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No. 07-055652-00007-0000

Fecha: 2011-05-12 15:02:05 Dep. 2020 DIR.NUEVASCR
Tra. 11 PATENTEYII Evt. 378 FASENACIONALI
Act. 523 RESPUESTA Folios: 12

Re: Expediente No. 07-055.652
Solicitud de patente a nombre de **CHEVRON PHILLIPS CHEMICAL
COMPANY L.P.**

Yo, DILIA RODRIGUEZ D'ALEMAN, identificada como aparece al pie de mi firma, domiciliada en la carrera 11 No. 86-53, piso 6, obrando como apoderada de la sociedad **CHEVRON PHILLIPS CHEMICAL COMPANY L.P.**, domiciliada en Texas, Estados Unidos de América, solicitante de la patente de la referencia, en respuesta al oficio No. 2752 notificado por fijación en lista el 18 de febrero de 2011, me permito acompañar el siguiente documento solicitado por ese despacho:

- KAROL, FREDERICK J. ET AL: "ETHYLENE POLYMERIZATION STUDIES WITH SUPPORTED CYCLOPENTADIENYL, ARENE AND ALLYL CHROMIUM CATALYST". Journal of polymer sciences, polymer chemistry edition, 13(7), 1607-17, CODEN:JPLCAT, ISSN: 0449-296X, 1975, XP008050661

Espero con esto haber dado cabal cumplimiento a lo solicitado por ese despacho y de conformidad con lo indicado en los artículos 3º, inciso 3, 35 inciso 2 y 59 inciso 2 del CCA, al analizar este memorial, atentamente solicito se traten todas las cuestiones planteadas con motivo del mismo.

Señor Superintendente,

DILIA MARÍA RODRÍGUEZ D'ALEMAN
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Ethylene Polymerization Studies with Supported Cyclopentadienyl, Arene, and Allyl Chromium Catalysts

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Synopsis

Highly active catalysts for low pressure ethylene polymerization are formed when chromocene, bis (benzene)- or bis (cumene)-chromium or tris- or bis (allyl)-chromium compounds are deposited on high surface area silica-alumina or silica supports. Each catalyst type shows its own unique behavior in preparation, polymerization, activity, isomerization, and response to hydrogen as a chain transfer agent. The arene chromium compounds require an acidic support (silica-alumina) or thermal aging with silica to form a highly active catalyst. At 90°C polymerization temperature arene chromium catalysts produced high molecular weight polyethylene and showed, in contrast to supported chromocene catalysts, a much lower response to hydrogen as a chain transfer agent. An increase in polymerization temperature caused a significant decrease in polymer molecular weight. Addition of cyclopentadiene to supported bis (cumene)-chromium catalyst led to a new catalyst which showed a chain transfer response to hydrogen typical of a supported chromocene catalyst. Polymerization activity with tris- or bis (allyl)-chromium appears to depend on the divalent chromium content in the catalyst. Changes in the silica dehydration temperature of supported allyl chromium catalyst have a significant effect on the resulting polymer molecular weight. High molecular weight polymers were formed with catalysts that were prepared using silica dehydration temperatures below about 400°C. Dimers, trimers, and oligomers of ethylene were usually formed with catalysts that were prepared on silica dehydrated much above 400°C. The order of activity of the different types of catalysts was chromocene/silica > chromocene/silica-alumina > bis (arene)-chromium/silica-alumina $\approx$ allyl chromium/silica.

INTRODUCTION

Publications in the scientific and patent literature have described ethylene polymerization with arene¹⁻⁶, allyl⁷⁻⁹, and cyclopentadienyl¹⁰⁻¹³ chromium compounds. In many cases substantial improvement in polymerization activity occurs when these compounds are deposited on supports and the supported compounds used as ethylene polymerization catalysts.^{2,4,8,10} Studies with a chromocene catalyst, $(C_5H_5)_2Cr/SiO_2$, have shown a support is required for formation of an active catalyst. This paper describes polymerization studies with supported cyclopentadienyl, arene, and allyl chromium compounds and compares some general features of ethylene polymerization with these catalysts.

RESULTS

Polymerization with Supported Chromocene Catalysts

A previous publication¹⁰ from this laboratory contains many results of polymerization studies with chromocene catalysts. Some additional experi-

ments (Table I) were carried out to provide additional data for comparison with arene and allyl chromium compounds. These studies showed lower activity occurred when silica-alumina (13% Al_2O_3) was substituted for grade 56 silica¹⁴ as the catalyst support. The presence or absence of hydrogen did not significantly alter polymerization activity. On silica-alumina, chromocene catalysts produced higher molecular weight, lower high-load melt index (HLMI) polymers than on silica.

Polymerization with Supported Arene Chromium Catalysts

Bis (benzene)- and bis (cumene)-chromium were deposited from hexane solution on dehydrated silica-alumina to form active catalysts for ethylene polymerization. At 90°C polymerization temperature these catalysts produced high molecular weight polymers with a low HLMI (Table I). Addition of hydrogen to the polymerization system led to a modest increase in HLMI. With Davison grade 56 silica dehydrated at 600°C bis (benzene)- and bis (cumene)-chromium did not form an active ethylene polymerization catalyst. However, an initial aging of silica with bis (cumene)-chromium at 150°C did provide a method for obtaining catalytic activity.

Polymerization temperature has a significant effect on the melt index and branching of the polymer. Polymer melt index increased from "no-flow" to 33 for an increase in polymerization temperature from 71 to 167°C (Table II). The methyl content¹⁵ ($\text{CH}_3/1000$ carbon atoms) in these polymers increased with an increase in polymerization temperature up to 137°C. The high methyl contents of 4.8 to 12.1 $\text{CH}_3/1000$ carbon atoms suggest that some branching occurs in these polymers. The measured polymer densities in Table II support this view. The presence of internal *trans* unsaturation in the polymers suggests that a chain isomerization-elimination process, of the type previously described,¹⁰ occurs during ethylene polymerization. The vinyl contents¹⁶ of the polymers fell in the range of 1-4 $[-\text{CH}=\text{CH}_2]$ groups/1000 carbon atoms, which would indicate that most polymer chains were terminated with a vinyl group.

A control experiment at 90°C was carried out to measure the amount of butene formed during the polymerization. The butene content of the vapor phase amounted to 1-2% and appeared almost exclusively as butene-1. Generation and subsequent copolymerization of α -olefins may be another reason for the high methyl content and lower densities.

Addition of Cyclopentadiene to Bis (Cumene)-Chromium Catalyst

Addition of cyclopentadiene to bis (cumene)-chromium deposited on silica-alumina caused a remarkable change in catalyst response to hydrogen and led to polymers with a low vinyl unsaturation content.¹⁷ The vinyl content (Table III) of the polymers decreased from 2.4 to 0.2 $[-\text{CH}=\text{CH}_2]$ groups/1000 carbon atoms indicating a significant change in the polymerization transfer reaction. In addition, polymer melt index increased sharply when catalysts modified with cyclopentadiene were used. The lower polymer yields in the presence of cyclopentadiene were probably the result of rapid polymerization of cyclopentadiene¹⁸ catalyzed by the silica-alumina support.

TABLE I
Comparison of Supported Chromium Compounds as Ethylene Polymerization Catalysts^a

Chromium Compound		Support ^b		C ₂ H ₄ psi	H ₂ /C ₂ H ₄	Activity g/mmole Cr/100 psi C ₂ H ₄ /hr	HLMI, dg/min
Type	mmole	Type	Dehydration Temp, °C				
chromocene	0.083	56	600	200	0	967	no flow
chromocene	0.066	56	600	185	0.08	1090	41
chromocene	0.066	SiO ₂ ·Al ₂ O ₃	600	185	0.08	606	12
bis (benzene)-	0.19	56	600	300	0	0	—
bis (cumene)-	0.15	56	600	300	0	0	—
bis (cumene)- ^c	0.30	56	600	300	0	59	1.2
bis (benzene)-	0.19	SiO ₂ ·Al ₂ O ₃	600	300	0	192	0.2
bis (cumene)-	0.15	SiO ₂ ·Al ₂ O ₃	600	300	0	364	0.8
bis (cumene)-	0.15	SiO ₂ ·Al ₂ O ₃	600	250	0.2	240	12
bis (cumene)-	0.15	SiO ₂ ·Al ₂ O ₃	600	200	0.5	283	21
allyl- ^d	0.2	56	600	200	0	240	oligomers and low molecular wt. solid
allyl- ^d	0.2	56	600	200	0.25	220	
allyl- ^d	0.3	56	300	200	0	100	0.2
allyl- ^d	0.3	56	300	200	0.25	87	1.5

^a All polymerizations carried out at 90° C for one hour.
^b 0.4 g support except for footnote^c.
^c 0.8 g support; chromium compound and silica aged at 150° C for one hour.
^d Cr(II)/Cr(III) = 2 as determined by polarography.

Such a polymer may coat the support surface and cause deactivation of chromium sites. In the absence of bis (cumene)-chromium, cyclopentadiene reacts with silica-alumina to form an orange-to-dark-red amorphous solid.

Polymerization with Supported Allyl Chromium Compounds

Tris (allyl)-chromium (III), $(C_3H_5)_3Cr$, was synthesized in ether using allyl magnesium bromide and chromic (III) chloride at $-20^\circ C$. Similarly bis (allyl)-chromium (II) dimer, $[(C_3H_5)_2Cr]_2$, was prepared at $25^\circ C$ using chromous (II) chloride.^{19,20} These chromium compounds, because of limited thermal stability and sensitivity in air and moisture, were not isolated from the reaction mixture. Instead, the solutions in ether were filtered at $-20^\circ C$, the filtrate stripped in vacuum and hexane flash-distilled through the system to remove any residual ether. Polymerization experiments were carried out using the allyl chromium compounds in hexane.

Tris (allyl)-chromium (III) in hexane decomposes on standing, even at $-17^\circ C$. Samples of the hexane solution were examined periodically by polarography¹⁰ to determine the divalent and trivalent chromium contents. The divalent chromium content, which depended upon the extent of decomposition, was 30–70%. Clearly tris (allyl)-chromium (III) is unstable in hexane, presumably decomposing to bis (allyl)-chromium (II) dimer. Bis (allyl)-chromium (II) dimer in ether solution was quite stable at ambient temperature with essentially no decomposition after two weeks. In hexane solution bis (allyl)-chromium (II) dimer, although more stable than tris (allyl)-chromium (III), decomposed in an unknown fashion within a few hours.

Polymerization studies with tris (allyl)-chromium (III) and bis (allyl)-chromium (II) dimer show these two compounds behave in a similar catalytic manner when deposited on grade 56 silica dehydrated at $300^\circ C$ (Table IV). High molecular weight polymers (low HLMI) were formed at a moderate polymerization rate. Since catalyst response to hydrogen is low, hydrogen addition does not provide a route to a significant increase in melt index. A rigorous comparison of polymerization activity with the two allyl chromium catalysts was not made since the concentration of the chromium compounds was not quantitatively established.

Polymerization activity with supported allyl chromium catalysts was substantially better than the activity reported in the literature for unsupported catalysts.^{7,9} However, at the chromium concentrations examined in our studies, the silica must be dehydrated above $100^\circ C$ prior to use as a support for allyl chromium.

A significant change in polymerization behavior occurred with catalysts prepared on silicas dehydrated above $400^\circ C$. Although polymerization activity remained high, only a minor portion of the polymer was insoluble in the hexane diluent. The majority of the product was a mixture of butenes and hexenes with lesser amounts of higher olefins. Olefin double bond isomerization was extensive with butene-2 present in significant quantity.

DISCUSSION

Polymerization behavior of supported cyclopentadienyl, arene, and allyl chromium catalysts depends to a considerable extent upon factors affecting

TABLE II
Influence of Polymerization Temperature on Supported Bis (Cumene)-Chromium Catalyst^a

Polymerization temperature, °C	Yield, g	MI, dg/min	Polymer density, g/cc	Polymer microstructure ^b		
				CH ₂ /1000C	—CH=CH ₂ /1000C	—CH=CH—/1000C
71	113	no flow	—	very low	1.1	very low
93	164	no flow	—	4.8	2.5	0.16
118	123	2.2	0.948	7.0	3.7	0.38
137	92	11	0.945	12.1	4.2	0.86
167	69	33	0.957	5.7	3.4	0.27

^a 0.4 g SiO₂-Al₂O₃ dehydrated at 500° C, 40-45 mg bis(cumene)-chromium, 300 psi C₃H₆.
^b negligible vinylidene content.

TABLE III
Effect of Cyclopentadiene Addition on Supported Bis (Cumene)-Chromium Catalysis^a

Cyclopentadiene, mole x 10 ⁵	Bis (cumene)-chromium, mole x 10 ⁴	Cyclopentadiene/chromium, molar ratio	Polymer yield, g	MI, dg/min	Vinyl content, —CH=CH ₂ /1000C
0	1.5	0	90	0.05	2.4
0.6	1.4	0.04	136	0.03	1.6
1.2	1.4	0.09	33	0.86	0.36
6.0	1.4	0.42	20	2.4	0.2
120	1.4	8.6	11	3.5	0.2

^a 0.4 g SiO₂-Al₂O₃ (500° C), 92° C polymerization temperature using 50 psi H₂ and total pressure of 300 psig.

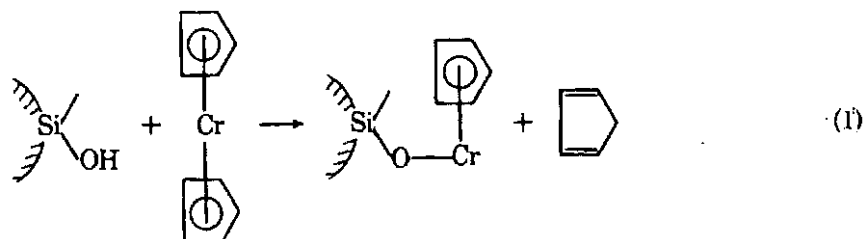
TABLE IV
Ethylene Polymerization Catalyzed by Supported Allyl Chromium Catalysts

Allyl chromium, source	Polarographic analyses, Cr(II)/Cr(III)	Support		H ₂ , psi	C ₂ H ₄ , psi	Polymerization time, min	Yield, g	MI, dg/min	HLMI, dg/min
		Type	Dehydration temp, °C						
CrCl ₃ ^a	2/1	56	100	0	200	60	0	—	—
CrCl ₃ ^a	2/1	56	200	0	200	50	53	no flow	0.2
CrCl ₃ ^a	2/1	56	300	0	200	60	60	no flow	0.2
CrCl ₃ ^a	2/1	56	300	50	200	60	52	no flow	1.5
CrCl ₂ ^b	—	56	300	0	200	40	130	0.01	1.6
CrCl ₂ ^b	—	56	300	70	200	90	86	0.03	5.0
CrCl ₃ ^c	2/1	56	600	0	200	100	21/~75 ^d	waxy solid	—
CrCl ₃ ^c	2/1	56	600	50	200	30	13/~75 ^d	waxy solid	—
CrCl ₃ ^c	not measured	56	700	0	200	35	4/~75 ^d	waxy solid	—

^a 0.3 mmole chromium.
^b <1.4 mmole chromium.
^c 0.2 mmole chromium.
^d Grams solid polymer/grams oligomer.

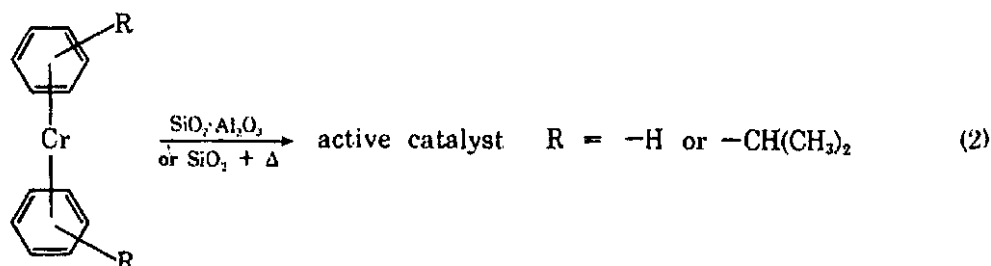
47

chromium deposition, valence state, and ligand environment of the supported chromium sites, and catalyst sensitivity to poisons. Deposition of chromocene on silica liberates cyclopentadiene indicating there is a chemical reaction of chromocene with surface silanol groups (eq. 1).



Silica-alumina, although less satisfactory for catalyst activity purposes than silica, can also serve as a suitable support for chromocene. Rapid and essentially complete deposition of chromocene in less than 30 min takes place on both supports.

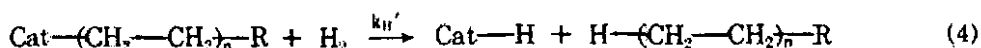
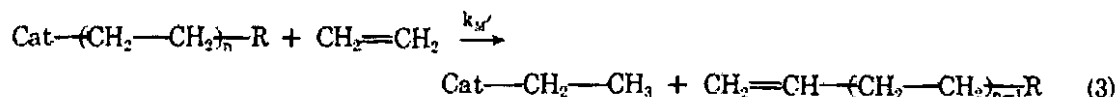
With bis (benzene)- or bis (cumene)-chromium catalyst, significant polymerization activity at 90°C occurs only when an acidic support like silica-alumina is used. Presumably the acidic support serves to destroy the original π -bonding in these arene compounds, which leads to chromium sites capable of polymerizing ethylene. Aging at 150°C of bis (cumene)-chromium and grade 56 silica did lead to formation of an active catalyst. Destruction of the π -bonding in bis (cumene)-chromium probably occurs during this aging process (eq. 2).



It seems reasonable that the support surface can serve a dual role of reactant and anchoring substrate, which permits maximum chromium efficiency. We believe that chemisorption of bis (arene)-chromium probably takes place by an oxidation-reduction reaction with surface silanol groups. This reaction could lead to a chemisorbed divalent chromium compound. The differences in polymerization activity of bis (cumene)-chromium and chromocene supported on silica-alumina (Table I) probably reflect differences in active site concentration and intrinsic activity of these sites.

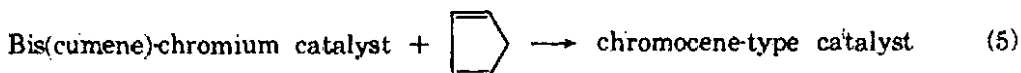
The high vinyl content (2-3 $[-\text{CH}=\text{CH}_2]$ groups/1000 carbon atoms) of polymers prepared at 90°C with supported bis (cumene)-chromium catalyst in the presence of hydrogen suggests the relative rates of the transfer reactions with monomer (eq. 3) and hydrogen (eq. 4) differ significantly from similar reactions with the chromocene catalyst. A vinyl content of 0.05 $[-$

CH=CH₂] groups/1000 carbon atoms represents a typical value for polymers prepared with the supported chromocene catalyst under identical conditions.

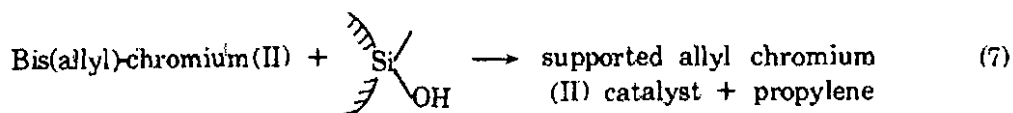


With bis (cumene)-chromium catalyst at a 90°C polymerization temperature, changes in hydrogen-ethylene ratio do not lead to the comparable changes in polymer melt index that occur with the chromocene catalyst. Previous publications have attempted to show a cyclopentadienyl ligand remains attached to the chromium center in chromocene catalysts. The presence of this ligand in the catalyst leads to a high catalyst response to hydrogen. With supported bis (cumene)-chromium catalyst, no comparable ligand is present; consequently, chain transfer to monomer or spontaneous dissociation competes effectively with chain transfer to hydrogen. The presence of internal unsaturation and high methyl contents in these polymers suggests that polymerization and chain isomerization both occur using the arene chromium catalysts.

Ligand exchange at the active chromium site appears to take place when cyclopentadiene is added to bis (cumene)-chromium deposited on silica-alumina. The change in catalyst response to hydrogen, leading to a significant reduction in polymer vinyl content, suggests that formation of a chromocene-type catalyst can occur by addition of cyclopentadiene (eq. 5).



With allyl chromium (II, III) rapid and complete deposition takes place on silica and silica-alumina leading to formation of highly active catalysts. The poor thermal stability of tris (allyl)-chromium and polarographic valence measurements showing the presence of divalent chromium in solutions of tris (allyl)-chromium indicate tris (allyl)-chromium (III) is converted to bis (allyl)-chromium (II) prior to or during catalyst formation (eq. 6). The similarity in polymerization behavior of catalysts formed from tris (allyl)-chromium (III) and bis (allyl)-chromium (II) lends support to this hypothesis. Although no studies on the mechanism of deposition were carried out it seems reasonable, by analogy with chemisorption studies with chromocene, to assume that deposition occurs by displacement of at least one allyl ligand by a surface silanol group (eq. 7). Recent studies²² with a number of supported allyl-transition metal compounds have shown that propylene is liberated in the chemisorption process.



The allyl chromium catalysts show activity about 20% of the activity of a comparable chromocene catalyst. Complications arising from poor stability of allyl chromium and the supported catalyst probably serve to reduce polymerization activity by lowering the active site concentration.

The dramatic change from solid polymer to ethylene oligomers when the silica dehydration temperature of the supported catalyst is increased suggests that the structure of the active site is considerably altered. It is conceivable that the allyl chromium catalyst prepared on high-temperature silica retains a higher allyl ligand concentration than a similar catalyst prepared from a low-temperature silica. Deposition studies with the chromocene catalyst have shown that more cyclopentadiene was evolved when chromocene was deposited on supports which had minimal thermal treatment. The chromocene catalyst on silica of lower dehydration temperatures forms solid polymers of higher molecular weight.

Many unsupported transition-metal allyl compounds show weak catalytic activity in ethylene polymerization. In one study⁹ tris (allyl)-chromium (III) showed poor catalytic activity while bis (allyl)-chromium (II) was inactive. It does not appear possible to determine from published data the extent to which allyl chromium stability, dimer formation, or other factors contribute to the differences in catalytic activity between tris (allyl)-chromium (III) and bis (allyl)-chromium (II).

Studies of ethylene polymerization with arene chromium compounds have been concerned for the most part with oxidized or pyrolyzed arene chromium compounds which show low polymerization activity. Complex structures have been proposed for the oxidized chromium compounds.³ One study² does describe polymerization with supported arene chromium compounds prepared in the absence of oxygen. Silica-alumina was observed to be a better support than silica for polymerization at 138°C. However, insufficient data are recorded to draw any significant conclusions regarding the mechanism of polymerization.

EXPERIMENTAL

Materials

The sensitivity of the chromium compounds and catalysts to trace impurities such as oxygen and water requires high-purity raw materials and extreme care in catalyst handling. All gases and diluents used for polymerization were dried by using activated molecular sieves (Linde 5A) prior to use. Ethylene (99.8%) and n-hexane (85 vol-% minimum) were obtained from Phillips. Argon, hydrogen, and nitrogen were all high-purity grades from Linde. Chromocene was conveniently prepared by the method previously described.¹⁰ Solutions of sublimed chromocene in n-hexane or toluene (10–60 mg/ml) were routinely used for the preparation of supported chromocene catalyst.

Bis (benzene)-chromium was purchased from the Strem Chemicals Co., and purified by vacuum sublimation. Bis (cumene)-chromium was obtained from Union Carbide Chemicals. Solutions in toluene (10 mg/ml) were normally used in the preparation of supported arene catalysts.

A mixture of tris (allyl)-chromium (III) and bis (allyl)-chromium (II) dimer was formed by reacting slightly more than 3 molar equivalents of allyl magnesium bromide with anhydrous chromic (III) chloride in dry ether at -20°C . After 90 min reaction time at -20°C , excess dry carbon dioxide was added to destroy any unreacted Grignard reagent. After the solution was filtered at -20°C , the ether was removed from the filtrate by high-vacuum distillation at low temperature. After removing the majority of the ether a large amount of hexane was flash-distilled through the system in order to completely remove any residual ether. The deep-red hexane solution contained a brown precipitate, presumably inorganic decomposition products of allyl chromium. The solution was stored at -70°C and warmed to 20°C for removal of samples. Polarographic analysis of the solution showed some divalent chromium was present, which appeared to depend upon the extent of warming. With extended warming the concentration of tris (allyl)-chromium (III) in ether solution decreases rapidly. Simultaneously the concentration of bis (allyl)-chromium (II) increases. In the absence of ether, both allyl chromium compounds in hexane solution completely decomposed at 25°C within 1.5 hr.

Bis (allyl)-chromium (II) dimer was prepared by reacting approximately two molar equivalents of allyl magnesium bromide with one equivalent of chromous (II) chloride (Alpha Inorganics) in dilute ether solution. After 4 hr of reaction at 25°C , the solution was cooled to -20°C and carbon dioxide was added. On cooling to -70°C orange-yellow needles characteristic of bis (allyl)-chromium (II) dimer precipitate. A hexane solution was prepared in a manner described for tris (allyl)-chromium (III).

Silica supports were purchased from the Davison Chemicals Division of W. R. Grace and Co. The supports were dehydrated in a manner previously described.¹⁰

Preparation of Supported Chromium Catalysts

The supported chromium catalysts were prepared in a manner previously described for the supported chromocene catalyst. Sieve-dried (Linde 5A) n-hexane (100 ml) was added to an 8-oz serum-capped bottle and purged with argon for 30 min. Dehydrated silica (0.4 g) was added to the hexane through a small hole in the cap. A second serum cap was fitted over the first to prevent contamination by air and water. After purging the contents in the bottle for 15 min, a solution of the chromium compound in toluene or hexane was added by syringe. The contents were rapidly agitated by a magnetic stirring bar for 30 min during which time complete deposition usually takes place. During the deposition step the color of the silica changes from white to jet black (chromocene) or deep red (allyl chromium) and the hexane solution changes from a wine-red to colorless. The catalyst slurry is now ready for transfer to the reactor under argon pressure.

Ethylene Polymerization Studies

All polymerizations were carried out in a 1-liter chrome-plated, stainless-steel autoclave, equipped with pressure gauge, appropriate argon and ethylene inlets and outlets, and a propeller stirring blade for agitation. The cata-

lyst was suspended in the diluent by agitation and a constant pressure of ethylene was maintained on the reactor. The flow rate could be observed by means of a high pressure rotameter in the ethylene feed line. Control of reaction exotherm could be maintained to some extent by heat transfer to cold water circulating through the reactor jacket, but it was most expedient to avoid a large exotherm by limiting the amount of catalyst used.

Typically, polymerizations were carried out by adding 500 ml of n-hexane to the reactor and transferring the supported catalyst under argon to the reactor. The contents were heated approximately to the polymerization temperature, and hydrogen (if required) and ethylene added. The amount of gas added to the reactor was monitored by an externally mounted gauge. Polymerization commences in all cases almost immediately on ethylene addition. Usually the polymerizations were carried out under constant ethylene pressure for 30–60 min. At the end of this period ethylene was rapidly vented, the reactor cooled and polyethylene removed. A small amount of stabilizer was added and the polymer dried in vacuum to constant weight.

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Received January 21, 1975

12