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Comparison of Cr/SiO_2 and $Cr/AlPO_4$ Polymerization Catalysts.
2. Chain Transfer

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ABSTRACT: The polymerization of ethylene over $Cr/AlPO_4$ produces a polymer having a broader molecular weight distribution than is obtained from over Cr/SiO_2. This suggests that the aluminophosphate carrier produces a broader variety of active sites than does silica, because the chain-transfer rate on each site is probably influenced by the local environment. Varying the polymerization conditions allows different types of sites to be distinguished on Cr/aluminophosphate catalysts. Some, which are unusually responsive to transfer agents, seem to be associated with surface phosphate.

Introduction

On the Phillips catalyst, i.e., chromium oxide supported on silica (Cr/SiO_2), ethylene polymerization is always accompanied by chain transfer, the termination of one growing chain and the initiation of its successor on the same active site.[1] Transfer probably occurs through the shift of a β-hydride from the chain to the monomer. This yields a terminal vinyl on the end of the chain, while the new chain starts with methyl. The cycle occurs repetitiously on each site, the lifetime of each chain being less than a second.[1,2] The chain length is determined by the rate of propagation relative to chain transfer.

Chain Transfer by Beta-Hydride Elimination to Monomer

The chain-transfer rate on Cr/SiO_2 is highly sensitive to many factors, such as the polymerization temperature or monomer substituents. Even variations in the local electronic environment around the active center are thought to exert a powerful influence. For example, increasing the activation temperature, which diminishes the surface hydroxyl population, decreases the molecular weight of the polymer produced, which suggests an acceleration of the chain-transfer reaction.[3,4] Adding modifying agents to the catalyst, such as fluoride or titania, can have a similar effect.[5] Thus the heterogeneity of the catalyst surface is reflected in the polymer because each site probably has its own characteristic transfer rate.[6,7] For commercial purposes this permits fine control of numerous polymer properties like impact resistance, shear response, warpage, or die swell. These and other properties are often controlled by subtle variations in the molecular weight distribution of the polymer.

Therefore we find that replacing the silica carrier by an aluminophosphate support also has an effect on the polymer. On both carriers the chromium is thought to react with surface hydroxyls to yield a chromate or dichromate species,[1-4] which is the precursor of the active site. Despite structural similarities,[8,9] the surface character of $AlPO_4$ is quite different from that of silica.[10] Two types of hydroxyls have been reported on aluminophosphates (designated generally as $AlPO_4$) and may be available for stabilization of chromium. One is attached to phosphorus and the other to aluminum. Other differences in bonding also exist, such as the presence of some double-bond character in P–O. Support effects thus become very powerful, and many differences are seen between Cr/SiO_2 and $Cr/AlPO_4$. Part 1 of this series[11] described differences in the kinetics of polymerization over the two catalysts. This report looks at the polymer to gain further insight.

Experimental Section

Activity tests were conducted under slurry conditions at 95 °C (unless otherwise stated) in a 2-L stirred autoclave. A pressurized jacket filled with boiling alcohol held the internal temperature of the reactor constant to within 0.5 °C. About 0.05 g of the catalyst was charged under dry nitrogen, 1 L of liquid isobutane diluent sometimes containing triethylborane (TEB) was then charged, and finally ethylene was supplied on demand at 550 psig (unless otherwise stated) until about 200–250 g of solid polyethylene had been made. Under these conditions the polymer does not go into solution but remains as a slurry. The rate of polymerization was followed by monitoring the flow of ethylene into the reactor through a calibrated differential-pressure cell. Isobutane and ethylene stock were Phillips polymerization grade, further purified through activated alumina and, in the case of isobutane, through a CO-reduced Cr/SiO_2 column. Triethylborane (TEB), when used, was added to equal 5×10^{-5} mol/L of the reaction diluent, or generally about 5 TEB/Cr. Hydrogen, when used, was added to equal 50 psig unless otherwise stated.

Aluminophosphate catalysts were made for this study by quickly neutralizing a concentrated solution of aluminum nitrate and ammonium phosphate. The gel was washed, dried, and then impregnated with a solution chromium nitrate to equal 1 wt % Cr. Further details concerning the structure and morphology of these aluminophosphate catalysts can be found a previous report.[12]

To activate the catalyst, about 10 g was fluidized in a dry air stream for 3 h at 300–850 °C, as specified in each experiment. A quartz tube was used with sintered glass disk to support the sample, which was heated to temperature at 400 °C/h with a 1 cm/s flow rate through the bed. Gasses were predried through activated alumina or, where possible, through CO-reduced Cr/SiO_2. The silica used in this study was Davison grade 952 having a surface area of about 280 m^2/g after activation at 600 °C.

Melt index (MI) and high-load melt index (HLMI) values were obtained at 190 °C according to ASTM-D1238, conditions E and F, respectively. Intrinsic viscosity measurements were taken on a Schott automated viscometer, with Ubbelohde type Oc orifice. Solutions of polymer in 1,2,4-trichlorobenzene were run at 130 °C, and viscosity-average molecular weights were calculated from the intrinsic viscosity by using the Mark–Houwink equation

$$[\eta] = K(M_v)^a$$

where $K = 3.95 \times 10^{-4}$, $a = 0.0726$, $[\eta]$ is the intrinsic viscosity, and M_v is the molecular weight. Size-exclusion chromatography 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. Methyl and terminal vinyl end-group analysis of the polymer was done by infrared spectroscopy using the absorption bands at 1365 and 909 cm^{-1}, respectively.

Results and Discussion

Hydroxyl Population. The activity of chromium oxide on silica is a sensitive function of the temperature at which the catalyst has been calcined. Surface hydroxyls are

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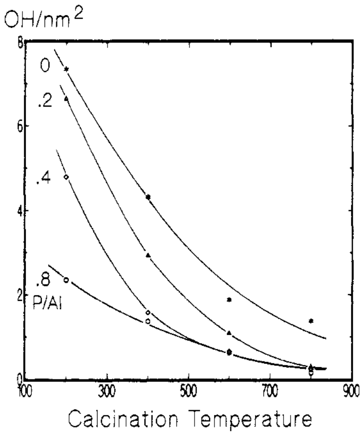


Figure 1. Surface hydroxyl population, as measured by reaction with methylmagnesium iodide, on four different carriers as a function of calcining temperature: P/Al = O; P/Al = 0.2; P/Al = 0.4; P/Al = 0.8.

thought to interfere with the polymerization process, perhaps by coordinating to active centers. The calcining step removes many of these hydroxyls by condensation to release water. Thus, increasing the calcining temperature improves the activity, possibly by increasing the percentage of active chromium. This amount is difficult to estimate, but may lie somewhere from 1 to 30% of the total chromium.[2] What distinguishs active from inactive Cr is not entirely clear but probably involves the extent of coordinative unsaturation at each site. In fact, several different types of sites which differ in their chemisorption behavior[2,13,14] have been identified on silica.

A similar situation seems to exist on the aluminophosphate carriers as well. The activity of Cr/AlPO$_4$ catalysts depends on the calcining temperature in a similar manner, as was shown in part 1 of this series.[11] However, a new variable also becomes important. The hydroxyl population depends not just on the calcining temperature but also on the amount of phosphate in the carrier. This is shown in Figure 1, which plots the hydroxyl population found on a series of carriers against calcining temperature. As the amount of phosphate in the carrier (the P/Al ratio) increases, a tetrahedral structure is increasingly imposed on the otherwise octahedral aluminate composition,[12] and the surface hydroxyl population decreases.

Thus in Figure 2 activity varies with the P/Al ratio much as it does with the calcining temperature, probably because in both cases the hydroxyl population is affected. The activity of these catalysts goes from near zero for pure alumina (P/Al= O) up to a peak at P/Al = 0.8–0.9. Then it declines as the onset of crystallinity at P/Al = 1 destroys the surface area. (These structural changes have been described in a previous report.[12]) As Figure 2 shows, this is true whether or not triethylborane (TEB) is used in the reactor as a cocatalyst.

In addition to activity, the molecular weight (MW) of the polymer also depends on the hydroxyl population.[2-5] Again this seems to be true of both Cr/silica and Cr/AlPO$_4$ catalysts. MW decreases with increasing calcining temperature, at least up to the point of sintering. As with activity, the aluminophosphate carriers also display a similar dependency on the P/Al ratio. This is shown Figure 3, where three indications of the MW are plotted. The melt indices provide a very sensitive indication of the fluidity of the molten polymer at 190 °C. In Figure 3 the HLMI, or high-load melt index, refers to a particular condition under which the test is run. Also plotted is the MW of the polymer as determined by two independent methods. The viscosity average (M_v) was calculated from the intrinsic viscosity, and the weight average (M_w) was obtained from size-exclusion chromatography. Whatever the measurement, MW decreases with increasing phosphate. Again this probably reflects, at least in part, the decreasing hydroxyl population. However, the presence of phosphate may contribute another effect too, which will be described below.

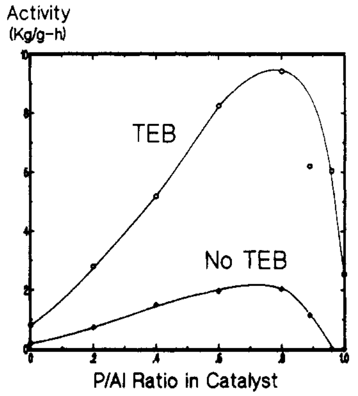


Figure 2. Series of aluminophosphate catalysts made by coprecipitation to contain varying amounts of phosphate and 1% Cr. Each was calcined in air at 600 °C, which converts the Cr to the hexavalent oxide, and allowed to polymerize ethylene in a high-pressure autoclave. Activity is enhanced by the phosphate. In half the runs, triethylborane (TEB) was added to the reactor as a cocatalyst to help reduce the chromium.

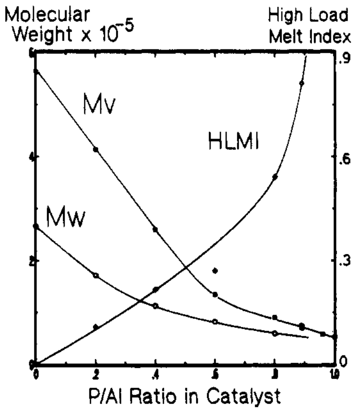


Figure 3. Chain transfer depends on the amount of phosphate in Cr/aluminophosphate catalysts, as shown by three different measurements on the polymer. High-load melt index (HLMI) increases with phosphate due to better fluidity from shorter chains. Viscosity-average molecular weight (M_v) and weight-average molecular weight (M_w) decrease with increasing levels of phosphate. Three different reactor conditions are represented: (HLMI) no additives; (M_v) with TEB; (M_w) with TEB and H_2.

Effect of TEB. Normally, on chromium oxide catalysts the chromium is hexavalent after calcining. On contact with ethylene it is reduced to a lower valent active state, probably Cr^{2+}.[2,15] Part 1 of this series[11] noted that stronger reducing treatments improve the activity of Cr/AlPO$_4$ catalysts, and triethylborane (TEB) is especially effective, increasing activity about 5-fold. It was concluded that TEB and other reducing treatments bring to life a new population of sites which would not otherwise become active. We call this effect the "Type A" interaction between TEB and Cr, and it can be seen in Figure 2, which plots the activity of various catalysts with and without TEB. Notice that the promotional effect of TEB on activity is almost independent of the amount of phosphate in the catalyst. All catalysts benefited by the addition of TEB.

Other reducing treatments also improve the activity of Cr/AlPO$_4$, but TEB displays another effect which seems

Table I
HLMI Obtained from Different Reducing Treatments

reduction by	$Cr/AlPO_4$	Cr/SiO_2
ethylene at 95 °C	0.95	6
TEB at 95 °C	144.0	4
CO at 350 °C	1.4	3
CO then TEB	47.5	
TEA at 95 °C	0.80	4

Table II
Summary of the Response to Triethylborane

	type of response[a]	
catalyst	Type A (activity)	Type B (transfer)
$Cr/AlPO_4$	strong	strong
CO-reduced	none	strong
Cr/SiO_2	weak[b]	none
Cr/Al_2O_3	strong	none

[a] In Type A interaction the TEB acts as a reducing or scavenging agent to increase the activity, probably by creating a new population of sites. In Type B interaction the TEB accelerates the chain-transfer rate possibly by an exchange mechanism. [b] Described as weak because TEB accelerates the development of activity but does not greatly change the maximum rate observed.

to be unique to the boron alkyls. It decreases the polymer MW. This is shown in Table I, where TEB is shown to increase the HLMI by over 2 orders of magnitude. Other reducing treatments, such as triethylaluminum (TEA) or CO at 300 °C, do not produce this effect. If the $Cr/AlPO_4$ catalyst is already reduced, say by CO at 300 °C, then adding TEB to the reactor has no effect on the activity, but it still accelerates the transfer rate, as is evident in Table I by the rise in HLMI. We call this lowering of the MW the "Type B" interaction between TEB and the chromium, because it seems to be independent of the Type A influence.

It seems unlikely that activation by TEB preferentially generates low MW producing sites. Other reducing treatments also activate $Cr/AlPO_4$ without changing the MW. And as seen in Table I, the CO-reduced catalyst was not activated by TEB, even though the transfer rates were enhanced.

Instead, the Type B interaction with TEB could be an exchange between the alkyls on the boron and the active center, which is not unknown for boron alkyls.[16] However, the amount of TEB in the reactor is so minute, only about 0.002 mol/(mol of polymer), that it could hardly have such a profound influence on the molecular weight of the polymer unless the process is somehow catalytic. This is accomplished if the boron alkyl then reacts with ethylene in the reactor which has been reported to be a strong displacing olefin in this temperature range.[16-19] TEB is then regenerated, and the driving force for the overall reaction is the irreversibility of the second step. Once incorporated into the polymer lattice, the polymer chains are probably unavailable for further reaction. Of course this is only one interpretation of the TEB Type B influence. It is also conceivable that the TEB merely adsorbs on some sites and changes their termination behavior.

Exchange Between Boron Alkyl and Active Site

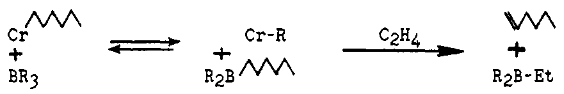


Table II summarizes the response to TEB of the various catalysts. The Type B response seems to be very specific to supports containing phosphate. Notice that TEB does not have this effect on Cr/SiO_2, as Table I also shows. Transfer rates on Cr/SiO_2 remain fairly constant or even decrease slightly when TEB is added to the reactor. Neither is it seen on Cr/Al_2O_3 even though it too is activated by TEB. The MW obtained from Cr/Al_2O_3 is the same with or without TEB in the reactor.

Table III
Phosphate Loading Affects Chain-Transfer Sensitivity

P/Al ratio in catalyst	base HLMI (no additives)	HLMI response factor on addition of TEB	H_2
0	0	1[a]	40[a]
0.2	0.1	2	45
0.4	0.2	47	43
0.6	0.3	410	69
0.8	0.6	690	53
1.0	0.7	260	65

[a] Since the base HLMI was zero, these factors were estimated from the intrinsic viscosity. TEB caused almost no change in the IV, and H_2 affected it much as it affected a P/Al = 0.6 catalyst.

Table III further demonstrates the dependence of the Type B interaction on phosphate. Here the response to TEB and H_2 is listed as a function of the P/Al ratio in the catalyst. Notice that the base HLMI, which was obtained with no additives in the reactor, increases with the P/Al ratio. This could reflect the decreasing hydroxyl population, as mentioned earlier. Adding TEB to the reactor, (third column) does not have the same effect for each catalyst. TEB does not change the MW when P/Al = 0, hence the response factor to TEB is 1. But as the support contains increasingly more phosphate, TEB produces a greater response. By P/Al = 0.8, adding TEB to the reactor increases the HLMI by nearly 700-fold. Thus the presence of phosphate seems to predispose at least some sites to react with the TEB.

Interaction with Hydrogen. Among Ziegler and some organochromium catalysts,[20-22] wide control of MW is achieved by adding hydrogen to the reactor, which interrupts the normal growth of polymer chains, yielding a methyl on each end. Since H_2 is consumed in the reaction, we call it termination by hydrogenation. This behavior is not typical of chromium oxide on silica, which terminates by β-H elimination, and exibits very little sensitivity to hydrogen. In contrast, $Cr/AlPO_4$ is found to be highly responsive to hydrogen, but the polymers are still high in vinyl unsaturation even when hydrogen is added to the reactor. In addition to hydrogenation, hydrogen also seems to accelerate β-H elimination through an unknown mechanism. Hogan found this to a limited extent even on Cr/silica.[1] Adding D_2 yielded HD and prominent $-CH_2D$ end groups in the polymer.

Hydrogen Accelerates Chain Transfer by Two Different Mechanisms

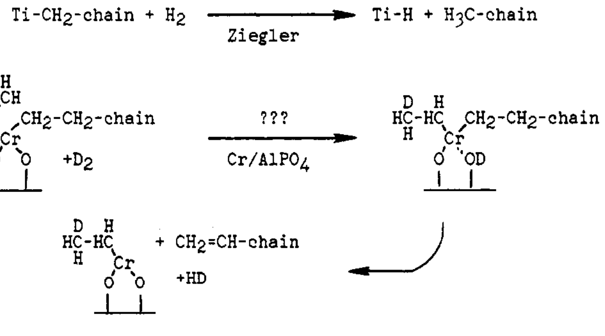


Table IV shows the end-group analysis of various polymers as determined by infrared absorption and how hydrogen affects the methyl and vinyl populations. Notice that on $Cr/AlPO_4$ hydrogen promotes both vinyl and methyl end groups. However, the methyl absorption is

Table IV
End-Group Analysis by Infrared Absorption[a]

catalyst	additives during polymerization		
	none	H_2	TEB
$Cr/AlPO_4$			
vinyl	1.1	1.4	1.3
methyl	0.8	1.7	1.0
Cr/SiO_2			
vinyl	0.7	0.8	
methyl	0.4	0.5	
Cr/Al_2O_3			
vinyl	0.5	0.7	0.5
methyl	0.5	2.5	0.5

[a] Vinyl and methyl IR absorptions are not on the same absolute scale, but it is useful to note changes when polymerization conditions are varied. Methyl also includes side branching.

Table V
Hydrogen Sensitivity of Various Catalysts

test*	H_2	catalyst type		
		Cr/SiO_2	$Cr/AlPO_4$	Cr/Al_2O_3
HLMI	no	0.80	0.04	0
	yes	3.60	21.1	0.93
M_v	no	250000	579000	1615000
	yes	184000	124000	435000

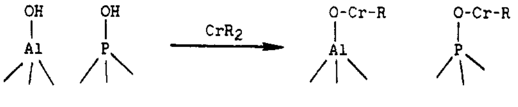
[a] Polymerization at 95 °C with 350 psi of ethylene and 150 psi of hydrogen when indicated.

increased slightly more, implying that some hydrogenation may also accompany the β-hydride elimination. This is in contrast to the effect of triethylborane, which increases methyl and vinyl proportionally. In comparison, hydrogen has very little effect on the Cr/SiO_2 catalyst, and TEB has no effect on Cr/Al_2O_3, indicating no Type B interaction.

Table V shows the relative magnitude of the response to hydrogen by the various catalysts. On Cr/SiO_2 the effect of H_2 is minor, increasing the HLMI from 0.8 up to 3. But on $AlPO_4$, where the starting HLMI is only 0.04, there is a greater response, increasing the HLMI up to 21.1. Cr/Al_2O_3 catalysts respond to H_2, but the starting point is much different, and even with H_2 they tend to make much higher MW polymer.

The response to H_2, in contrast to TEB, does not depend on the phosphate content of the catalyst. In Table III the HLMI increases proportionally for each catalyst when H_2 is added, usually about 30–60-fold. Cr/Al_2O_3 exhibits about the same sensitivity to H_2 as $Cr/AlPO_4$. Since Cr/SiO_2 is relatively insensitive, the H_2 response may be somehow related to the presence of aluminum in the carrier.

MW Distribution. The $Cr/AlPO_4$ catalysts tend to produce polymer having a broader molecular weight distribution than is seen from Cr/SiO_2, other conditions being equal. Figure 4 provides an illustration, where for simplicity the catalyst was not chromium oxide but an organochromium compound, bis(2,4-dimethylpentadienyl)-Cr(II). Such organochromium complexes are thought to react with hydroxyls on the support, losing one ligand, to yield a Cr center bound to the carrier through one link.[2,20,21] Since $AlPO_4$ contains two types of hydroxyls,[10] two types of sites could presumably be formed. Although P–OH is probably more acidic than Al–OH, both are expected to react rapidly with this organochromium complex due to its high reactivity.



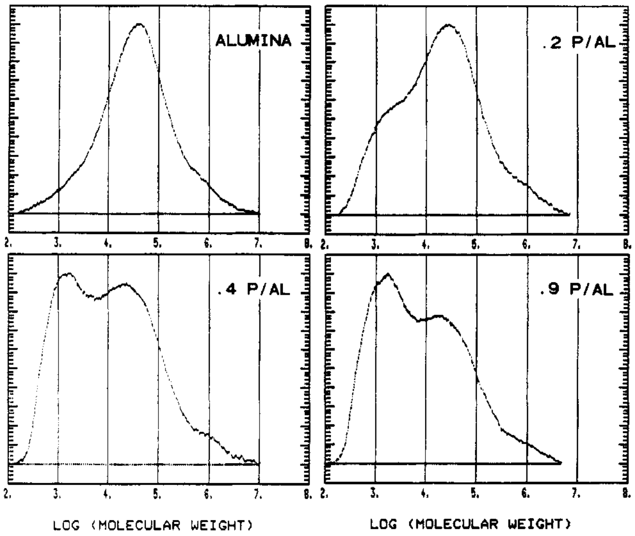


Figure 4. Two types of sites are suggested in the molecular weight distributions of these polymers. They were obtained from bis(dimethylpentadienyl)Cr(II) deposited on four supports in which the P/Al ratio was varied. The low MW peak probably results from chromium associated with surface phosphate.

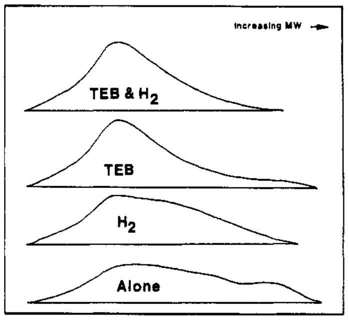


Figure 5. Size-exclusion chromatograms from polymers obtained under different reactor conditions. Catalyst: $Cr/AlPO_4$ 300 °C. Hydrogen: 50 psig. Both TEB and H_2 decrease the average MW but in different ways. TEB shifts material from the center of the distribution to lower MW, while H_2 also decreases the high MW tail.

Figure 4 describes the polymers made by four such catalysts. In each case, only the carrier was different, varying in P/Al ratio between 0 and 0.9. The alumina catalyst (P/Al = 0) produced only one polymer peak in the size exclusion chromatogram (SEC), but as phosphate was added to the carrier, a second, lower MW, peak also emerged and became almost dominant at P/Al = 0.9. The low MW peak probably comes from sites associated somehow with phosphate because it parallels the amount of phosphate in each support. The other peak may be associated only with aluminum because a similar peak is obtained from the alumina-supported catalyst. Thus it seems plausible that the two types of sites originate by reaction with the two types of hydroxyls. An alternative interpretation, however, is that the phosphate exerts its influence more indirectly, through changes in the catalyst structure or through secondary coordination around the chromium.

Supported chromium oxide catalysts are a little different from the above example in that Cr can probably attach through two links, not just one, giving rise to a greater number of species. So although a similar trend is obtained from chromium oxide (decreasing MW with increasing phosphate), the SEC curves are not bimodal. Again the influence of phosphate may be due to the formation of P–O–Cr bonds, but we cannot rule out a more indirect

Table VI
Molecular Weights Calculated from SEC Curves

additive	M_w	M_n	M_w/M_n
none	516 000	15 800	32.7
H_2	171 000	13 000	13.2
TEB	124 000	8 600	14.4
H_2 + TEB	67 000	8 300	8.1

Table VII
Sensitivity of $Cr/AlPO_4$ to 1-Hexene

reactor additive	polymer properties					
	density	MI	HLMI	vinyl	methyl	M_v
none	0.959	0	0.04	1.1	0.8	579 000
1-hexene	0.953	0.4	45	1.9	4.8[a]	110 000

[a] Includes branching.

contact. Since the type of sites is controlled by the amount of phosphate in the support, the molecular weight distribution is also affected, and this gives a valuable way of controlling many of the commercial polymer properties.

Figure 5 shows some size-exclusion chromatagrams of polymers from chromium oxide on $AlPO_4$ (P/Al = 1). The base polymer, obtained without additives in the reactor, always has a broad molecular weight distribution, with M_w/M_n typically greater than 25. By analogy with the organochromium catalyst (Figure 4), we might expect to see the influence of phosphate in the low MW part of Figure 5, whereas the high MW tail may originate from sites resembling those on Cr/alumina.

Adding hydrogen to the reactor, which is shown in the second SEC curve, lowers the average MW by decreasing the high MW tail. This is consistent with the earlier suggestion that hydrogen sensitivity may come from the influence of the aluminum.

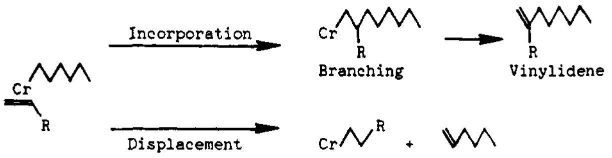
Adding TEB to the reactor, shown in the third SEC curve, also decreases the average MW, but in a different way. Material from the center and low MW side of the distribution seems to have been shifted to lower MW. This is the Type B response by the mid and low MW sites associated with phosphate. In contrast, the high MW tail, presumably from sites more like those on alumina, is less affected.

Finally in the upper curve of Figure 5 both hydrogen and TEB have been added to the reactor, and the effects are seen to be additive. The high MW tail is decreased as a result of the hydrogen, while TEB shifts other material to lower MW. Typically the molecular weight distribution narrows to M_w/M_n = 4–8. The molecular weights calculated from SEC curves tend to confirm these trends. An example is listed in Table VI.

Figure 6 shows another series of SEC traces. This time the amount of phosphate in the catalyst was varied from P/Al = 0 to P/Al = 0.8. Both TEB and H_2 were added in each run. The low MW side expands as the amount of phosphate in the catalyst increases, but the high MW tail shrinks. This is consistent with the previous peak assignments.

Copolymerization. On Cr/SiO_2 1-olefins accelerate termination, reportedly because after their incorporation into the chain the abstraction of β-hydride from a tertiary carbon is easier than from the usual secondary carbon.[1]

Possible Interactions with 1-Olefins



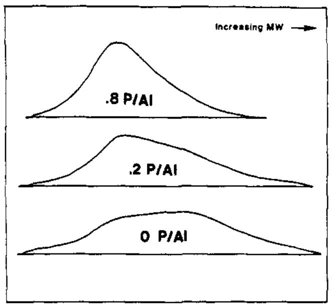


Figure 6. Size-exclusion chromatograms of polymers obtained from three different catalysts varying in phosphate content. Catalysts were activated at 700 °C and run with 50 psig of H_2 and triethylborane.

On $Cr/AlPO_4$ the change in MW is magnified. Table VII lists some data from two runs, one with 20 mL of hexene added to the reactor, the other with only ethylene. The catalyst was $Cr/AlPO_4$ (P/Al = 0.8). Notice that hexene decreases the molecular weight, enhancing both terminal vinyl and methyl.

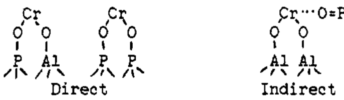
Hogan's suggestion of a tertiary H shift only partly explains the effect of 1-hexene on $Cr/AlPO_4$. It accounts for the presence of vinylidene in the polymer, but to understand the enhanced levels of terminal vinyl we must conclude that hexene can also displace the chain through the usual β-H transfer. The two reactions, incorporation and displacement, probably compete with each other. In Table VII we see evidence for both: lower MW indicates displacement, and the lower density reflects branching.

Conclusions

$Cr/AlPO_4$ polymerization catalysts probably contain a wider variety of sites than is typical of Cr/SiO_2. One type of site (P-site) seems to be closely associated with phosphate, which renders the chromium–polymer bond less stable. Thus it exhibits high reactivity toward β-H elimination and is very responsive to TEB as a chain-transfer agent. Aluminophosphate catalysts are also more sensitive to hydrogen than is Cr/SiO_2 However, hydrogen seems to decrease the polymer MW through another mechanism and is not related to the presence of phosphate. Since even Cr/Al_2O_3 responds to H_2, this characteristic may reflect an influence by aluminum.

It is not clear exactly how the P-sites are associated with phosphate. A direct attachment to surface phosphate, as below, is not unreasonable. But we cannot rule out a more indirect influence, such as a coordination to phosphate.

Influence by Surface Phosphate



Registry No. TEB, 97-94-9; TEA, 97-93-8; $H_2C{=}CH_2$, 74-85-1; Cr, 7440-47-3; $AlPO_4$, 7784-30-7; $H_2C{=}CH(CH_2)_3CH_3$, 592-41-6; H_2, 1333-74-0; CO, 630-08-0; polyethylene, 9002-88-4.

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Factors Influencing the Rate of Tungsten Hexachloride/Tetramethyltin-Catalyzed Olefin Metathesis Polymerization: Monomer Ring Strain Is Not Important

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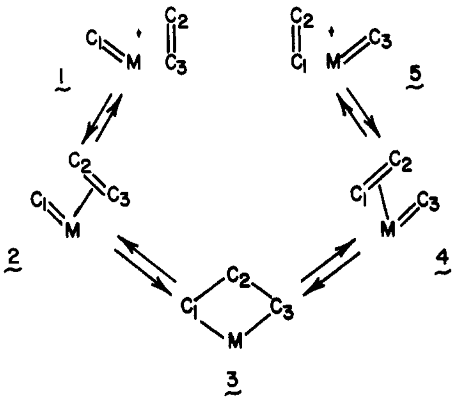
ABSTRACT: Competitive kinetics in tungsten hexachloride/tetramethyltin-catalyzed olefin metathesis copolymerizations demonstrate that monomer ring strain does little to affect reaction rates. The species in the catalytic cycle that appears to be kinetically pertinent is the metal carbene; the nature and geometry of the growing polymer chain about the catalyst and specifically the ability of the penultimate double bond to coordinate to the metal determine the reactivity of the metal carbene toward monomer. Relative reactivities for carbenes derived from cyclobutene, cyclopentene, cyclohexene, cycloheptene, cyclooctene, 1,5-cyclooctadiene, cyclodecene, cyclododecene, norbornene, bicyclo[2.2.2]oct-2-ene, and α-pinene are determined.

Introduction

Although the skeleton of the presently most widely accepted mechanism for olefin metathesis propagation was proposed in 1970,[1] certain subtleties remain undetailed. The interconversion of carbene/olefin and metallacyclobutane complexes (Scheme I) has a large amount of experimental support,[2,3] but questions such as the relative stabilities of **2**, **3**, and **4** (it has been suggested[4] that **3** is not an intermediate, but a transition state for some systems and **3** has been isolated as an intermediate in other systems[5]), the geometry of **2** and **4** (with regard to the dihedral angles between the olefin and carbene)[6] and whether a direct [2 + 2] reaction occurs instead of the formation of a distinct olefin/carbene complex[4] are still issues. Explanations of reactivity and stability differences and origins of selectivity and stereoselectivity depend on these mechanistic details; hence rational control of this catalysis depends on the answers to these questions.

We have been concerned with factors affecting the rate of olefin metathesis polymerization, in particular the structure of the propagating carbene and the monomer ring strain, and have published a preliminary account of this work.[7] This paper presents evidence that, contrary to popular assertions,[2,8,9] the rate of polymerization of cyclic olefins by metathesis catalysis is not a function of ring strain in the monomer and that "reactive monomers" such as norbornene[4,10] are not reactive because of their ring strain. We offer another interpretation of the kinetic data, namely that reactivity differences between different cyclic olefins can be ascribed to the relative reactivity of the propagating carbene. The geometry of the growing polymer chain about the catalyst site determines the reactivity. Our interpretations are derived by using tungsten hexachloride/tetramethyltin catalysis, and we recognize that other catalysts may have different kinetically pertinent species. Comparison with other cyclic monomers (ethers, lactones, lactams, see below) suggests that our observations are general.

Scheme I



Experimental Section

All manipulations were carried out under an atmosphere of prepurified nitrogen. Norbornene, cyclooctene, cyclooctadiene, cyclohexene, cyclopentene, cycloheptene, bicyclo[2.2.2]oct-2-ene, α-pinene, cyclodecene, cyclododecene, cyclohexane, cyclopentane, chlorobenzene, and tetramethyltin were obtained from Aldrich; cyclobutene was prepared by a published procedure.[11] Each was dried over calcium hydride and distilled under nitrogen. Tungsten hexachloride was zone refined under vacuum at 350–400 °C and stored under nitrogen. Gas chromatographic analyses were performed with a Hewlett-Packard 5790A gas chromatograph using a 6 ft × $^1/_8$ in. 5% OV 101 on Chromosorb W column.

Competitive kinetics measurements were obtained by two different procedures:

Procedure A. Chlorobenzene (55 mL), 0.43 mmol of tetramethyltin (0.24 mL of a 1.8 M solution in chlorobenzene), and 1.5 mL of cyclohexane or cyclopentane (GC internal standards) are introduced via syringe to a nitrogen-purged Schlenk flask containing a stirring bar. Tungsten hexachloride (0.43 mmol) is

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