agent, usually (but not always (*21, 25, 30*)) shortens chains by hydrogenation, as shown by

$$\begin{aligned}&CH_2{=}CH_2\\ &\quad Cr{-}CH_2{-}chain + H_2 \rightarrow\\ &\qquad\qquad Cr{-}CH_2{-}CH_3 + CH_3{-}chain.\end{aligned}$$

Figure 4 shows the SEC traces of four polymers made from dicumene Cr(0) on aluminophosphate, each with a different amount of H_2 in the reactor. Note that H_2 significantly shifted the high MW, Al-associated peak to lower MW, while the phosphate-associated peak was less affected. The result was a narrowing of the distribution. $Cr(DMPD)_2$ catalysts also displayed this trend, as well as chromium oxide on aluminophosphate. Table 1 summarizes results from various chromium compounds on aluminophosphate support with different amounts of hydrogen added to the reactor.

Other examples of the two types of sites behaving differently could be seen in poisoning experiments. Polar or other coordinating ligands are usually strong poisons for all the Cr-based catalysts, probably because they inhibit the adsorption of ethylene onto the site. The diarene Cr(0) compounds were less sensitive than most, but they too were affected. Upper Fig. 5 shows the SEC trace of polymer made from dicumene Cr(0) on aluminophosphate in which 61 μmol/liter of ethanol was added to the reactor (3.5 EtOH/Cr, or 2.3×10^{-5} EtOH/C_2H_4). Activity dropped to about 10% of its former value. Note in Fig. 5 that the high MW peak seems to have been preferentially diminished. Apparently these sites (the Al-associated sites) were inhibited more than the sites associated with phosphate.

In another series of experiments using bis-benzene Cr(0) on aluminophosphate, the polymerization time was varied so that polymer yield varied from 150 g polymer/g catalyst to over 2300 g/g. However, no difference in the product was found. Thus the results from the above poisoning experiments do seem to indicate a preferential inhibition of one site over the other.

TABLE 1

Effect of Hydrogen on the MW Distribution

psi H_2:	0	5	10	20	40
Dicumene Cr					
M_w	High	94,800	52,800	50,400	31,500
M_w/M_n	—	39.7	23.4	20.8	19.2
$Cr(DMPD)_2$					
M_w	High	—	66,200	60,300	43,900
M_w/M_n	—	—	32.7	30.7	18.9
Cr Oxide					
M_w	471,000	—	—	—	143,000
M_w/M_n	33.0	—	—	—	14.2

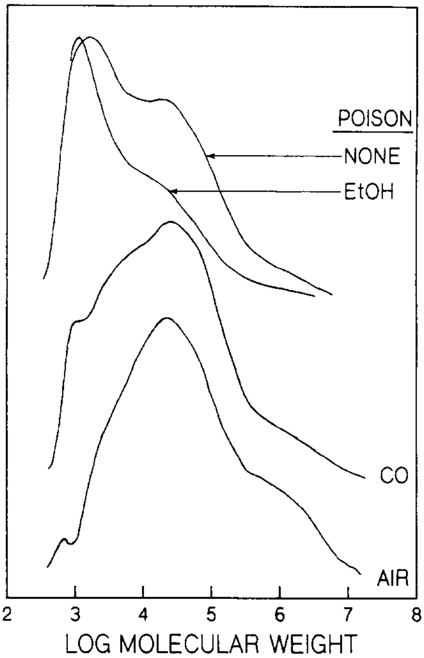


FIG. 5. Size exclusion chromatograms of polyethylene obtained from dicumene chromium on calcined aluminophosphate (0.4 P/Al, 600°C). In one run ethanol was added to the reactor to inhibit polymerization. In others the catalyst was exposed to carbon monoxide or air before polymerization.

Other poisons had the opposite effect. The lower portion of Fig. 5 shows the SEC traces of polymers made from the same dicumene Cr(0) catalyst, but exposed to carbon monoxide at 25°C before contact with ethylene. Activity dropped to about 40% of its former value, mostly from inhibition of the phosphate-associated sites. Note the selective decrease in the low MW peak. Also in Fig. 5, the catalyst was exposed to an excess of dry air at 25°C before being charged to the reactor. Again the activity dropped about 60% and the phosphate-associated sites were preferentially inhibited. The loss of the low MW peak, almost total in this case, compared to the loss in activity, indicates a very selective poisoning. The emergence of a small new peak at MW = 10^6 may also signify the generation of a new species by oxidation.

These experiments were repeated with a dibenzene Cr(0) on aluminophosphate catalyst and similar results were obtained. In this case the poisoning was not as serve. Pre-exposure to carbon monoxide lowered the activity about 40% and again decreased the size of the low MW peak. A quick pre-exposure to air decreased activity very little but did diminish the phosphate-associated SEC peak.

Another way of destroying the organochromium catalysts was to heat them in an inert atmosphere, which probably stripped off some of the remaining organic ligands. In Part II of this series $Cr_4(TMSM)_8$ on alumina was heated to 300°C in N_2, and a new high MW peak developed in the SEC. In these experiments aluminophosphate-supported organochromium catalysts behaved in much the same way. In Fig. 6 are shown the SEC traces of three polymers from dicumene Cr(0) catalysts, two heat-treated and one not heat-treated. One can see that heating the catalyst gradually removed the low MW peak, replacing it with high MW polymer in the 10^6 MW range. Dibenzene Cr(0) behaved similarly in another series of experiments. Therefore the phosphate-associated sites may be less stable to heat treatment. All of the organochromium compounds tested, even chromocene, yielded a similar pattern—a shift to high MW's, with accompanying broadening of the distribution. Indeed, the final species after heating, perhaps an oxide, may have been identical regardless of the initial organochromium compound used.

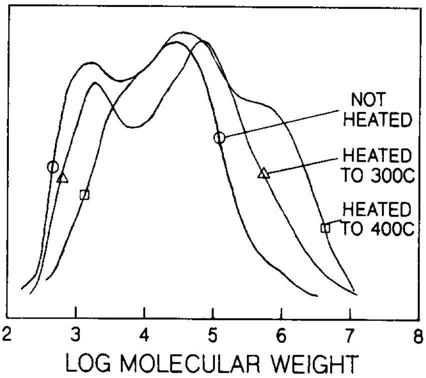


FIG. 6. Size exclusion chromatograms of polyethylene obtained from dicumene chromium on calcined aluminophosphate (0.4 P/Al, 600°C). After preparation the catalyst was heated under nitrogen for 30 min at various temperatures.

Since the two types of sites on these catalysts were poisoned or even destroyed preferentially, it was of interest to see if they also formed preferentially. In several experiments various organochromium compounds were impregnated onto the activated aluminophosphate support at different loadings, ranging from 0.1 to 2.0% Cr by weight. It was hoped that the most reactive surface sites would adsorb the chromium compound first, and that at low loadings only these sites would be formed. Using $Cr(DMPD)_2$, a very reactive compound (*21*), no dependence on the loading was found. The relative intensities of the two SEC peaks remained constant. However, dicumene Cr(0), which is less reactive and probably requires an oxidation to Cr(I) for adsorption, yielded a different result. The SEC traces shown in Fig. 7 indicate that the high MW or Al-associated peak, formed first, followed by the phosphate peak. Dibenzene Cr(0) behaved similarly in another series of experiments. These results were a little surprising since P–OH might be expected to be more acidic than Al–OH. However, surface strain introduced during calcination may also influence reactivity.

The ratio of the two SEC peaks was also affected by the temperature at which the support was first calcined before deposition of the organochromium compound. In one experiment the SEC traces of two polymers obtained from dicumene Cr(0) on aluminophosphate (P/Al = 0.4) were compared. In one case the support had been calcined at 300°C, in the other case at 700°C. The low MW peak, from the phosphate-related sites, was favored by the higher calcining temperatures. The main change in peak intensity occurred between the 300 and 700°C samples. Little further

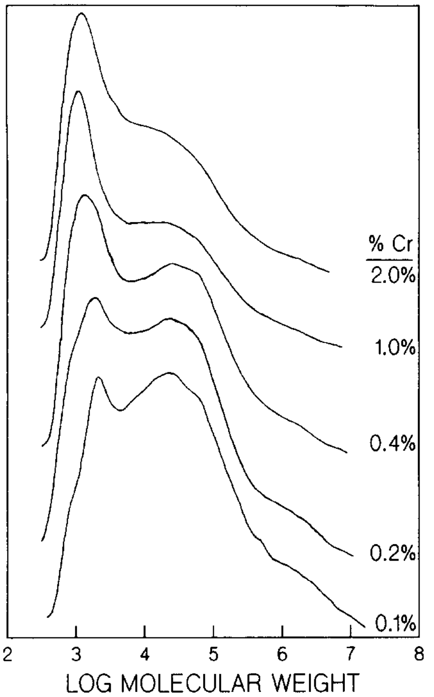


FIG. 7. Size exclusion chromatograms of polyethylene obtained from impregnating various amounts of dicumene chromium on calcined aluminophosphate (0.4 P/Al, 600°C).

change up to 850°C was noted. The activity of the catalyst doubled between 300 and 700°C calcining temperature (from 2000 to 4000 g/(gh)) but increased only slightly more to 850°C.

Changing the calcining temperature did not greatly affect the ratio between the two peaks from the more reactive Cr(DMPD)$_2$, but it did cause some minor differences. The 0.6 P/Al support was calcined at 850 and at 300°C for comparison. At 300°C the high MW peak was broadened and included more high MW material than at 850°C, while the low MW peak was less distinct and was also shifted to higher MW. This would account for the overall trend of higher average MW, which is a common characteristic of most supported chromium catalysts, even the oxide (*8, 9, 25*). It could reflect interference by neighboring hydroxyl groups.

As always, our interpretation of these results may be oversimplified. A close examination of some SEC curves suggests that the low MW peak could contain subspecies. Another small peak between 10^6 and 10^7 is also sometimes barely visible. Whether these extra peaks represent additional catalytic species or subspecies is unclear. Surface irregularities after calcination probably make possible many different types of environments within a species.

Alumina Supports

Alumina can also serve as a carrier for chromium oxide and the organochromium compounds to form polymerization catalysts. Usually, however, we have found the activity to be low, only about 10–20% of that of the best aluminophosphates. Whatever chromium compound was used, the polymer product was normally of extremely high molecular weight compared to that of other supports. Impregnating H_3PO_4 onto the alumina before calcination provided a surface layer of aluminophosphate, which greatly increased the activity of the resultant catalyst and recreated the same bimodal MW distribution described above (*25*).

Adding fluoride to the support before calcining also tended to increase activity, probably by replacing surface hydroxyl groups (*25*). This was true of most chromium-based catalysts, but especially when the support was alumina, which has a relatively high OH population (*20, 25*). Figure 8 shows that it also can affect the MW distribution of the resultant polymer. The SEC traces of two polymers are shown, both from dibenzene chromium on 500°C calcined alumina. In one case the alumina was impregnated with NH_4HF_2 before being calcined, and in the other case it was not. Without fluoride two high MW peaks were obtained, one described earlier at about log MW = 4.7 and another very high MW peak centered near log MW = 6.0. Such high MW material is often visible as a tail on the SEC traces from other catalysts

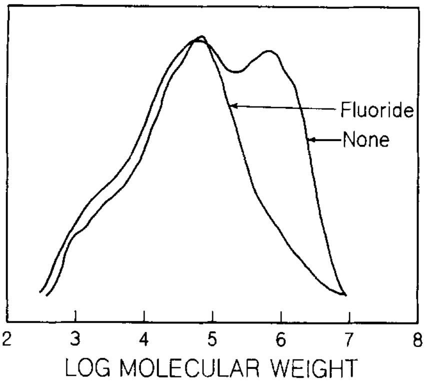


FIG. 8. Size exclusion chromatograms of polyethylene obtained from dibenzene chromium impregnated onto aluminas calcined at 500°C. In one case the alumina was impregnated with 8% NH_4HF_2 before being calcined.

too, such as $Cr(DMPD)_2$ or $Cr_4(TMSM)_8$ on aluminophosphates. It seems to be most evident on alumina calcined at low temperatures, and therefore is particularly exaggerated in Fig. 8. One can see in Fig. 8 that fluoriding reduced the second peak. It had a similar effect on $Cr(DMPD)_2$ on alumina and $Cr_4(TMSM)_8$ on alumina, narrowing the MW distribution and decreasing the very high MW tail. Possibly in these cases the chromium could react with more than one hydroxyl to yield an oxide-like species. If so, the fluoride may discourage this reaction by diminishing the OH population.

Silica Supports

Silica, the best support for chromium oxide, functioned very poorly for most organochromium compounds in our tests. Others have also reported this (*24*, *34*). Activity was often much lower than that of the best aluminophosphates. Surface hydroxyls on silica exhibit little acidity in comparison to the other carriers, so only the more reactive organochromium compounds, such as $Cr(DMPD)_2$ functioned as catalysts when impregnated onto silica at 25°C. Surprisingly, the best activity, about 800 g/(gh), was obtained when the silica had been calcined at only 250°C. In our experiments silicas calcined at higher temperatures provided much less activity. These results are summarized in Table 2.

In contrast, the less reactive dicumene Cr(0) did not form an active polymerization catalyst when impregnated at 25°C onto calcined silica. When the impregnated material was then heated to 150–200°C under nitrogen to encourage reaction with the surface, some activity did develop. Of if the silica contained acidic impurities, such as Al, V, or other metal ions, or just a trace of sulfuric acid, activity did develop on impregnation of dicumene Cr(0) at 25°C (*35*). Silica–alumina supports could even compare favorably in activity to the aluminophosphates in some cases.

Figure 9 shows some SEC traces obtained from $Cr(DMPD)_2$ on silicas calcined at various temperatures. When the silica was calcined at 250 and 400°C a single broad high MW polymer peak was obtained. However, calcining at 600°C produced an entirely different composition, most of the product being liquid, as shown by the sharp low MW peak. Bis-allyl Cr has also been reported to behave in a similar way, exhibiting extreme MW dependence on the calcining history of the silica (*24*). A silica calcined at 800°C also produced mostly liquids and wax. The product was heated under vacuum overnight to remove most of the lighter material. The SEC trace

TABLE 2

Activity and Percentage High MW Polymer Recovered

	250°C	400°C	600°C	850°C
Plain silica				
(% polymer)	95%	91%	27%	10%
(activity g/(gh))	820	180	170	200
With titania coating				
(% polymer)	—	97%	58%	—
(activity g/(gh))		750	890	
Silica-titania cogel				
(% polymer)	—	99%	—	91%
(activity g/(gh))		1194		1909

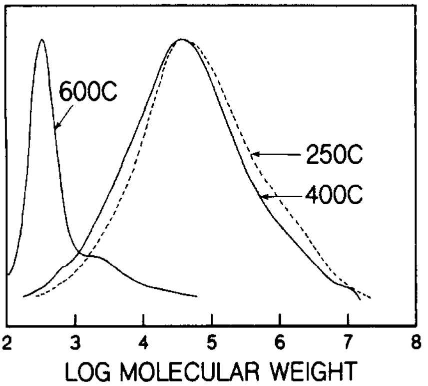


FIG. 9. Size exclusion chromatograms of ethylene polymerization products from Cr(DMPD)$_2$ on silicas calcined at various temperatures.

of the remaining high polymer resembled that obtained from 400 and 250°C silica except that there was a slight shift to the lower MW region.

What happened between 400 and 600°C to change the SEC patterns so dramatically is not clear. One possibility is that the spacing of the hydroxyls was involved. Calcining the silica dehydroxylates the surface, and the higher the temperature, the more hydroxyls are removed. At the lower calcining temperatures these hydroxyls are spaced closely enough that they can react in pairs with many reagents such as BCl_3 or $TiCl_4$ *(36–39)*. By 600°C, however, only "single" or isolated hydroxyls remain. Therefore on the 400 or 250°C silicas, the sites may have reacted with or at least coordinated to a second hydroxyl. Presumably this becomes more difficult when the silica has been calcined at 600°C or above. Such a pattern has also been observed in this laboratory from chromyl chloride *(33)*.

In two experiments the silica support was impregnated with phosphoric acid, then calcined at 250 and 400°C. After being impregnated with Cr(DMPD)$_2$ these also functioned as active catalysts. The SEC traces from these samples were compared to nonphosphated controls. The phosphate seems to have had much the same effect on silica that we saw previously on the aluminophosphates. It introduced a lower MW component and tended to decrease the average MW. It was not so clearly resolved into two peaks as was seen on the aluminophosphates though. The lower MW component came in the third decade as before, and was not the very low MW peak obtained from 600°C silica, which came in the second decade.

Titania is often added as a promoter to chromium oxide polymerization catalysts *(11–13)*. Although it does not serve as a support in itself, the activity of silica-based catalysts is usually enhanced when a surface coating of titania is applied, or when 5–10% titania is coprecipitated with the silica. Typically the molecular weight distribution of the resultant polymer is broadened by a new contribution from the lower MW region. For Cr(DMPD)$_2$ catalysts as well titania was found to provide a great enhancement of the activity, in fact much greater than for Cr oxide, as Table 2 shows. Note in Fig. 10 that the molecular weight distribution was similarly affected. Two silica samples were treated with titanium isopropoxide *(11)* and then calcined at 400 and 600°C, to yield a support coated with about 8 wt% titania. Afterward each sample was impregnated with Cr(DMPD)$_2$ and allowed to polymerize ethylene. In Fig. 10 the SEC trace from the 400°C sample is broadened to lower MW regions compared to the 400°C silica control. Again this suggests that the chromium may be coordinated to titania neighbors.

The sample titanated and calcined at 600°C also performed differently from its 600°C silica counterpart; SEC traces are shown in lower Fig. 10. Whereas the control catalyst produced mainly liquids, this effect was less pronounced on the titanated sample. A small low MW peak did become apparent by 600°C, but the amount of high MW polymer recovered was much higher. This was also found for Cr(DMPD)$_2$ on silica–titania cogel; even the 850°C sample produced mostly high MW polymer. This is summarized in Table 2.

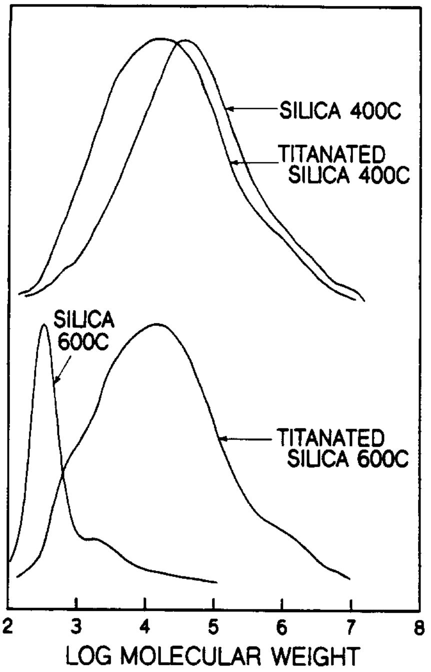


FIG. 10. Size exclusion chromatograms of polyethylene obtained from $Cr(DMPD)_2$ on silica treated with $Ti(OC_3H_7)_4$ and calcined at 400 and 600°C. Samples from untreated silicas are also shown for comparison.

It is not clear why silica calcined at 600°C or above produced mainly olefins when treated with $Cr(DMPD)_2$, but silica–titanias did not. Even coprecipitated silica–titania, where the titania was not as concentrated on the surface (*11*), produced mainly high MW polymer after calcination at 600 and 850°C. Perhaps the isolated hydroxyls on pure silica provide a "bare" environment which encourages chain termination, whereas surface titania provides something to which the chromium can coordinate. Indeed, the extreme boost in activity by titania suggests that the $Cr(DMPD)_2$ somehow reacted with it, or at least that surface hydroxyls were rendered more reactive by the titania.

As mentioned above, this pattern was not seen with dicumene Cr(0) which was less reactive with the support and thus provided only marginal activity on silica. But even on 600 or 800°C silica the small amount of product from dicumene Cr(0) was always high MW polymer.

CONCLUSIONS

Clearly the polymerization behavior of most supported chromium catalysts is very dependent on the carrier used. The acidity of surface hydroxyls probably determines the reactivity of the carrier with an organochromium compound, and thus the activity of the resultant catalyst. The chemistry of each site is then intimately related to what atom the chromium is attached, i.e., Al, P, Si, Ti, etc. Even when the attached element is the same, say Si, great differences in the polymerization behavior can still exist between sites. The change in SEC pattern from 400 to 600°C silica in Fig. 9 is a dramatic example. This suggests that coordination of the chromium site to neighboring hydroxyl or oxide groups may also play a powerful role in the chain transfer behavior of the site. If so, coordination to phosphate or titania rather than direct attachment may also influence the chemistry of the site.

Finally local steric conditions, such as strain introduced through calcination, may also influence the chemistry of the site. This may be especially true of the chromium oxide-based catalysts where the chromium is doubly attached to the surface. This may partly explain why these catalysts give broad SEC traces but do not contain well-resolved multiple peaks as do the organochromium catalysts.

REFERENCES

1. Morys, P., Gorges, U., and Krauss, H. L., *Z. Naturforsch. B: Anorg. Chem. Org. Chem.* **39**, 458 (1984).
2. Fubini, B., Ghiotti, G., Stradella, G., Garonne, E., and Morterra, C., *J. Catal.* **66**, 200 (1980).
3. Ghiotti, G., Garrone, E., Della Gatta, G., Fubini, B., and Giamello, E., *J. Catal.* **80**, 249 (1983).
4. Ghiotti, G., Garrone, E., and Zecchina, A., *J. Mol. Catal.* **46**, 61 (1988).
5. Krauss, H. L., *J. Mol. Catal.* **46**, 97 (1988).
6. Clark, A., and Bailey, G. C., *J. Catal.* **2**, 230 (1963).

7. Clark, A., and Bailey, G. C., *J. Catal.* **2,** 241 (1963).
8. McDaniel, M. P., and Welch, M. B., "The Influence of Hydroxyls on the Cr/Silica Polymerization Catalyst," *Amer. Chem. Soc. Symp. Ser.* No. 212, Paper 15, p. 191. Las Vegas, 1983.
9. McDaniel, M. P., and Welch, M. B., *J. Catal.* **82,** 98 (1983).
10. McDaniel, M. P., *J. Catal.* **76,** 37 (1982).
11. McDaniel, M. P., Welch, M. B., and Dreiling, M. J., *J. Catal.* **82,** 118 (1983).
12. Pullukat, T. J., Hoff, R. E., and Shida, M., *J. Polym. Sci. Polym. Chem. Ed.* **18,** 2857 (1980).
13. Pullukat, T. J., Hoff, R. E., and Shida, M., *J. Appl. Polym. Sci.* **26,** 2927 (1981).
14. Hill, R. W., Kehl, W. L., and Lynch, T. J., U.S. Patent 4,219,444, (Aug. 1980).
15. McDaniel, M. P., and Johnson, M. M., *J. Catal.* **101,** 446 (1986).
16. McDaniel, M. P., and Johnson, M. M., *Macromolecules* **20,** 773 (1987).
17. Wilson, D. R., Liu, J.-Z., and Ernst, R. D., *J. Amer. Chem. Soc.* **104,** 1120 (1982).
18. Smith, P. D., and Hsieh, E. T., U.S. Patent 4,587,227 (May 1986).
19. Hafner, W., and Fisher, E. O., U.S. Patent 2,953,586.
20. Cheung, T. T. P., Willcox, K. W., McDaniel, M. P., and Johnson, M. M., *J. Catal.* **102,** 10 (1986).
21. Freeman, J. W., Wilson, D. R., Ernst, R. D., Smith, P. D., Klendworth, D. D., and McDaniel, M. P., *J. Polym. Sci. Polym. Chem. Ed.* **25,** 2063 (1987).
22. Karol, F. J., Karapinka, G. L., Wu, C., Dow, A. W., Johnson, R. N., and Carrick, W. L., *J. Polym. Sci. Part A-1* **10,** 2621 (1972).
23. Karol, F. J., Brown, G. L., and Davison, J. M., *J. Polym. Sci. Part A-1* **11,** 413 (1973).
24. Karol, F. J., and Johnson, R. N., *J. Polym. Sci. Part A-1* **13,** 1607 (1975).
25. McDaniel, M. P., *in* "Advances in Catalysis" (D. D. Eley, H. Pines, and Paul B. Weisz, Eds.), Vol. 33, p. 47. Academic Press, New York, 1985.
26. Ballard, D. G. H., *in* "Advances in Catalysis" (D. D. Eley, H. Pines, and Paul B. Weisz, Eds.), Vol. 22, p. 263. Academic Press, New York, 1973.
27. Peri, J. B., *Disc. Faraday Soc.* **52,** 55 (1971).
28. Although one ligand is thought to be lost from the divalent Cr compounds on reaction with surface OH, it is not obvious that this should happen to the diarene Cr(0) compounds where oxidation to Cr(I) probably occurs. Comparison to known Cr(I) complexes would suggest that both rings should remain. In a personal communication, J. H. Lunsford has described ESR evidence indicating that this may indeed be the case.
29. Wharry, W. M., Martin, S. J., and McDaniel, M. P., *J. Catal.* **115,** 463 (1989).
30. Hogan, J. P., *J. Polym. Sci. Part A-1* **8,** 2637 (1970).
31. McDaniel, M. P., *J. Catal.* **67,** 71 (1981).
32. McDaniel, M. P., *J. Catal.* **76,** 29 (1982).
33. McDaniel, M. P., *J. Catal.* **76,** 17 (1982).
34. Rebenstorf, B., *J. Mol. Catal.* **46,** 109 (1988).
35. McDaniel, M. P., and Smith, P. D., U.S. Patent 4,619,980 (Oct. 1986).
36. Armistead, C. G., Tyler, A. J., Hambleton, F. H., Mitchell, S. A., and Hockey, J. A., *J. Phys. Chem.* **73**(11), 3947 (1969).
37. Peglar, R. J., Hambleton, F. H., and Hockey, J. A., *J. Catal.* **20,** 309 (1971).
38. Kunawicz, J., Jones, P., and Hockey, J. A., *Trans. Faraday Soc.* **67**(3), 848 (1971).
39. McDaniel, M. P., *J. Phys. Chem.* **85,** 532 (1981).