Ethylene polymerization by Cr(III) salts on acidic carriers

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A B S T R A C T

Chromium tris-2,4-pentanedionate becomes quite active as an ethylene polymerization catalyst when sublimed onto an acidic high-porosity carrier and in the presence of aluminum alkyl cocatalyst. The resultant catalyst produces a broad MW distribution of mostly linear polyethylene. Because the MW distribution reflects the active site distribution, it has been studied in this paper as the catalyst was probed by changing the organic ligand, the acidic carrier, the cocatalyst and reactor additives. The MW distribution was quite responsive to changes in the carrier and the cocatalyst, but not to changes in the organic ligand.

These responses were then compared to those of a commercial relative, the Phillips chromium (VI) oxide catalyst system anchored on the same supports. Many common behaviors were observed, and also some contrasting ones. For example, the incorporation of 1-hexene, and the resulting branch placement within the MW distribution were identical between the two catalysts. On the other hand, the role of the support calcination temperature as a MW regulator was greatly reduced from the experimental catalyst, but the response to reactor H_2 was much more pronounced than that of Phillips catalysts. Thus, the experimental catalyst offers many of the same features of commercial Cr catalysts, but with some environmental and operational advantages too.

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1. Introduction

One of the most important ways of studying polymerization catalysts is to examine the polymer that they produce. This is because the active site population is usually only a small fraction of the total metal loading. Thus the only certain way of *selectively* probing the active sites is by examining the catalyst activity, and the character of the polymer produced.

Acidic, high-porosity oxide carriers have been found to activate a wide variety of transition metal compounds to generate olefin polymerization catalysts. This includes Phillips hexavalent Cr/silica catalysts, in which the addition of titania, alumina or other metal oxides increase the surface acidity. Consequently the polymerization rate and some polymer characteristics are significantly enhanced [1,2]. In other examples, the addition fluoride, phosphate or sulfate to Cr(VI)/alumina, which also enhances surface acidity, produced a similar boost in activity [3–6]. Indeed, many lower-valent Cr alkyl or arene compounds do not polymerize ethylene unless deposited onto an acidic oxide support [1,7–10]. Other examples include nickel compounds which were enhanced by acidic aluminophosphate carriers [11,12], and vanadium (II) and

titanium (II) alkyls [13]. Even metallocenes [14–17] and single-site coordination compounds [18–22] can be activated by deposition onto a wide variety of such solid acid supports. In each of these catalytic systems the acidic support is thought to withdraw electron density from the transition metal, thus rendering it more reactive with the olefinic pi-orbitals.

In this paper we report that chromium (III) 2,4-pentanedionate, i.e. $Cr(AcAc)_3$, can also be activated by these acidic carriers [23]. This compound has long been used as a source of Cr in the production of Phillips Cr(VI)/silica catalysts [24–29]. However, in this capacity it is calcined in air at >500 °C, which burns off the 2,4-pentanedionate ligands, leaving a typical Cr(VI) oxide (Phillips) catalyst. In contrast, we report here that $Cr(AcAc)_3$ can itself initiate ethylene polymerization at high rates in the absence of calcination, if it is supported on an acidic carrier. Unlike the Cr alkyl and arene compounds described above, which already contain a potential Cr-alkyl initiation site, $Cr(AcAc)_3$ requires an aluminum alkyl cocatalyst in order to generate polymerization activity. Possibly one of the 2,4-pentanedionate ligands is replaced by an alkyl group as the initiating species.

In this report we describe some of the unusual characteristics of this catalyst system, and the polyethylene it produces. These observations suggest that the choice of acidic support has a much stronger influence on the catalyst than the initial organic ligands.

2. Experimental

2.1. Preparation of catalysts

Solid acids used in this study were made as described below. Commercially available silica, alumina, or silica-alumina was impregnated with other materials to enhance or modify surface acidity, followed by calcination at 400–800C°C. For example, a particularly effective solid acid which was used in many of these experiments (often called the "standard" solid acid in this report) was silica-alumina (60% alumina) which was then treated with 3.7 mmol of HF, followed by calcination at 600 °C. In other cases alumina was treated with 1.5 mmol/g ammonium sulfate and then calcined at 600 °C. Some solid acids were also chlorided, which was accomplished by passing 2–4 mmol/g of carbon tetrachloride vapor up through a fluidized bed at 500 °C.

Samples of these solid acids were then treated with chromium (III) tris-acetylacetonate. Unless otherwise noted, the Cr loading was 0.4 mmol per gram of support. The chromium was added in one of two ways. In some experiments the solid acid was impregnated with a toluene solution of the chromium. Then the toluene was boiled away so that the catalyst was exposed to maximum temperature of only 110 °C. In other experiments, the dry chromium (III) tris-acetylacetonate crystals were mixed with the solid acid powder, which was then fluidized in dry nitrogen (or CO or H_2 as noted) while the temperature was raised to between 150 °C and 600 °C. In most preparations, and if not otherwise stated, the $Cr(AcAc)_3$ was sublimed onto the solid acid at 250 °C in nitrogen. During this Cr deposition step, the original purple color of the catalyst changed to bright green, indicating reaction between Cr and the solid acid surface.

2.2. Polymerization

Polymerization runs were made in a 2.2 L stainless steel reactor equipped with a marine stirrer rotating at 400–500 rpm. The reactor was surrounded by a stainless steel jacket through which a stream of hot water was circulated, which permitted precise temperature control to within half a degree centigrade, with the help of electronic control instruments. Unless otherwise stated, a small amount, typically 0.05–0.15 g, of the solid catalyst was first charged under nitrogen into the dry reactor. Next, 1.2 L of isobutane liquid was added. However, half way through the addition 1 mL of 1 M triisobutylaluminum (or other cocatalyst if so stated) was added, which was then flushed into the reactor with the remainder of the isobutane liquid. The reactor was then heated to 100 °C and ethylene was added to the reactor to equal 3.79 MPa (550 psig), which was maintained during the experiment to yield a steady 1.7 mol/L ethylene concentration. The slurry was stirred for the specified time, usually about 1 h, and the polymerization rate was noted by recording the flow of ethylene into the reactor to maintain the set pressure. After the allotted time, the ethylene flow was stopped, and the reactor was slowly depressurized and opened to recover a granular polymer powder. In nearly all cases, the reactor was clean with no indication of any wall scale, coating, or other forms of fouling. The polymer powder was then removed and weighed. Activity was determined from this weight and the measured time.

2.3. Gel permeation chromatography

The molecular weight and MW distribution of these polymers was then obtained using a Waters 150 CV gel permeation chromatograph with trichlorobenzene (TCB) as the solvent, and a flow rate of 1 mL/min at 140C. BHT (2,6-di-tertbutyl-4-methylphenol) was used as a stabilizer in the TCB at a concentration of 1.0 g/L. An injection volume of 220 μL was used with a nominal polymer concentration of 0.3 g/L at room temperature. Dissolution of the sample in stabilized TCB was carried out by heating at 160–170 °C for 20 h with occasional gentle agitation. Two Waters HT-6E columns (7.8 × 300 mm) were used. These columns were calibrated with a broad linear polyethylene standard (Phillips Marlex BHB 5003), for which the molecular weight had been determined [30].

Short-chain branch distributions were measured using a SEC-FTIR high-temperature heated flow cell obtained from Polymer Laboratories [31].

2.4. Rheology

Rheology measurements were obtained as follows: Polymer powder was first stabilized with 0.1 wt% BHT dissolved in acetone and then vacuum-dried before molding. Samples for viscosity measurements were then compression molded at 182 °C for a total of 3 min. The samples were allowed to melt at a relatively low pressure for 1 min and then subjected to a high molding pressure for an additional 2 min. The molded samples were then quenched in a press at 25 °C. Disks (2 mm × 25.4 mm diameter) were stamped out of the molded slabs for rheological characterization.

Small-strain oscillatory shear measurements were performed on a Rheometrics Inc. rms-800 or ARES rheometer using parallel plate geometry over an angular frequency range of 0.03 100 rad/s. The test chamber of the rheometer was blanketed in nitrogen to prevent polymer degradation. The rheometer was heated to 190 °C. Upon loading the sample, and after thermal equilibration of the oven, the specimens were squeezed between the plates to a 1.6 mm thickness, and the excess was trimmed away. A total of ~8 min elapsed between the time the sample was inserted between the plates and the time the frequency sweep was started.

Strains were generally maintained at a single value throughout a frequency sweep, but larger strain values were used for low viscosity samples to maintain a measurable torque. Smaller strain values were used for high viscosity samples to avoid overloading the torque transducer and to keep within the linear viscoelastic limits of the sample. The instrument automatically reduces the strain at high frequencies if necessary to avoid overloading the torque transducer. These rheological data were fitted to the Carreau-Yasuda equation to determine zero shear viscosity (η_0), relaxation time (τ), and a measure of the breadth of the relaxation time distribution (CY-a) [32]. The long-chain branching (LCB) levels in polymers were calculated using the method of Janzen and Colby [33–35] from values of zero shear viscosity and measured values of weight-average MW obtained.

## 3. Results and discussion

3.1. Influence of the carrier

Some typical polymerization results from this $Cr(AcAc)_3$ catalyst system are shown in Table 1. In these tests the catalysts were made by depositing chromium (III) 2,4-pentanedionate onto a variety of diverse oxide supports. The catalysts were then used to polymerize ethylene at 100 °C using 1.0 mmol/L of triisobutylaluminum (TiBA) in the isobutane diluent. It is clear in Table 1 that the solid acid chosen had a profound influence on the activity of the catalyst, which varied from as little as 50 g of PE per gram of catalyst per hour, to over 6700 gPE/g/h. Scheme 1 shows some of the possible ways in which chromium or metallocene catalysts may interact with the support, although this list is by no means exhaustive.

Some of these same supports were also quite successful at activating metallocene catalysts [14,15], and there is a fair correlation between the two systems. That is, the supports that were most successful at activating metallocenes also seemed to perform best

Table 1
Typical results from Cr(2,4-pentanedionate)$_3$ deposited onto various supports.

Support	Calc. Temp.	Deposit. Temp.	Activity gPE/g/h	HLMI g/10 min	Density g/mL	M_N kg/mol	M_W kg/mol	M_Z kg/mol	M_W/M_N
Silica	600 °C	110 °C	56	1.5	0.9505	8.8	637	3139	72
Ti/Silica	600 °C	250 °C	147	0.1	0.9515	8.0	866	3644	108
Alumina	600 °C	110 °C	103	1.2	0.9512	9.5	653	3205	69
" e	"	250 °C	57	0	0.9515	8.7	1301	4263	149
Aluminophosphate (P/Al 0.9)	600 °C	110 °C	150	9.4	0.9612	5.6	468	3086	84
"	"	250 °C	240	13.1	0.9570	2.8	352	2246	126
Aluminophosphate (P/Al 0.2)	600 °C	250 °C	157	0.6	0.9536	6.3	658	3137	105
F-Aluminophosphate (P/Al 0.6)	600 °C	250 °C	563	6.2	0.9546	3.8	412	2573	109
Silica-Alumina (60% alumina)	600 °C	110 °C	141	0.5	0.9515	9.6	801	3427	84
F-Silica-Alumina (60% alumina)	600 °C	110 °C	2167	0.4	0.9472	10.2	770	3116	76
"	"	250 °C	5200	0.1	0.9495	13.1	699	3049	53
Cl-F-Silica-alumina (60% alumina)	600 °C	250 °C	6734	0.1	0.9492	10.8	723	3101	67
F-Silica-Alumina (13% alumina)	500 °C	110 °C	1270	5.3	0.9531	5.1	494	3229	96
"	"	250 °C	1220	5.6	0.9529	5.3	427	2617	81
SO$_4$/Alumina	600 °C	110 °C	2083	0.9	0.9506	7.9	734	3449	93
"	"	250 °C	1100	0.4	0.9517	8.5	662	3136	78
SO$_4$/Alumina	400 °C	110 °C	276	1.5	0.9538	9.3	739	2881	80
Cl-Zn/Alumina	600 °C	110 °C	43	1.1	0.9565	9.5	796	3177	83

Catalysts contained 2 wt% Cr and were tested at 100 °C, 1.7 mol/L ethylene and with 0.5–1.0 mmol/L TiBA cocatalyst.
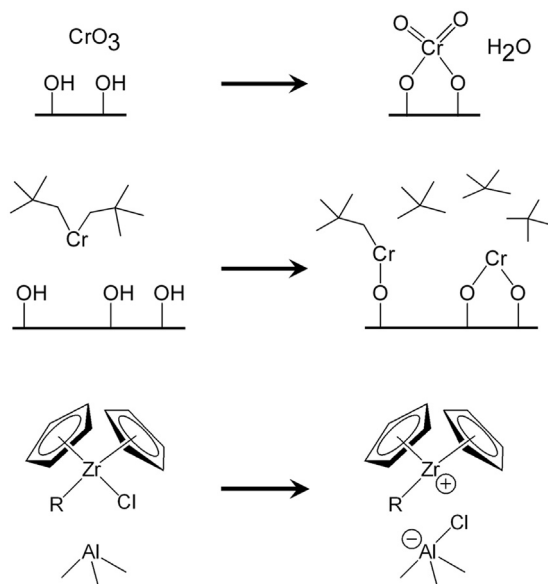
Scheme 1. Anchoring of Cr oxide, Cr alkyl, or metallocene to an acidic oxide support.

for this chromium system. These carriers are known to contain an assortment of both Lewis and Bronsted acid surface sites of varying strength, and this possibly suggests that the activating species may be the Lewis-acidic sites, which are known to activate metallocenes, as shown in Scheme 1. In fact, Monoi [36] has reported that chromium (III) 2,4-pentanedionate can be activated by methylaluminoxane (MAO), another Lewis-acidic metallocene activator. The most active catalyst in this study was a silica-alumina treated with both chloride and fluoride. This recipe has been a favorite for metallocene activation as well [37]. However, the correlation is not perfect. For example, one of the best Lewis-acidic supports for activation of metallocenes, chlorided zinc-alumina (the last entry in Table 1), exhibited little activity in this Cr(AcAc)$_3$ catalyst system. This support has only Lewis, not Bronsted, acidity.

Comparison of the activities in Table 1 to the performance of analogous Phillips catalysts, that is chromium (VI) oxide on these same supports, indicates little similarity [1,2]. For example, the Phillips catalysts Cr/silica, Cr/silica-titania and Cr/aluminophosphate tend to produce outstanding activity, unlike the Cr(AcAc)$_3$ catalyst system. In the Phillips system, the Cr is

thought to bind to the support through two oxide links, as shown in Scheme 1, whereas Cr(AcAc)$_3$ almost certainly attaches in a different way.

Further comparison of Table 1 to hydrocarbyl-chromium compounds, such as the Cr alkyls, chromocenes, or bisarene Cr, when deposited on these same supports [1,8,10,13,38–41] also indicates some major differences. For example the aluminophosphates or even plain alumina perform well for hydrocarbyl-Cr compounds, but less so for Cr(AcAc)$_3$. Hydrocarbyl-Cr compounds are thought to be activated by reacting with Bronsted acid sites on the surface as shown in Scheme 1. This again suggests that the attachment of Cr(AcAc)$_3$ to these solid acids takes place through a different pathway.

3.2. Polymer structure

Also shown in Table 1 are some of the properties of the polymers that were produced by these catalysts. This includes the high load melt index (HLMI), an industrially convenient viscosity measurement (ASTM D1238-F, Condition 190/21.6), and three moments of the molecular weight distribution: M_N (number average), M_W (weight average), and M_Z (double-weight average). All of the Cr(AcAc)$_3$ catalysts produced extremely high MW and a broad MW distribution, as indicated by the high polydispersity values (M_W/M_N). In this they are different from metallocenes and other single site catalysts, which produce a much narrower MW distribution ($M_W/M_N \sim 2$). This indicates a diverse multitude of active site types on the catalysts in Table 1, in which the support contributes to the character of each. That is, some sites produce low-MW polymer while others produce high-MW polymer. Like other Cr-based catalysts, the MW distribution produced is strongly influenced by the support, indicating that surface oxide or other species must be part of the coordination sphere of the active sites.

For example, Fig. 1 shows the MW distribution from three aluminophosphate catalysts in Table 1 (runs 6–8). In each case Cr(AcAc)$_3$ was deposited onto an aluminophosphate support which varied in the amount of phosphate it contained. Notice that the alumina support (P/Al = 0) produced a wide variety of polymer MW, but mostly it produced chains greater than 1 million g/mol. However, as the phosphate level in the support was increased (P/Al = 0.2 up to 0.9) one can see progressively greater contributions in the low-MW range. In other words, surface phosphate species, which tend to be more acidic than silanols, influence the Cr to produce lower-MW polymer chains. This same
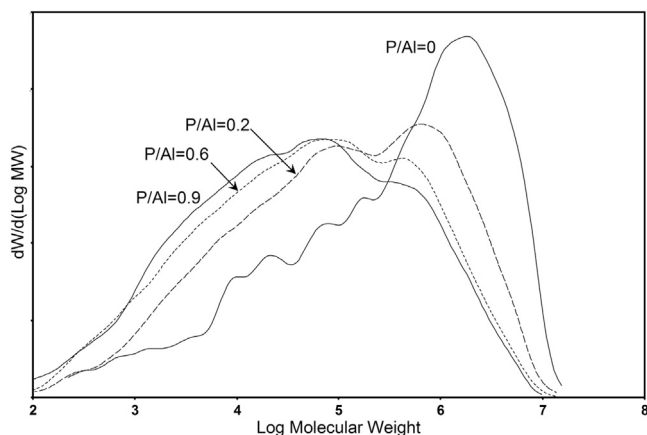
Fig. 1. MW distributions of polymer from Cr(AcAc)$_3$ on three aluminophosphate carriers varying in composition.

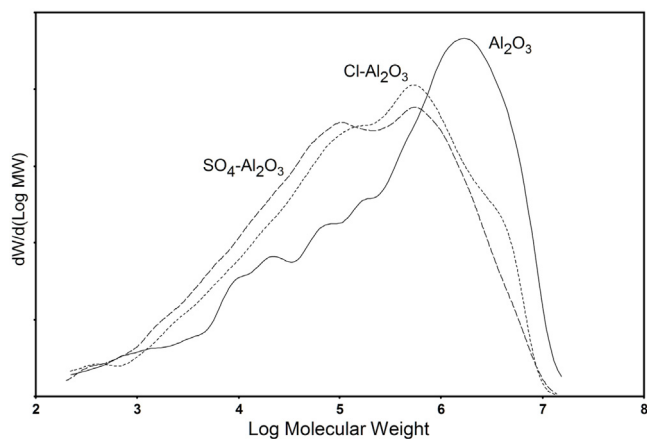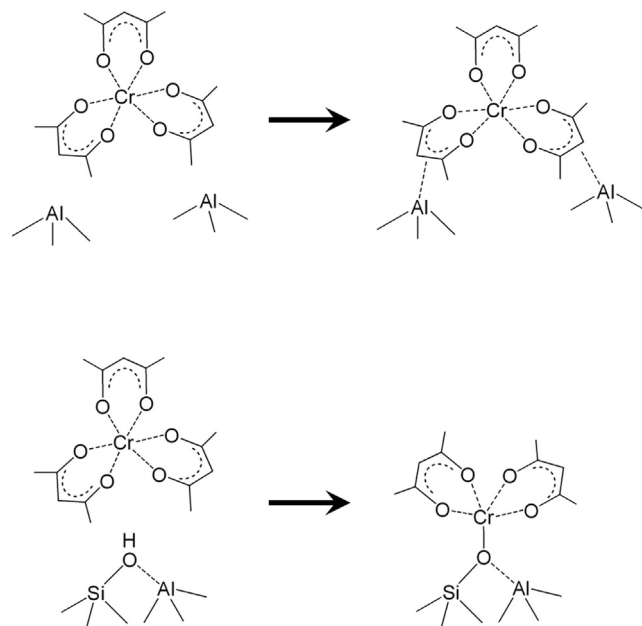**Fig. 2.** MW distributions from Cr(AcAc)$_3$ on three alumina carriers varying in acidity.

Scheme 2. Showing possible ways of anchoring Cr(AcAc)$_3$ to an acidic carrier: a) intact, and b) by losing a ligand.

behavior has been observed from analogous Phillips catalysts (Cr(VI)/aluminophosphate) [1,42–45] and hydrocarbyl-Cr catalysts (Cr alkyls, etc. on aluminophosphate) [1,8,10], but not from metallocene catalysts activated by these same supports. This indicates that the support contributes to the coordination sphere of the Cr, but not of the metallocene, which is thought to be ionized by removal of one ligand to a Lewis acid as shown in Scheme 1.

The other supports shown in Table 1 also produced subtle changes in the otherwise very broad MW distribution. Fig. 2 shows three other examples, this time of polymers obtained with an alumina support (runs 3, 16 and 18 in Table 1). In one case Cr(AcAc)$_3$ was supported on the unmodified alumina, then in the other two cases the alumina had been treated with chloride or sulfate in order to enhance the surface acidity. All were calcined at 600 °C. As in Fig. 1 so again in Fig. 2 we see that the addition of surface acidity to the catalyst produces more polymer (higher activity) and also it introduces a new lower-MW peak at about MW ∼ 10^5 g/mol.

Thus although the composition of the support may vary widely, the same main peaks seem to reoccur in the MW distribution from various supports, although varied somewhat in amount. This perhaps suggests some similarity in the active site populations. The peak at MW = 10^5 appears to be associated with the addition of phosphate, fluoride or sulfate, and therefore it may be derived from an acidic surface site. Even the highest-MW peak, at ∼$10^{6.3}$ g/mol also seems to be shifted to lower MW by the increased acidity.

3.3. Reaction of Cr(AcAc)$_3$ with the support

When heated, Cr(AcAc)$_3$ sublimes near 100 °C. Thus it can be dry-mixed with the desired support and heated to various temperatures in an inert gas such as nitrogen. During the heating step it sublimes into the gas phase where it is then carried up through the fluidized support bed on which it is adsorbed. The reaction of Cr(AcAc)$_3$ with the support is indicated visually by a color change from the original deep purple of the free compound, to a bright green color on the support. The nature of its reaction with silica has been the subject of several studies [24,46–48] because Cr(AcAc)$_3$ has often been used a Cr source for Phillips catalysts, in which the Cr is then calcined at >500 °C to convert it to Cr(VI) oxide. In these studies, surface silanols were found to react with Cr(AcAc)$_3$ at 200–280 °C to replace one 2,4-pentanedionate ligand, as shown in the lower half of Scheme 2, although this reaction pathway is by no means certain. The reaction between Cr(AcAc)$_3$ and dehydroxylated alumina was also studied [49]. In addition to the reaction with surface hydroxyls, which is shown in the lower half of Scheme 2, an additional type of interaction was also identified between the 2,4-pentanedionate ligands and surface Lewis-acidic Al species. This is depicted in the upper half of Scheme 2.

Once the chromium complex has attached to the support, according to Scheme 2 or perhaps by some other pathway, it then reacts with the alkylaluminum cocatalyst to produce the active site. This reaction may involve a reduction of the chromium to Cr(II) possibly with simultaneous removal of AcAc ligands and alkylation to form the active site. Although this reaction must occur to form the active site, the exact details are at this point, still unknown.

Fig. 3 shows the polymerization activity from a series of experiments in which samples of fluorided silica-alumina (60% Al$_2$O$_3$), as shown in Table 1, were dry-mixed with Cr(AcAc)$_3$ and heated in a nitrogen-fluidized bed to various temperatures. The activity passes through a maximum near 250 °C. The amount of carbon left on the catalyst was measured by combustion analysis, and is listed in Table 2. After treatment at 250 °C and 300 °C, the catalyst still contained all of the carbon, that is, the equivalent of about 3 AcAc groups per Cr. Of course this does not necessarily prove that the Cr(AcAc)$_3$ remains intact because even liberated AcAc or decom-
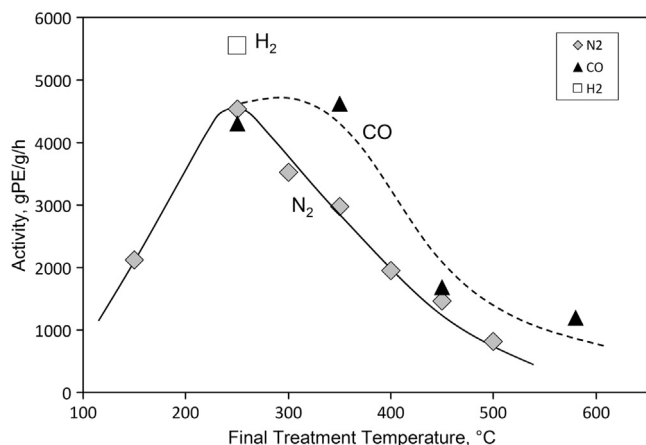
Fig. 3. Fluorided silica-alumina was dry-mixed with Cr(AcAc)$_3$, heated to the temperature shown in N$_2$, CO or H$_2$, and then tested for polymerization activity.

Table 2
Amount of carbon found on catalysts.

Deposition Temperature	% Carbon Remaining	Maximum Possible AcAc/Cr
250 °C	3.65	3.06
300 °C	3.63	3.32
400 °C	2.85	2.58
450 °C	1.43	1.16

Combustion analysis of fluorided silica-alumina after deposition of Cr(AcAc)$_3$. Shown as% C and also as AcAc ligands per Cr if all C were present as AcAc.

position products could be strongly adsorbed on this very acidic support. At higher temperatures, however, it is clear that the Cr begins losing its AcAc ligands.

It is interesting to compare the polymers made by depositing the Cr(AcAc)$_3$ at different temperatures. The MW distribution of polymers from such an experiment is shown in supplemental Fig. S1. One might expect the loss of ligands to change the active site population significantly, and therefore the polymer character as well. However, there was barely any change in the MW distribution as the Cr(AcAc)$_3$ deposition temperature was raised from 110 °C to 500 °C. Only a very slight shift to higher MW was observed, and the activity dropped, as shown in Fig. S1. The shift in weight-average MW is plotted against temperature in supplemental Fig. S2.

Also shown in Fig. 3 is a series of similar experiments, except that the Cr(AcAc)$_3$ deposition was done in carbon monoxide rather than nitrogen, under the assumption that this might result in some reduction of the chromium valence. The activity of this series was slightly higher, but it went through the same maximum near 250 °C. Still another sample was treated with hydrogen at 250 °C, which yielded still a little more activity. However, the polymer MW distribution was again barely affected by heating in a reducing atmosphere and there was little difference between N$_2$ versus CO or H$_2$. The distribution retained is distinctive broad shape, but with the weight-average MW increased slightly versus the samples heated in N$_2$. These MW distributions are shown in supplemental Fig. S3.

3.4. Cocatalyst

The Cr(AcAc)$_3$ catalysts did not polymerize ethylene unless a metal alkyl cocatalyst was also added to the reactor. This is in contrast to the commercial Phillips Cr oxide catalysts, which are reduced by ethylene and in the process self-alkylate to form the active sites. However, unlike the commercial Cr(VI) sites, which are strongly oxidizing and thus interact with ethylene rather easily, the
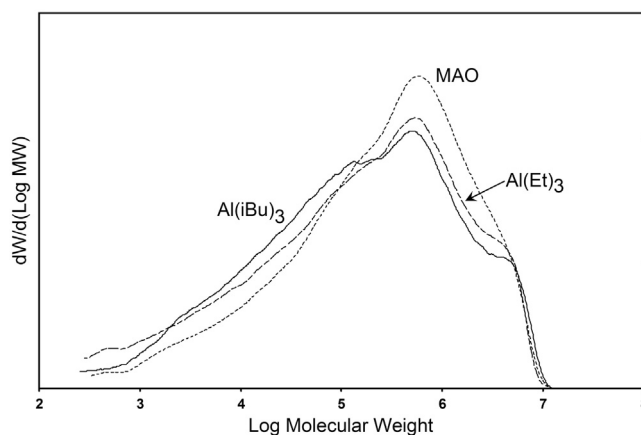

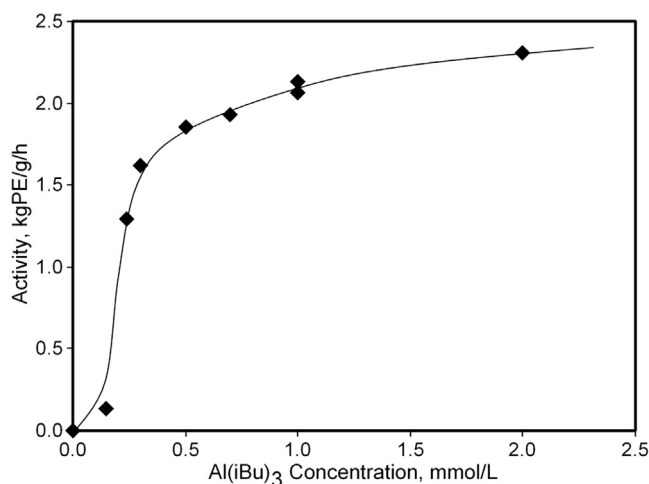**Fig. 4.** Influence of the cocatalyst type on the polymer MW distribution.

Fig. 5. Polymerization activity as a function of cocatalyst reactor concentration, for Cr(AcAc)$_3$ on fluorided silica-alumina.

trivalent Cr(AcAc)$_3$ sites are not reactive with ethylene, and thus a metal alkyl cocatalyst is needed to alkylate, and perhaps reduce, the initial Cr(III) sites.

Aluminum alkyls produced the highest activity, and of these tri-isobutylaluminum was preferred. Table 3 lists some examples of the use of different cocatalysts with the same catalyst, i.e. Cr(AcAc)$_3$ deposited on the standard fluorided silica-alumina. Note that the trialkylaluminum compounds worked best, and the presence of chloride killed the catalyst. Even methylaluminoxane (MAO) was tested, but it was less effective.

In addition to the activity varying widely with the choice of cocatalyst, the polymer character seems also to have been affected. This is indicated by the MW moments in Table 3, which are all high. The MW distribution also changed in subtle ways as the cocatalyst was varied. An example is shown in Fig. 4 in which fluorided silica-alumina was used along with 1 mmol of three different cocatalysts, triisobutylaluminum, triethylaluminum, and MAO. Again the same main peaks seem to reappear, but in slightly different amounts, which perhaps indicates similarity in the active site populations. MAO was the most different of the three cocatalysts shown, both in its chemistry and also in its influence on the MW distribution.

The amount of cocatalyst used also had an influence on the observed activity. Fig. 5 shows one example in which Cr(AcAc)$_3$ was deposited onto standard fluorided silica-alumina, and then it was tested with varying amounts of triisobutylaluminum added to the reactor. Notice that the activity rises sharply at first as the con-

Table 3
Comparison of various cocatalysts with a single carrier.

Cocatalyst	Al(iBu)$_3$	AlEt$_3$	AlEt$_2$Cl	MAO	ZnEt$_2$	BEt$_3$	Al(iBu)$_3$	AlEt$_3$	AlMe$_3$
N$_2$ Temperature	110 °C	110 °C	110 °C	110 °C	110 °C	110 °C	250 °C	250 °C	250 °C
Activity, gPE/g/h	2067	1808	0	918	0	0	3303	3623	1303
Melt Indices									
MI, g/10 min	0.0011	0.0009	na	0.0002	na	na			
HLMI, g/10 min	0.049	0.047	na	0.018	na	na	0.0519	0.0553	0.2569
Molecular Weight									
M_N, kg/mol	10.9	11.2	na	16.9	na	na	10.2	10.3	10.8
M_W, kg/mol	790	801	na	876	na	na	701	783	666
M_Z, kg/mol	3519	3634	na	3031	na	na	2952	3333	2794
MW Breadth									
M_W/M_N	72.8	71.5	na	52.0	na	na	68.7	76.1	61.7
M_Z/M_W	4.5	4.5	na	3.5	na	na	4.2	4.3	4.2
Density, g/mL	0.9493	0.9476	na	0.9462	na	na	0.9484	0.9477	0.9493

Catalyst: Cr(AcAc)$_3$ deposited onto fluorided silica-alumina (60% alumina) at 110 °C or at 250 °C. Polymerization at 100 °C and 1.7 mol/L ethylene using 1 mmol/L cocatalyst.

centration of cocatalyst is increased. Then it levels off, and there is no further effect. In these experiments the amount of chromium used was approximately 0.07 mmol/L. Therefore, all of the points in Fig. 5 represent a considerable stoichiometric excess.

This response to cocatalyst is unusual among Cr-based catalysts. The cocatalyst levels used in these experiments with Cr(AcAc)$_3$ catalysts is one to two orders of magnitude greater than is typically used with Phillips chromium oxide catalysts. In fact, the latter usually reach maximum activity with sub-stoichiometric amounts of cocatalyst (less than or equal to 1 Al/Cr) and large amounts of trialkylaluminum cocatalyst even tend to kill the reaction [1]. However, in Fig. 5, there seems to be no loss in activity for the Cr(AcAc)$_3$ catalyst, even at the highest cocatalyst concentration.

The amount of cocatalyst used had only a modest influence on the MW distribution. An example is shown in supplemental Fig. S4 in which triisobutylaluminum was used. The main difference is an increase in the peak at MW = 10^5 g/mol with the highest triisobutylaluminum concentrations.

3.5. Support calcination temperature

One of the main methods of controlling the MW and MW distribution from Phillips chromium oxide catalyst is through variation of the initial calcination temperature of the support. Consequently this variable was also explored with the Cr(AcAc)$_3$ catalyst. Simple silica-alumina was calcined at temperatures ranging from 400 °C to 800 °C before being treated with Cr(AcAc)$_3$ at 250 °C. As is usually observed with chromium oxide catalysts, the polymerization activity increased with calcination temperature and the molecular weight dropped. In Fig. 6 the activity, weight-average MW and the low-shear melt viscosity are all plotted as a function of calcination temperature. The MW distribution of the polymers, which is shown in supplemental Fig. S5, was not greatly affected. There was only a slight shift of the entire curve to lower MW with higher calcination temperature, which accounts for the responses in Fig. 6. A similar, although more pronounced, trend is observed from the chromium oxide catalysts.

3.6. Cr(AcAc)$_3$ loading

Like many other chromium-based catalysts the activity of this system does not have a linear dependence on the amount of Cr on the catalyst. Instead, the first increment of Cr(AcAc)$_3$ added exhibits disproportionate activity. This is illustrated in Fig. 7. In this series of experiments, standard fluorided silica-alumina was dry-mixed with various amounts of Cr(AcAc)$_3$ and heated in a nitrogen-fluidized bed to 250 °C where it was held for one hour.
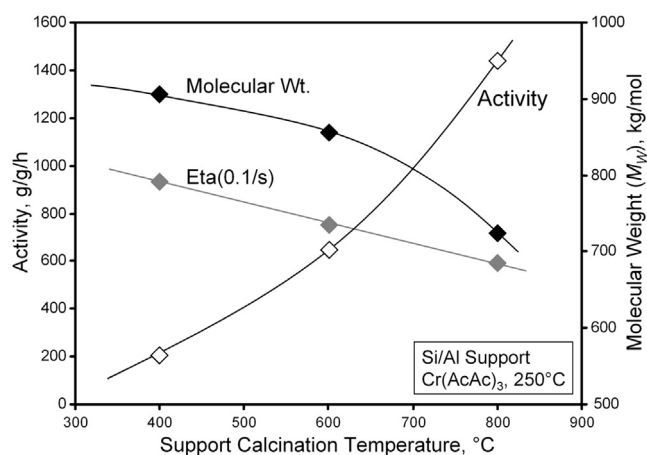

Fig. 6. Influence of the support calcination temperature on catalyst activity and polymer MW from a Cr(AcAc)$_3$ sublimed onto non-fluorided silica-alumina support.
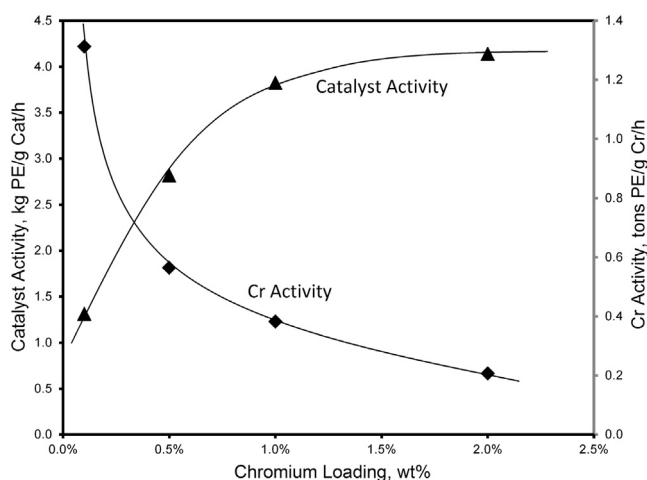

Fig. 7. Activity of Cr(AcAc)$_3$ on fluorided silica-alumina as a function of Cr loading.

In Fig. 7 the polymerization activity per gram of catalyst is plotted as a function of Cr loading. It rises at first, but then as more Cr is added the activity eventually levels off and the addition of still more Cr has no effect. This behavior, which suggests some kind of saturation, is very typical of commercial chromium oxide catalysts [1].

Also plotted in Fig. 7 is the activity per gram of chromium on the catalyst. It is initially very high, over one million grams of PE
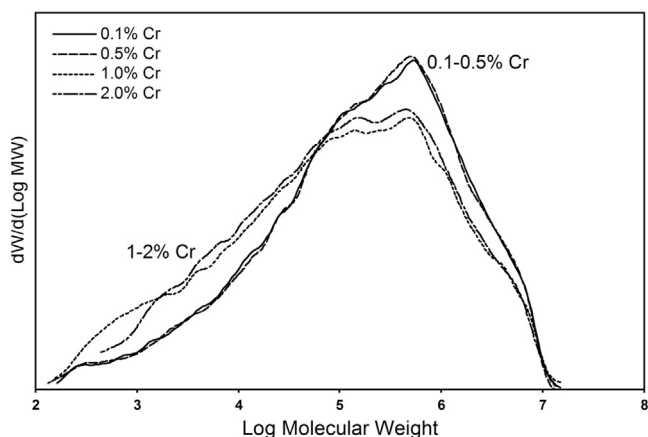
Fig. 8. Influence of Cr loading on the MW distribution from Cr(AcAc)$_3$ sublimed onto fluorided silica-alumina.

Table 4
Response to H$_2$ as a MW regulator.

H$_2$ Partial Pressure, atm	0	3.4	7.5
H$_2$/Et Pressure Ratio	0	0.22	0.67
Activity, kgPE/g/h	2167	994	841
Melt Indices			
MI, g/10 min	0.0011	2.05	15.2
HLMI, g/10 min	0.0485	107	713
Molecular Weight			
M_N, kg/mol	10.86	5.96	4.14
M_W, kg/mol	790	119	69
M_Z, kg/mol	3519	648	350
MW Breadth			
M_W/M_N	72.8	20.0	16.6
M_Z/M_W	4.5	5.4	5.1
Density, g/mL	0.9469	0.9625	0.9645

Catalyst: Cr(AcAc)$_3$ on fluorided silica-alumina, 600 °C. Reaction at 100 °C and total pressure of 550 psig.

per gram of Cr per hour. Then it drops as more Cr(AcAc)$_3$ is added, indicating that less is being translated into active sites. The reason for this behavior has long been a puzzle. It cannot be attributed to diffusion [1] because it is observed even in solution-phase polymerization. It suggests that there is something different about that first chromium added that makes it more capable of supporting polymerization. Perhaps the most acidic surface sites are the first to be occupied by Cr(AcAc)$_3$, and these are consequently the most active.

If one extrapolates the Cr activity line in Fig. 7 to near zero percent Cr, one conservatively obtains an activity of about 2 tons of PE per gram of Cr per hour. Taking this value as representative of all active sites, one can calculate that no more than 10% of the chromium could be active on a catalyst containing a loading of 2% Cr.

The polymer was also examined as a function of Cr(AcAc)$_3$ loading, and the MW distributions obtained are shown in Fig. 8. It is interesting that the first chromium sites added produce a significantly narrower MW distribution than do catalysts containing higher Cr loadings. That is, the later increments of Cr added tend to generate more sites producing low-MW polymer. Thus, the earlier sites are different, or perhaps there is some kind of interaction between sites at higher loading, although this seems unlikely given the sparse density of sites.

3.7. Hydrogen

Hydrogen is often added during commercial ethylene polymerization to lower the average molecular weight. Growing PE chains are "clipped" by hydrogenolysis on some sites which causes a rise in the melt index (lower melt viscosity) and it may also affect the MW distribution. Ziegler catalysts can produce the entire commercial MW range just by adding the appropriate amount of hydrogen to the reactor. However, Phillips chromium oxide catalysts typically exhibit very poor response to hydrogen, which is often a problem during commercial operations.

Table 4 shows the effect of adding hydrogen when the catalyst is Cr(AcAc)$_3$ deposited onto standard fluorided silica-alumina at 110 °C. The activity was lowered by the addition of hydrogen, partly because the ethylene concentration had to be lowered to accommodate the additional pressure of H$_2$. The melt index (both MI and HLMI), which is a measure of the flow of the molten polymer, increased exponentially in response to the lowered MW. Note the huge drop of all three moments of the molecular weight. The breadth of the MW distribution also narrowed, indicating that the high MW part of the distribution was disproportionally affected by
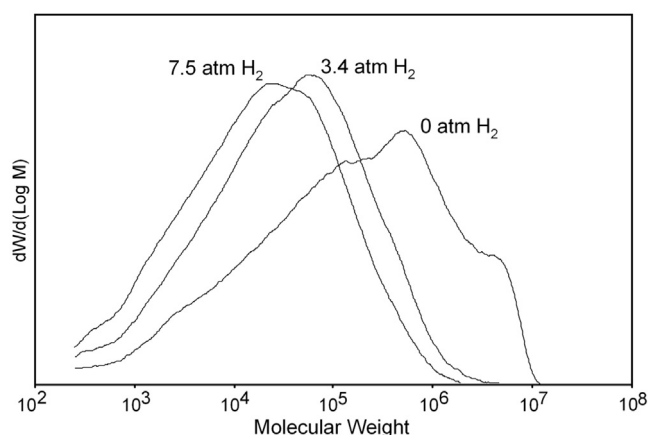

Fig. 9. A major shift in the MW distribution is observed when H$_2$ is added to the reaction (the catalyst was Cr(AcAc)$_3$ on fluorided silica-alumina).

hydrogen. This can be understood as a statistical response [1] rather than (or perhaps in addition to) a genuine chemical selectivity of the high-MW sites to hydrogen.

Fig. 9 shows the change in MW distribution when hydrogen is added. The huge shift to lower MW on this log scale is remarkable and it indicates an unusual sensitivity to the presence of hydrogen. This would be considered desirable in commercial operations. Note that, as suggested by the data in Table 4, the high-MW portion of the MW distribution is preferentially altered.

3.8. Short-chain branching

Alpha-olefins, such as 1-butene or 1-hexene, are frequently added to the ethylene polymerization reaction in order to impart "short-chain" branching onto the otherwise linear PE backbone. Such short-chain branches disrupt the polymer crystallinity and consequently lower the density of the polymer. Thus the density serves as a quick industrial measure of the degree of branching in the polymer. Note that Tables 1,3 and 4 list the density of the polymers. The density of typical HDPE homopolymers ranges from 0.975 down to about 0.935 depending on the molecular weight and MW distribution. Consequently the density values in the above tables suggest that these polymers naturally contain a small amount of branching. This is a result of the very broad MW distribution, which contains oligomeric and even light olefins that can then become incorporated again as branches. One could also detect these α-olefins in the reactor by the slight, but distinctive,
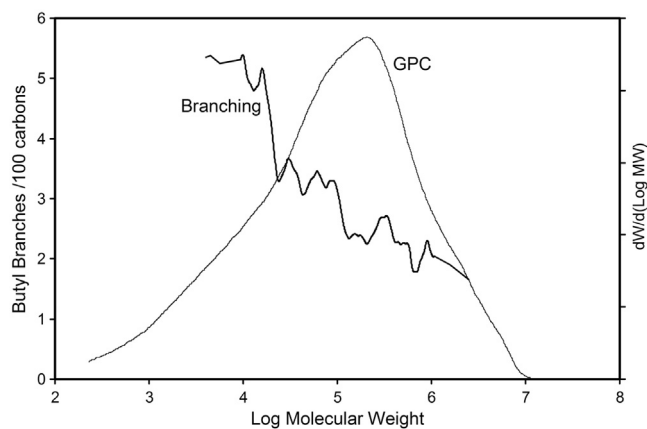
Fig. 10. Branch placement as a function of MW in an ethylene-hexene copolymer made using Cr(AcAc)₃ on fluorided silica-alumina.

Table 5
Long-chain branching as a function of the support.

P/Al	LCB per
molar raio	10^6 carbons
0	1.4
0.2	1.6
0.6	2.3
0.9	3.4

Aluminophosphate supports calcined at 600 °C were treated with Cr(AcAc)₃ at 250 °C.

sweet odor. Branching derived from incorporation of these light α-olefins is usually termed "in-situ" branching and it is often observed from chromium alkyl or arene catalysts [1,7,8,10,50–56] or from chromium oxide catalysts under some conditions [1,57–59].

One important aspect of copolymerization is the incorporation efficiency, that is, the ease with which the catalyst can insert α-olefins versus ethylene. Poor efficiency means that more comonomer must be added to the reactor to achieve a target amount of branching. To determine the response of the Cr(AcAc)₃ system to comonomer, a copolymerization reaction was carried out using Cr(AcAc)₃ deposited onto standard fluorided silica-alumina at 250 °C. 1-Hexene was added to yield a concentration of 0.31 mol/L. The copolymerization was conducted at 95 °C and 1.41 mol/L ethylene. The addition of 1-hexene did not increase the activity, but it did yield polymer of 0.9388 g/mL density, equivalent to about 0.6 mol% 1-hexene incorporated. Note that to achieve a 1-hexene/ethylene ratio of only 0.06 in the polymer, it was necessary to use a concentration ratio of 0.22 in the reactor. This reflects how much more reluctantly the α-olefins incorporate compared to ethylene. Actually this is a fairly typical response that is characteristic of other chromium catalysts, including commercial chromium oxide catalysts.

Such short-chain branching increases flexibility, toughness and stress-crack resistance in the finished polymer. Catalysts that contain a variety of active site types, such as Ziegler or Phillips catalysts, usually tend to concentrate branching into the low-MW portion of the MW distribution [1,60]. This is in large part because the strong Lewis acidity of some polymerization sites enhances reactivity with the more electron-donating α-olefins, but it also enhances β-hydride coordination with the polymer chain which is a precursor to chain termination. Thus the sites that incorporate α-olefin best also terminate best. In addition, the act of α-olefin incorporation also stimulates chain termination [1] because the resultant tertiary β-hydride is more reactive than the usual secondary β-hydride. Consequently copolymers tend to have lower MW than homopolymers made under the same conditions, regardless of the catalyst.

To determine the behavior of the Cr(AcAc)₃ catalyst, the 0.9388 density ethylene/1-hexene copolymer described above was also analyzed by FTIR-SEC, which detects where the branches are within the MW distribution. The results are shown in Fig. 10. Note that, with this system too, the branching tends to be concentrated into the low-MW region. This is the expected behavior, and the response is nearly identical to many commercial chromium oxide catalysts. It is consistent with the idea that the most Lewis acidic sites produce lower MW polymer and are also more reactive with α-olefins. The result is a disproportional amount of branching in the low-MW part

of the MW distribution. Unfortunately this is not the preferred profile for best polymer mechanical performance, and much research effort has been expended over the years to counteract this natural tendency. The Cr(AcAc)₃ catalyst does perhaps offer the advantage of having a much higher MW component, which does still contain branching. This should improve impact and tear resistance compared to Phillips catalysts.

3.9. Long-chain branching

In addition to the short-chain branching described above, typically 2–6 carbons long, commercial polyethylene often contains long-chain branching (LCB) too, branches longer than about 150 carbons which is the critical entanglement length for PE rheology. This is because PE chains growing on Cr-based catalysts are usually terminated by β-hydride elimination leaving a vinyl end-group on the liberated chain. This vinyl end-group can then become incorporated into another growing chain as a branch. The process is much like copolymerization of other α-olefins, only the incorporated chain is called a "macromer" rather than a comonomer. Long-chain branching occurs very rarely, in comparison to incorporation of short-chain branching, but it has a profound influence on the flow behavior of the molten polymer during molding operations [1,61–63]. LCB content controls the ease of flow during extrusion, melt strength in all applications, bubble stability and melt fracture in film, slump resistance in pipe and blow molding, die swell during extrusion of bottles, warpage upon cooling, and dozens of other behaviors in as many different applications and products.

While much of the behavior of the Cr(AcAc)₃ system is similar to Phillips chromium oxide catalysts, some characteristics were quite different. In general the degree of long chain branching in the polymers from Cr(AcAc)₃ tends to be quite low compared to that from chromium oxide catalysts. Most of the usual variables that influence LCB content from chromium oxide catalysts have no effect on the Cr(AcAc)₃ catalyst system. For example, variation of the calcination temperature of silica-alumina between 400 and 800 °C produced no significant difference in long chain branch content. Janzen-Colby calculations produced relatively constant values of 1.2 to 1.4 branches per million carbons. Similarly the chromium loading, which has a strong influence on LCB content from chromium oxide catalysts, produced relatively constant LCB values of 1.2 to 1.3 branches per million carbons from Cr(AcAc)₃ as Cr was varied between 1 and 4 wt%. Other major variables also had little or no effect on LCB content, such as the temperature of Cr(AcAc)₃ deposition or the atmosphere used (CO or H₂ versus N₂).

Even the type of support seemed to make little difference in LCB content. Silica, silica-alumina, or fluorided silica-alumina produced similar LCB content, as did alumina versus sulfated alumina. The one notable exception to this rule was the aluminophosphate family. As was observed with chromium oxide catalysts [64], the LCB content from Cr(AcAc)₃ catalysts seemed to increase with rising phosphate content. An example of this behavior is shown in Table 5. The presence of phosphate is thought increase the acidity of surface −OH groups to which Cr binds, and which could promote macromer retention and/or insertion [65].

3.10. Other organic ligands

In comparison to catalysts made with Cr alkyls, or bisarene Cr, or Cr oxide (Phillips), the 2,4-pentanedionate ligand on the chromium constitutes a different kind of catalyst when deposited onto a support and treated with cocatalyst. It differs from these earlier catalysts in having the presence of coordinated oxygen in the ligand itself. Thus it is different from these earlier catalysts in that it has no initiating Cr-alkyl or hydride group (or any accessible route to such a species) nor is it capable of reducing and self-alkylating upon contact with ethylene. This is why a cocatalyst is needed, much like Ziegler catalysts. Presumably the aluminum alkyl attacks and removes at least one of the AcAc ligands.

In an effort to probe the importance of the remaining AcAc ligands to the active site, other chromium compounds containing oxygen-coordinated ligands were also tested and compared to the original Cr(AcAc)$_3$ compound. In one experiment, the standard fluorided silica-alumina was impregnated with four such chromium compounds dissolved in toluene. These catalysts were then dried in nitrogen at 150 °C and tested for polymerization activity in the presence of 1 mmol of triisobutylaluminum cocatalyst. The results are summarized in Table 6.

The most similar compound tested was chromium tris-hexafluoroacetylacetonate, *i.e.* Cr(HF-AcAc)$_3$. One might expect the presence of so many fluoride moieties on the ligand to withdraw electron density from the chromium and thus have a major influence on both the activity and polymer character. However, this was not the case. Table 6 summarizes the results of such a comparison. Both compounds produced about 2000 g of PE per gram of catalyst per hour. And, as shown in Table 6, the character of the polymer produced by both compounds was almost identical, i.e. the molecular weight and MW distribution.

To further probe the contribution of the organic ligand, two chromium (III) carboxylates were also tested, under the same conditions noted above. One was chromium (III) 2-ethyl, hexonate and the other was chromium (III) naphthenate. The results of these tests are also summarized in Table 6. Again an activity of about 2000 gPE/g/h was obtained from the 2-ethyl hexanoate, and less was observed from the naphthenate. The MW distributions obtained from all four compounds are shown in Fig. 11. They are identical, within the accuracy of the test. This indicates that the original ligand does not play an important role in the final catalyst, perhaps because it is not longer present. This observation is discussed further in the Conclusions section.

3.11. Comparison with Cr(VI) oxide catalysts

Another equally relevant comparison is between the Cr(AcAc)$_3$ catalysts described herein and chromium oxide (Phillips) catalysts
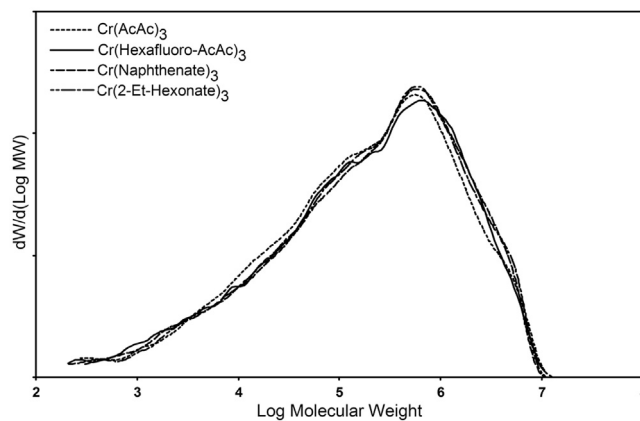

Fig. 11. Influence of the Cr organic ligand on the polymer MW distribution.

made using the same acidic supports. Because the latter catalysts have no organic ligands, such a comparison provides an insight into the importance of the remaining organic ligands on the Cr(AcAc)$_3$ catalyst system after Cr deposition and reaction with the triisobutylaluminum cocatalyst.

Therefore chromium (VI) oxide was deposited onto an acidic support described above for Cr(AcAc)$_3$ catalyst, i.e. sulfated alumina, which was then calcined in dry air at 600 °C. This preserves the chromium in the hexavalent state. Consequently such Cr(VI), i.e. Phillips, catalysts are reduced upon contact with ethylene and transformed into an alkylated lower-valent chromium catalyst [1]. This catalyst was then tested under standard conditions, both in the absence of cocatalyst (because these catalysts can self-alkylate), and also in the presence of triisobutylaluminum cocatalyst (which mimics the treatment used to make the Cr(AcAc)$_3$ catalysts). In one case a Cr(VI) catalyst was subjected to an additional treatment in carbon monoxide at 350 °C which is known to convert the Cr(VI) surface species into a "naked" Cr(II) or Cr(III) surface species [1]. The results of such testing are summarized in Table 7.

Upon viewing Table 7, one is immediately struck by the similarity of the Cr(AcAc)$_3$ and the Cr(VI) catalysts when used in the presence of triisobutylaluminum (TiBA) cocatalyst. The MW and MW distribution, and even the density, of the polymers are especially similar. In contrast, the Cr(VI) and even the CO-reduced, i.e. the Cr(II), catalyst are quite different in character when used without triisobutylaluminum cocatalyst. This is especially clear when comparing the various moments of average MW, i.e. M_N, M_W and M_Z, as well as the polymer density and the MW distribution (M_W/M_N), of the Cr oxide catalysts in Table 7 when used with versus without cocatalyst. It is obvious that the cocatalyst plays a

Table 6
Influence of the organic ligand on catalyst behavior.

Cr Source	Cr(AcAc)$_3$	Cr(HFAcAc)$_3$	Cr(2-Et Hexonate)$_3$	Cr(Napthenate)$_3$
Activity, gPE/g/h	1976	2267	1887	601
Melt Indices				
MI, g/10 min	0.00093	0.0009	0.00034	0.00027
HLMI, g/10 min	0.0364	0.07	0.0285	0.0220
Molecular Weight				
M_N, kg/mol	13.7	10.9	15.7	11.8
M_W, kg/mol	785	791	829	809
M_Z, kg/mol	3145	2932	3010	2865
MW Breadth				
M_W/M_N	57.2	72.4	53.0	68.5
M_Z/M_W	4.0	3.7	3.6	3.5
Density, g/mL	0.9422	0.9477	0.9482	0.9471

Catalyst: Various Cr(III) salts were deposited onto fluorided silica-alumina, then tested with tri-isobutyl aluminum for polymerization activity.

Table 7
Comparison of Cr(AcAc)3 catalysts to Phillips chromium oxide catalysts.

Catalyst	Cr(AcAc)$_3$[a]	Cr(VI)[b]	Cr(VI)[b]	Cr(II)[c]
Cocatalyst	TiBA	TiBA	None	None
Activity, g/g/h	755	1126	3152	1313
Density, g/mL	0.9527	0.9526	0.9386	0.9378
HLMI, g/10 min	0.04	0.39	0.00	0.00
M_N, kg/mol	6.1	6.7	127	26.4
M_W, kg/mol	613	692	1269	1190
M_Z, kg/mol	2602	3242	3176	3088
MW Breadth, M_W/M_N	100	103	10	45
LCB per million carbons	1.49	3.18	1.42	1.30

Catalyst: a) Cr(AcAc)$_3$ was sublimed at 250 °C onto a sulfated alumina which had been calcined at 600 °C; b) CrO3 was impregnated onto sulfated alumina and calcined in air at 600 °C; c) the catalyst in b was then further treated in CO at 350 °C for half an hour, then cooled after the CO was purged out.
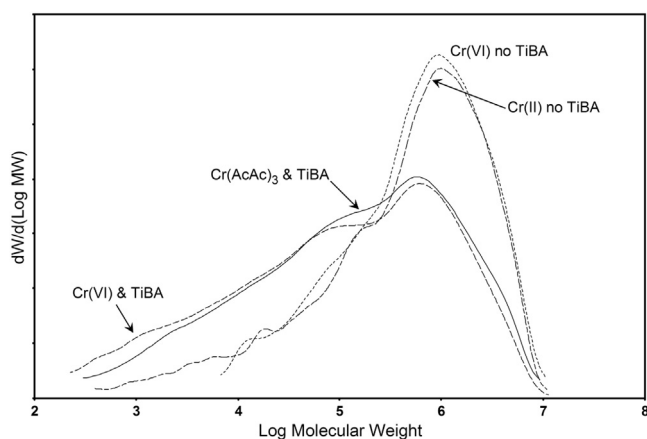

Fig. 12. MW distribution from Cr(AcAc)$_3$ and Phillips chromium oxide catalysts, both on the same sulfated alumina carrier, in the presence or absence of triisobutylaluminum (TiBA) cocatalyst.

major role in the determining the behavior of the catalyst and the character or the polymer, even on the Cr oxide catalysts.

The MW distribution, shown in Fig. 12, also makes the point quite clearly. It is obvious that the presence of cocatalyst makes a major difference in the MW distribution, and hence the diversity of the active site population, of the Cr(VI) oxide catalyst. In the presence of cocatalyst the MW distribution obtained is identical to that from the Cr(AcAc)$_3$ catalyst, but in the absence of cocatalyst Cr(VI) and Cr(II) oxides produce a completely different MW distribution. This strongly suggests that the AcAc ligands, if any remain after treatment with triisobutylaluminum cocatalyst, have little or no influence on the character of the catalyst. It further indicates that the presence of cocatalyst can have a major influence on the catalyst, whether derived from Cr(AcAc)$_3$ or Cr oxide. This is discussed further below in the Conclusions section.

One can also see in Table 7 the activities of the various catalysts. The activity indicates that the presence of triisobutylaluminum cocatalyst is actually detrimental to the development of active sites from Cr(VI) catalysts. That is, Cr(VI) catalysts are actually more effectively reduced and alkylated into active sites in the absence of cocatalyst. Note also in Table 7 that cocatalyst has a huge effect on the density of the polymer, which is actually increased. This counter-intuitive response is because cocatalyst also broadens the MW distribution.

4. Conclusions

This catalyst system, i.e. Cr(AcAc)$_3$ or other trivalent Cr salts deposited onto an acidic oxide carrier, has been found to polymerize ethylene at high activity, comparable to the commercial Phillips

Cr oxide catalysts. This is an advantage in commercial operations because hexavalent chromium has been classified as carcinogenic. The catalyst is only active when the carrier contains strongly acidic sites, and also when in the presence of a trialkylaluminum cocatalyst. The purpose of the carrier is clearly to increase the electron deficiency of the chromium and the purpose of the cocatalyst must be to alkylate the chromium. However, the cocatalyst may also reduce the initially trivalent chromium, possibly to a divalent form. Thus the 60 year old debate about the valence of the active site on the commercial Phillips catalysts also spills over into this related system as well. At present, we have no information as to whether the alkylated active site is trivalent or divalent.

Only the most acidic carriers were found to activate Cr(AcAc)$_3$ to form a polymerization catalyst. Of the many supports tested, a fluoride-treated silica-alumina, a fluoride- and chloride-treated silica alumina, and a sulfate-treated alumina seemed to perform best in these experiments. However, as has been discovered in metallocene activation studies using these same types of carriers [14–17], there are probably many other variations that are at least equal in their performance.

It is clear from the polymer MW distribution that these Cr(AcAc)$_3$ catalysts contain an extremely wide variety of active sites compared to the usual Phillips chromium oxide/silica catalysts. No doubt this indicates a variety of ligand environments around the chromium sites after exposure to aluminum alkyl cocatalyst. These ligands could come from the initial organic ligand (AcAc), or through interaction with the acidic support, or they could even be new compounds made by reaction of the aluminum alkyl cocatalyst with the AcAc or the support.

The similarity of the MW distributions shown in Fig. 11 and Table 6, where four very different chromium (III) organic salts were used, suggests that the initial organic ligand does not play a major role in determining the character of the active sites. Neither did the MW distribution change as the Cr(AcAc)$_3$ catalyst was heated from 90 °C, where it probably contained three AcAc ligands per Cr, up to nearly 600 °C, where the initial organic ligands should have been removed or pyrolized (see Table 2 and supplemental Figs. S1 and S3). Furthermore, Fig. 12 shows almost identical MW distributions from Cr(AcAc)$_3$ and also from chromium oxide when both were supported on the same sulfated alumina and treated triisobutylaluminum. All of these observations suggest a minor, if any, role for the AcAc ligand in determining the character of the active site population. It seems likely that the AcAc ligands are removed upon contact with the alkylaluminum cocatalyst.

In contrast, one can see a strong influence from the acidic support in Figs. 1 and 2 and in Table 1. The addition of acidic modifiers such as fluoride, phosphate or sulfate made an especially pronounced change in the MW distribution. Increased acidity often enhanced the activity of the catalyst by adding a large new population of sites producing low-MW polymer. This has also been observed from Phillips chromium oxide catalysts [1,2,42,43]. Also like Phillips catalysts, these Cr(AcAc)$_3$ catalysts responded to the calcination temperature of the support. Higher temperatures lowered the molecular weight (Fig. 6 and supplemental Fig. S5), although the effect was more subtle than from Phillips catalysts.

Finally there is also the contribution of the aluminum alkyl cocatalyst to consider. Fig. 4 and supplemental Fig. S4 show that the cocatalyst can have an influence on the active site population. Only aluminum alkyls produced active sites, not zinc or boron alkyls, and even diethylaluminum chloride was ineffective. This suggests that the cocatalyst plays a strong role in site development, beyond mere alkylation, perhaps reacting with or removing ligands. In Fig. 4 one can see in the MW distribution a significant difference between methylaluminoxane, triethylaluminum, and triisobutylaluminum cocatalyst. Supplemental Fig. S4 shows that the amount of cocatalyst can also influence the MW distribution.

Perhaps the data that is most revealing concerning the role of the cocatalyst is found in Fig. 12 and Table 7. A large shift in MW distribution was observed when two chromium oxide catalysts (one hexavalent and one divalent) were tested with and then without triisobutylaluminum cocatalyst. The addition of cocatalyst caused a pronounced broadening of the MW distribution from these Cr oxide catalysts to become identical to that from the Cr(AcAc)$_3$ catalyst on the same sulfated alumina when also tested with triisobutylaluminum cocatalyst.

In contrast to chromium oxide catalysts, note that the activity and the MW distribution from Cr(AcAc)$_3$ catalysts were not greatly affected by heating, even at temperatures where the organic ligands were pyrolized (Fig. 3 and supplemental Figs. S1, S2 and S3). This again strongly indicates that the organic ligand is not contributing and probably removed. Nor was much difference observed in the MW distributions whether the heating was done in N$_2$, CO or H$_2$. Perhaps this is because the cocatalyst removes the organic ligand and also reduces the chromium anyway.

Acknowledgement

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata.2016.08.023.

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