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(57) Abstract

Disclosed is a catalyst system for the homopolymerization of alpha-olefins having 2-8 carbon atoms, said catalyst system comprising a Group 6b metal-alkali metal compound wherein said Group 6b metal is a cyclopentadienyl Group 6b metal trialkaryl complex anion in which the Group 6b metal has an oxidation state +3 and wherein said complex anion is balanced by an alkali metal cation such as lithium and wherein the alkali metal cation is, optionally, coordinately linked to a neutral hydrocarbyl based ligand containing a heteroatom such as oxygen, nitrogen, phosphorus or sulphur, said Group 6b metal-alkali metal compound being supported on an inorganic support. The catalyst system can contain, in addition, a Group 2 or Group 3 metal-alkyl compound.

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CYCLOPENTADIENYL GROUP 6B METAL-ALKALI METAL ALPHA-OLEFIN POLYMERIZATION CATALYSTS AND THEIR USE IN POLYMERIZATION PROCESSES

FIELD OF THE INVENTION

The present invention relates to catalyst systems for polymerizing alpha-olefins and processes for polymerizing alpha-olefins using such catalysts.

BACKGROUND OF THE INVENTION

Chromium based catalysts are used in the commercial polymerization of small alpha-olefins such as ethylene and propylene. One such catalyst is prepared by depositing chromocene (bis(cyclopentadienyl) chromium (II)) on an inorganic metal oxide support, as disclosed in British Patent No. 1,253,063 to Karapinka. U.S. Patent No. 4,015,059, issued March 29, 1977 to Karol, describes the use of bis(indenyl) - bis(fluorenyl) - chromium (II) compounds supported on activated inorganic oxide supports as catalysts for the polymerization of ethylene.

Recently, new synthetic methods have been described for preparing Cr^{+3} organometallic compounds. Theopold, J. Am. Chem. Soc. (1988), 110, 5902 entitled "Cationic Chromium (III) Alkyls as Olefin Polymerization Catalysts," Theopold, Acc. Chem. Res. (1990), 23, 263 entitled "Organochromium (III) Chemistry: A Neglected Oxidation State" and Thomas et al., J. Am. Chem. Soc., (1991), 113, p. 893 et seq. disclose that certain pentamethylcyclopentadienyl chromium (III) alkyls can be prepared, and that they can be used for making polyethylene homogeneously in CH_2Cl_2. However, these homogenous Cr (III) polymerization catalysts have several deficiencies. These include low polymer productivity, rapid deactivation, and the need to use polar, non-coordinating solvents. Additionally, since they are homogeneous catalysts, they are unsuitable for gas phase olefin polymerization.

U.S. Patent No. 4,530,914, issued July 23, 1985 to Ewen et al., discloses a catalyst system for the polymerization of alpha-olefins which comprises two or more metallocenes, each having different propagation and termination rate constants, and aluminoxane. The metallocenes are cyclopentadienyl derivatives of a transition metal of Group 4b, 5b, and 6b metals of the Periodic Table. They are described by the formulas $(C_5R'_m)_pR''_s(C_5R'_m)MeQ_{3-p}$ and $R''_s(C_5R'_m)_2MeQ'$ where $(C_5R'_m)$ is a cyclopentadienyl or substituted cyclopentadienyl, each R' is hydrogen or a hydrocarbyl radical, R" is an alkylene radical, a dialkyl germanium or silicon or an alkyl phosphine or amine radical bridging two $(C_5R'_m)$ rings, Q is a hydrocarbon radical, ME is a Group 4b, 5b, or 6b metal, s is 0 or 1, p is 0, 1, or 2; when $p=0$, $s=0$; m is 4 when s is 1 and m is 5 when s is 0.

U.S. Patent No. 4,939,217, issued July 3, 1990 to Stricklen, also discloses a process for polymerizing olefins where the polymerization is conducted in the presence of hydrogen, and a catalyst system is used which contains aluminoxane and at least two metallocenes, each having different olefin polymerization termination rate constants. The metallocenes disclosed are similar to those described in aforementioned U.S. Patent No. 4,530,914.

U.S. Patent No. 4,975,403, issued December 4, 1990 to Ewen, discloses a catalyst system for use in the polymerization of olefins. The catalyst system includes at least two different chiral, stereo-rigid metallocene catalysts of the formula $R''(C_5(R')_4)_2MeQ_p$ (where Me is a Group 4b, 5b, or 6b metal and $(C_5(R')_4)$ is a cyclopentadienyl or substituted cyclopentadienyl ring) and an aluminum compound.

Canadian Patent Application No. 2,000,567, published April 13, 1990, discloses a process for producing polyethylene using a composite catalyst made up of a solid catalyst component typified by a selected chromium compound, a modified aluminum compound typified by a trialkylaluminum, and an alkylaluminum alkoxide compound. The chromium compound may be chromium oxide, and the modified aluminum compound may be the reaction product of an organoaluminum compound and water.

European Patent Application 0,509,294 A2, published on October 21, 1992, relates to a cyclopentadienyl Group 6b metal hydrocarbyl compound in which the metal has an oxidation state of +3 and which compound is supported on an inorganic support as a catalyst for the homopolymerization or copolymerization of alpha-olefins having from 2 to 8 carbon atoms.

The catalyst system can also contain a Group 2 or Group 3 metal-alkyl compound such as an aluminum trialkyl.

SUMMARY OF THE INVENTION

In accordance with the present invention, there is provided a catalyst system for the homopolymerization of alpha-olefins, having from 2 to 8 carbon atoms, said catalyst system comprising a Group 6b metal-alkali metal compound wherein said Group 6b metal is a cyclopentadienyl Group 6b metal trialkaryl complex anion in which the Group 6b metal has an oxidation state +3 and wherein said complex anion is balanced by an alkali metal cation selected from lithium, sodium, potassium and cesium and wherein said alkali metal cation is, optionally, coordinately linked to a neutral hydrocarbyl based ligand containing a heteroatom selected from oxygen, nitrogen, phosphorus and sulphur, said Group 6b metal-alkali metal compound being supported on an inorganic support.

There is also provided in accordance with the present invention, a catalyst system as described above which contains in addition a Group 2 or Group 3 metal-alkyl compound.

In the above catalyst systems and processes, chromium is a preferred Group 6b metal; silica, aluminum phosphate and alumina aluminum phosphate are preferred supports, and aluminoxanes and trialkylaluminum compounds are preferred Group 2 or 3 metal-alkyl compounds.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The present invention provides catalyst systems for use in the homopolymerization of alpha-olefins, including ethylene, propylene, 1-butene, 1-hexene, 4-methyl-1-pentene, and 1-octene.

It has quite surprisingly been found that, even though the productivity of many cyclopentadienyl Group 6b metal hydrocarbyl compounds is quite low when employed as catalysts in the homogeneous polymerization of alpha-olefins, when these compounds are supported on an inorganic metal oxide or inorganic phosphate solid support, their productivity increases dramatically, especially when co-catalysts are used. While the catalyst systems of the present invention can be used to polymerize a variety of alpha-olefins, they are especially useful in the polymerization of ethylene. These catalysts produce polyethylene in high yield. When the supports have a proper morphology, the resulting polymers have a highly desirable morphology, i.e., substantially spherical which is especially useful for gas phase polymerization. The catalysts of the present invention are unusually sensitive to the use of hydrogen during polymerization of polyethylene to reduce the molecular weight. In addition, the catalyst system of this invention produces polyethylene with a variety of molecular weight distributions, depending on the support used.

Activities for the catalyst systems of the present invention are greater than 3,000 grams of polymer per gram of chromium metal per hour ("g/g Cr/hr"), preferably greater than 30,000 g/g Cr/hr, and more preferably greater than 200,000 g/g Cr/hr.

The term molecular weight distribution ("MWD"), as used herein, is the weight average molecular weight ("M_w") divided by the number average molecular weight ("M_n"), i.e., M_w/M_n. The polymers produced in accordance with the present invention using silica supported catalysts have a MWD greater than 8, preferably greater than 9, and more preferably greater than 12. These polymers, which have broad MWDs, have improved ease of processing, better melt behavior, and other desirable properties such as impact resistance and environmental stress crack resistance. Large blow molded products have superior processability when made with broad MWD polymers. Additionally, film is more puncture resistant when made from polymers with a high molecular weight and broad MWD. The polymers made in accordance with this invention using aluminum phosphate supported catalysts possess high molecular weight and either a narrow or broad MWD depending upon the pre-heating conditions for the aluminum phosphate. Additionally, the MWD can be modified by the presence of hydrogen or a co-monomer.

The catalyst systems of the present invention comprise at least one cyclopentadienyl Group 6b metal-alkali metal compound wherein said Group 6b metal is a cyclopentadienyl Group 6b metal trialkaryl complex anion in which the Group 6b metal has an oxidation state of +3 and wherein said complex anion is balanced by an alkali metal cation selected from lithium, sodium, potassium and cesium, and which is catalytically active when deposited on an inorganic metal oxide or inorganic metal phosphate support. Optionally, the alkali metal cation is coordinately linked to a neutral hydrocarbyl based ligand containing a heteroatom selected from oxygen, nitrogen, phosphorus and sulphur.

As used herein, the term "cyclopentadienyl" refers to unsubstituted cyclopentadienyl as well as substituted derivatives of cyclopentadienyl in which the cyclopentadienyl ring contains one or more substituents which do not interfere with the Group 6b metal compound's ability to function as an alpha-olefin polymerization catalyst. Examples of substituted cyclopentadienyl include pentamethylcyclopentadienyl, methylcyclopentadienyl, t-butylcyclopentadienyl, and pentaphenylcyclopentadienyl, as well as compounds where the substituent forms a multi-cyclic ring with the cyclopentadienyl ring. Examples of these multi-cyclic rings include indenyl and fluorenyl rings. For the sake of simplicity, the abbreviation "Cp" will be used herein to refer to unsubstituted cyclopentadienyl, and the abbreviation "Cp*" will be used to refer to pentamethylcyclopentadienyl. Cp* is a preferred cyclopentadienyl group as it stabilizes the organometallic compound of this invention.

The Group 6b metal compounds useful in the present invention include compounds wherein the metal is chromium, molybdenum or tungsten. Compounds in which the metal is chromium are preferred. The Group 6b metal atom in the compound has an oxidation state of +3.

These Group 6b methyl compounds have, in addition to one cyclopentadienyl group, at least one alkaryl group bonded to the metal atom. Exemplary alkaryl radicals include, but are not limited to, benzyl, 3-methyl benzyl and 3, 5-dimethyl benzyl, and other similar groups. Additionally, silicon can be incorporated into such group as phenyl silyl, and the like. If more than one alkaryl group is bonded to the metal atom, they can be independent or linked.

The alkaryl group is sigma bonded to the Group 6b metal.

The Group 6b metal, cyclopentadienyl-alkaryl groups form a complex anion which is balanced in charge by an alkali metal cation selected from the group consisting of lithium, sodium, potassium and cesium.

Examples of the Group 6b metal compounds useful in this invention include, but are not limited to, compounds having the following general formula:

$$[A]^{+} - [Q]_{c} \, [(C_5(R')_5)_a M X_b]^{-}$$

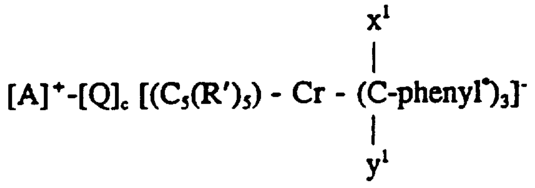
wherein M is a Group 6b metal such as chromium, molybdenum and tungsten;

$(C_5(R')_5)$ is a cyclopentadienyl or substituted cyclopentadienyl ring;

R' is at each independent occurrence hydrogen, a hydrocarbyl radical having 1-20 carbon atoms, or adjacent R' groups may together form one or more rings;

X is an alkaryl radical having 7-20 carbon atoms;

$a=1$ or 2, $b=1$, 2 or 3 where $a+b=4$; A is a cation selected from the group consisting of lithium, sodium, potassium and cesium; Q is at each independent occurrence a neutral hydrocarbyl based ligand containing a heteroatom selected from the group consisting of oxygen, nitrogen, phosphorus and sulfur and coordinately linked to the alkali metal cation and c is 0, 1, 2 or 3. Preferably the Group 6b metal compounds useful in this invention have the general formula:



$$[A]^{+}\text{-}[Q]_c\,[(C_5(R')_5) - \mathrm{Cr} - (\underset{\substack{|\\ y^1}}{\overset{\substack{x^1\\ |}}{C}}\text{-phenyl}^{*})_3]^{-}$$

wherein Cr is chromium; $(C_5(R')_5)$ is a cyclopentadienyl or substituted cyclopentadienyl ring; R′ at each independent occurrence is hydrogen, a hydrocarbyl radical having from 1-20 carbon atoms, or adjacent R′ groups may together form one or more rings; x^1 and y^1 are the same or different and are selected from hydrogen or hydrocarbyl radicals having from 1-6 carbon atoms; phenyl* is phenyl or a substituted phenyl ring where the substituents at each independent occurrence can be hydrogen or a hydrocarbyl radical having from 1-6 carbon atoms; A is an alkali metal cation selected from lithium, sodium, potassium or cesium; Q is at each independent occurrence a neutral hydrocarbyl based ligand containing a heteroatom selected from the group consisting of oxygen, nitrogen, phosphorus and sulphur and coordinately linked to the alkali metal cation; and c is 0 to 3 inclusive.

As used herein, term "hydrocarbyl" refers to the alkyl, alkenyl, aryl, aralkyl and alkaryl radicals and the like. Exemplary hydrocarbyl radicals include, but are not limited to, methyl, ethyl, propyl, butyl, amyl, isoamyl, hexyl, neopentyl, isobutyl, heptyl, octyl, nonyl, decyl, cetyl, phenyl, benzyl and other similar groups. Additionally, organosilyl groups, such as trimethylsilyl methyl, i.e., $(CH_3)_3SiCH_2$., and the like can be used. If more than one hydrocarbyl group is bonded to the metal atom, they can be independent or linked, i.e., they can form a 3-, 4-, 5-, 6-, or 7-membered metallocycle. Preferably, the hydrocarbyl group is sigma bonded to the Group 6b metal.

In part, the choice of Group 6b metal compound is based on the thermal stability of the compound and its ease of preparation. Of the Group 6b compounds useful in this invention, the organochromium compounds are preferred.

Theopold, J. Am. Chem. Soc. (1988), 110, 5902 entitled "Cationic Chromium (III) Alkyls as Olefin Polymerization Catalysts," Theopold, Acc. Chem. Res. (1990), 23, 263 entitled "Organochromium (III) Chemistry: A Neglected Oxidation State," and Thomas et al., J. Am. Chem. Soc., 113 (1991), p. 893 et seq. (all of which are incorporated herein by reference) describe syntheses useful in making some of the Group 6b metal compounds where the Group 6b metal is in the +3 oxidation state. Anyone with ordinary skill in the art, knowing the above references and reading the working examples below, would know how to prepare the Group 6b metal-alkali metal compound(s) which when deposited on a support form the catalysts of this invention. For example, benzyl lithium can be used — as shown in Example 2 below — to make a compound catalyst precursor of this invention.

In the catalyst systems of the present invention, the Group 6b metal compound is deposited on an inorganic support. Suitable inorganic metal oxide supports include silica, alumina silica-alumina mixtures, thoria, zirconia, magnesium oxide and similar oxides. Suitable inorganic metal phosphates include aluminum phosphate, zirconium phosphate, magnesium-containing alumina phosphate, silica aluminum phosphate, silica alumina-aluminum phosphate, and alumina aluminum phosphate. Silicas, aluminum phosphates and alumina aluminum phosphates are preferred. Suitable silica supports include Davison 952, Davison 955, Crosfield EP-10 and Crosfield EP17MS. Further examples of useful supports are the following: alumina aluminum phosphates with aluminum to phosphorus ratios of about 5:1 to 1:1 as disclosed in the U.S. Patents Nos. 4,080,311 and 4,219,444; magnesia-alumina-aluminum phosphates as described in U.S. Patent No. 4,210,560; zinc oxide-cadmium oxide-alumina-aluminum phosphates such as those disclosed in the U.S. Patent No. 4,367,067; and the calcium, barium, and/or strontium oxide-alumina-aluminum phosphates described in U.S. Patents Nos. 4,382,877 and 4,382,878. The acidity of these supports can be adjusted by judicious inclusion of basic metals such as alkali and alkaline earth metals (Ca, Be, Mg, K, Li) to counteract excessive acidity. Other useful supports include magnesium halides, particularly magnesium chloride, such as those described in "Transition Metals and Organometallics as Catalysts for Olefin Polymerization" (1988, Springer-Verlag) edited by W. Kaminsky and H. Sinn and "Transition Metal Catalyzed Polymerizations-Ziegler-Natta and Metathesis Polymerizations" (1988, Cambridge University Press) edited by R. Quirk.

The supports useful in this invention should have a high surface area. In general, these supports should have the characteristics listed in the following table:

Property	Broad Range	Preferred Range
Surface area	25-600 m^2/g	100-370 m^2/g
Pore volume	0.25-4 cm^3/g	0.7-3 cm^3/g
Mean particle diameter	30-200 microns	60-140 microns

Preferably, the pore size distribution is broad, with a significant percentage of the pores in the macropore range (>500 Angstroms). Preferably, at least 50% of the pores are macropores. It is also desirable that the support be substantially anhydrous before the Group 6b metal compound is deposited on it. Thus, it is desirable to calcine the support prior to deposition of the Group 6b metal compound.

The supported catalysts of this invention are readily prepared by techniques well known in the art. For example, a solution of the Group 6b metal alkali metal compound in aliphatic, aromatic or cycloaliphatic hydrocarbons, or ethers such as diethyl ether or tetrahydrofuran can be stirred with the support until the Group 6b metal alkali metal compound is adsorbed on or reacted with the support. The amount of Group 6b metal alkali metal compound relative to the amount of support will vary considerably depending upon such factors as the particle size of the support, its pore size and surface area, the solubility of the Group 6b metal compound in the solvent employed, and the amount of Group 6b metal compound which is to be deposited on the support. However, in general the amount of Group 6b metal alkali metal compound used is adjusted so that the final metal content (calculated as the element), relative to the support, is in the range of from about 0.01 to about 10 weight percent. In most cases, the most desirable level is in the range of about 0.1 to about 5 weight percent.

Preferably the supported Group 6b metal compounds of this invention are employed in conjunction with a co-catalyst in order to obtain increased activity. The co-catalysts useful in the practice of the present invention are Group 2 and Group 3 metal alkyls. As used herein, the term "Group 2 and Group 3 metal alkyls" refers to compounds containing a metal from Group 2 or Group 3 of the Periodic Table (such as Mg, Zn, B, or Al) to which is bonded at least one alkyl group, preferably a C_1 to C_8 alkyl group. Suitable Group 2 and Group 3 metal alkyls include dialkyl magnesium, dialkyl zinc, trialkylboranes, and aluminum alkyls. Suitable aluminum alkyls include trialkylaluminums (such as trimethylaluminum, triethylaluminum, triisobutylaluminum and trioctylaluminum). Trialkylaluminums with alkyl groups of four carbons or greater are preferred. Other aluminum alkyls useful in the practice of the present invention include alkylaluminum alkoxides (such as diethylaluminum ethoxide and ethylaluminum diethoxide), and alkylaluminum halides (such as diethylaluminum chloride, diethylaluminum bromide, diethylaluminum iodide, diethylaluminum fluoride, ethyl aluminum dichloride, ethyl aluminum dibromide, ethyl aluminum diiodide, ethyl aluminum difluoride, and ethyl aluminum sesquichloride).

Other suitable aluminum alkyls are aluminoxanes, including those represented by the general formula $(R\text{-}Al\text{-}O)_n$ for the cyclic form and $R(R\text{-}Al\text{-}O)_n\text{-}AlR_2$ for the linear form. In these formulas, R is, at each independent occurrence, an alkyl group (such as methyl, butyl, isobutyl and the like) preferably with more than two carbon atoms, more preferably with 3-5 carbon atoms, and n is an integer, preferably from 1 to about 20. Most preferably, R is an isobutyl group. Mixtures of linear and cyclic aluminoxanes may also be used. Examples of aluminoxanes useful in this invention include, but are not limited to, ethyl aluminoxane, isobutyl aluminoxane, and methyl aluminoxane. Aluminoxanes (also known as "alumoxanes") suitable for use in this invention are described in Pasynkiewicz, "Alumoxanes: Synthesis, Structures, Complexes and Reactions," *Polyhedron 9*, p. 429 (1990), which is incorporated by reference herein in its entirety.

The preferred Group 2 and Group 3 metal alkyls are the aluminoxanes and the trialkylaluminums.

When used, the Group 2 and Group 3 metal alkyls are used in a Group 2 or 3 metal alkyl to Group 6b metal compound mole ratio of from about 1:1 to about 1,000:1. The preferred mole ratio is from about 10:1 to about 200:1.

The catalyst systems of the present invention may be used in either solution, slurry or gas phase polymerization processes. After the catalysts have been formed, the polymerization reaction is conducted by contacting the monomer charge with a catalytic amount of the catalyst at a temperature and at a pressure sufficient to initiate the polymerization reaction. If desired, an organic solvent may be used as a diluent and to facilitate materials handling. The polymerization reaction is carried out at temperatures of from about 30°C or less up to about 200°C or more, depending to a great extent on the operating pressure, the pressure of the entire monomer charge, the particular catalyst being used, and its concentration. Preferably, the temperature is from about 30°C to about 125°C. The pressure can be any pressure sufficient to initiate the polymerization of the monomer charge, and can be from atmospheric up to about 1,000 psig. As a general rule, a pressure of about 20 to about 800 psig is preferred.

When the catalyst is used in a slurry-type process, an inert diluent medium is used. The diluent should be one which is inert to all other components and products of the reaction system, and be stable at the reaction conditions being used. It is not necessary, however, that the inert organic diluent medium also serve as a solvent for the polymer produced. The inert organic diluents which may be used include saturated aliphatic hydrocarbons (such as hexane, heptane, pentane, isobutane, isopentane, isooctane, purified kerosene and the like), saturated cycloaliphatic hydrocarbons (such as cyclohexane, cyclopentane, dimethylcyclopentane, methylcyclopentane and the like), aromatic hydrocarbons (such as benzene, toluene, xylene and the like), and chlorinated hydrocarbons (such as chlorobenzene, tetrachloroethylene, o-dichlorobenzene and the like). Particularly preferred diluents are cyclohexane, pentane, isopentane, isobutane, hexane and heptane.

When the catalyst is used in a gas phase process, it is suspended in a fluidized bed with, e.g., ethylene. Temperature, pressure and ethylene flow rates are adjusted so as to maintain acceptable fluidization of the catalyst particles and resultant polymer particles. Further descriptions of such a fluidized bed may be found in British Patent No. 1,253,063, to Karapinka, which is incorporated by reference herein.

The following examples are intended to further illustrate the present invention:

EXAMPLE 1

SUPPORTS

The $AlPO_4$ support was purchased from Grace-Davison. The silica support was an EP-10 purchased from Crosfield Catalysts. Some properties of the EP-10 support are:

Property	Crosfield EP-10
Surface area	320 m^2/g
Pore volume	1.80 cm^3/g
Mean particle diameter	105 microns

CATALYST PREPARATIONS

In the preparation of the following catalysts, all manipulations were performed under argon using glove box or Schlenk techniques. All solvents were thoroughly dried over

Na/benzophenone or calcium hydride and distilled prior to use.

EXAMPLE 2

$[Li]^+ [Cp^*Cr(Bzyl)_3]^-$

Lithium (η^5-pentamethylcyclopentadienyl)tris(benzyl)chromate(III) was formed by reacting $CrCl_3(THF)_3$ (1.845 g, 4.92 mmol) with Cp^*Li (0.700 g, 4.92 mmol)in the THF overnight. The THF was then removed in vacuo and the solid residue redissolved in 30 ml of toluene. To this solution 28.4 ml (3.00 eq.) of BzylLi (0.52 M in Et_2O) was added dropwise. Within minutes the color of the solution changed to bright purple. After stirring for 45 minutes the solvent was evaporated under vacuum. The residual solid was extracted with toluene. Crystallization from a mixture of pentane and toluene at -40°C gave purple crystals of $Li^+[Cp^*Cr(Bzyl)_3]^-$ in 63% yield.

X-ray diffraction indicates that the most unusual feature of the structure is the position of the lithium atom, which is sequestered by the benzyl groups and thereby forced into close proximity to the transition metal (Cr-Li:2.54A°). The lithium atom is bonded equally to all three benzyl groups in an allylic fashion.

EXAMPLE 3

SUPPORTED $[Li]^+$ $[Cp^*Cr(Bzyl)_3]^-$

The organochromium compound $[Li]^+$ $[Cp^*Cr(Bzyl)_3]^-$ (0.042 g, 7.81 x 10^{-5} mole), prepared as described in Example 2, was dissolved in 20 ml of benzene, giving a purple solution to which was added 0.5 g of the $AlPO_4$. The resulting mixture was stirred for 5 minutes, giving a purple colored solid and a clear supernatant. The resulting solid catalyst was washed with benzene and pentane, and dried to a free-flowing powder.

EXAMPLE 4

$[Li(TMEDA)_2]$ $[Cp^*Cr(Bzyl)_3]$

The catalyst for this example was prepared as follows:

Stir $CrCl_3(THF)_3$ (1.501 g, 3.98 mmol) and Cp^*Li (0.568 g, 4.00 mmol) together in 50 ml of THF for one hour. 6.0 ml (3.00 eq.) of BzylMgCl (2.05 M in THF, 12.30 mmol) was added dropwise to this blue solution. 1.4-dioxane (3 ml) was added after an hour and the solution was allowed to stir for an additional hour. The purple solution was filtered and 3 ml of TMEDA added to it. This solution was allowed to stir for an additional hour. After removing all volatiles the residue was extracted with ether and dried. Crude yield: 2.39 g (85 %).

EXAMPLE 5

SUPPORTED $[Li(TMEDA)]^+$ $[Cp^*Cr(Bzyl)_3]^-$

Bis(tetramethylethylenediamine) lithium (μ^5-pentamethylcyclopentadienyl) tris(benzyl) chromate (III) (0.086 g, 11.2 x 10^{-5} mole) was dissolved in 20 ml of benzene and treated all at once with 0.5 g of Crosfield EP-10 silica. The resulting mixtures was stirred for 15 minutes resulting in a very dark purple colored solid and a clear supernatant. The solid was washed with benzene and pentane, and dried to a free-flowing powder.

COMPARATIVE EXAMPLE A

ETHYLENE POLYMERIZATION USING AN UNSUPPORTED CATALYST

0.112 mmol of the catalyst from Example 2 above were dissolved in 50 ml of heptane in a 250 ml Fisher-Porter bottle, and pressured to 50 psig with ethylene. The reactor was stirred at 25°C for 2.6 hours. Initially, the ethylene uptake was rapid, but this rate decreased rapidly over the first half hour. The reaction was stopped by venting the pressure. The polymer produced was washed with isopropanol and then with acetone. The polymer was then dried under vacuum. The results of this polymerization are indicated in Run 1 in Table I below.

COMPARATIVE EXAMPLE B

ETHYLENE-BUTENE-1 COPOLYMERIZATION USING AN UNSUPPORTED CATALYST

Comparative Example A was repeated except 20 ml of butene-1 in 20 ml of benzene were added to the reactor which was stirred for 4 hours. The results are shown as Run 2 in Table I below.

EXAMPLE 6

ETHYLENE POLYMERIZATION USING A SUPPORTED CATALYST

Polymerization runs were conducted in two-liter autoclave reactors under particle form (slurry) conditions using 300 ml heptane as diluent, and a weighed amount of catalyst (typically 0.050 to 0.250 g). Run times of 0.5 to 1.0 hour were normally employed. For example, in a typical run, 0.050 g of the catalyst prepared in Example 3, i.e., $(Li)^+(Cp^*Cr(Bzyl)_3^-$ adsorbed on $AlPO_4$, was charged to a two-liter stirred autoclave along with 300 ml of heptane and 0.3 ml of a 1.0 M heptane solution of isobutylaluminoxane purchased from AKZO. The reactor temperature and pressure were adjusted to 80°C and 200 psig (with ethylene), respectively except in Run 6 where a partial pressure of 20 psig of hydrogen was used. The ethylene was supplied on demand from a pressurized reservoir. After 1.0 hour, the reaction was stopped by deactivating the stirrer and venting the pressure. The polymer produced was washed with isopropanol and acetone, and dried under vacuum to yield 140 g of white, granular solid. The results of these polymerizations are indicated in Runs 3, 4, 5, and 6 in Table I below.

It is to be noted that the $AlPO_4$ support used in Runs 3, 4, 5, and 6 was heat treated at a temperature of 600°C (Run 3) for 16 hours or at 400°C for 16 hours for Runs 4, 5 and 6.

In addition in Run 5, 30 ml of butene-1 were added to the reactor to determine if a co-polymerization product could be obtained.

Referring to Table I, it can be seen that the polymerization using the homogeneous chromium compound has extremely low activity (Runs 1 and 2).

In contrast, Runs 3 and 4 show an approximately 5,000-fold improvement in activity using a supported catalyst system of this invention.

A comparison of Runs 2 and 5 shows that while some butene-1 was co-polymerized with ethylene using the unsupported catalyst, no butene was incorporated, surprisingly, into the product using the supported catalyst systems of this invention. It also appears the butene is a molecular weight control agent and has an effect on MWD.

Additionally, higher molecular weight products are obtained with the catalyst system of the present invention compared to products obtained using an unsupported catalyst in a homogeneous type polymerization reaction. Compare the results in Run 1 in Table I below (a homogeneous operation) where the molecular weight of the product was 171,100 to the results in Run 3 in Table I below using the supported catalyst system of this invention where the molecular weight of the product is 1,408,000.

A comparison of Runs 3 and 6 shows the sensitivity of the catalysts of this invention to hydrogen. The molecular weight goes from 1,408,000 (Run 3) without hydrogen to 166,500 (Run 6) with a partial pressure of hydrogen of 20 psig.

The procedure of Example 6 was repeated except using the supported catalyst of Example 5 above. The results are shown in Table II below.

Referring to Table II below, it can be seen that 3 runs were made, i.e., Runs 7, 8, and 9. In each run the silica support was dehydrated at a temperature of 600°C for 16 hours. In each case, a co-catalyst (IBAO) was used and in Run 8, 20 psig of hydrogen was employed. In Run 9, 40 ml of butene-1 were added to determine if co-polymerization would occur.

Referring to Table II, it is again seen that the catalyst systems of this invention appear to be unsuitable for the co-polymerization of ethylene with other alpha-olefins (compare Runs 7 and 9). In Run 9, 0 % SCB (Side Chain Branching) was observed when butene was added to the reactor.

A comparison of Runs 7 and 8 shows that the catalyst systems of this invention are particularly sensitive to the presence of hydrogen to affect the molecular weight of the product. Thus, in Run 7, (without the presence of hydrogen), the molecular weight of the product was 436,200, whereas with a partial pressure of hydrogen (Run 8) the molecular weight of the product was 116,200.

The applicant's invention is not to be limited by the examples shown above, but only by the claims set forth below.

TABLE I

POLYMERIZATION DATA FOR $Li^+ [Cp^*Cr(Bzyl)_3]^-$

RUN	Support[a]	μ MOL Cr	Co-Catalyst	Al:Cr[b]	C_2H_4 psig	Co-Monomer psig	Temp. °C	Activity[c]	Activity[d]	MW[e]	MWD[f]	SCB[g]
1	None	128	None	0	50	0	25	4.9	0.54	171,100	9.54	0
2	None	128	None	0	50	24 ml C_4[h]=	25	5	0.56	20,440	2.41	12.37
3	$AlPO_4$	9	IBAO[i]	33	200	0	80	301,000	2800	1,408,000	2.61	0
4	$AlPO_4$	9	IBAO	29	200	0	80	397,436	3720	-------	-----	0
5	$AlPO_4$	9	IBAO	29	200	30 ml C_4[h]=	80	188,034	1760	742,900	19.29	0
6	$AlPO_4$	9	IBAO	29	180[j]	0	80	288,462	2700	166,500	10.36	0

[a] Precalcined at 400°C for Runs 4, 5 and 6 and 600°C for Run 3

[b] Mole Ratio

[c] g Polymer per g Cr per hour

[d] g Polymer per g catalyst per hour

[e] MW = Weight Average Molecular Weight

[f] MWD = $M_w \div M_n$ = Weight Average Molecular Weight ÷ Number Average Molecular Weight

[g] SCB = Ethyl Side Chain Branching/1000C

[h] Milliliters of Butene-1

[i] IBAO = Isobutylaluminoxane

[j] 20 psig of hydrogen also employed

TABLE II

POLYMERIZATION DATA FOR $[\mathrm{Li(TMEDA)}]^+$ $[\mathrm{Cr^{*}Cr(Bzyl)_3}]^-$

RUN	Support[a]	μ MOL Cr	Co-Catalyst	Al:Cr[b]	C_2H_4 psig	H_2 psig	Co-Monomer Psig	Temp. °C	Activity[c]	Activity[d]	MW[e]	MWD[f]	SCB[g]
7	EP-10	11.2	IBAO[i]	29	200	0	0	80	137,362	1600	436,200	14.84	0
8	EP-10	11.2	IBAO	29	180	20	0	80	46,360	540	116,200	9.72	0
9	EP-10	11.2	IBAO	29	200	0	40 ml C_4^{h}=	80	42,582	496	320,400	14.88	0

[a] Precalcined at 600°C for Runs 7, 8 and 9
[b] Mole Ratio
[c] g Polymer per g Cr per hour
[d] g Polymer per g catalyst per hour
[e] MW = Weight Average Molecular Weight
[f] MWD = $M_w \div M_n$ = Weight Average Molecular Weight ÷ Number Average Molecular Weight
[g] SCB = Ethyl Side Chain Branching/1000C
[h] Milliliters of Butene-1
[i] IBAO = Isobutylaluminoxane

PROPOSED CLAIMS FOR CASE T-5105:

1. A catalyst system for the homopolymerization of alpha-olefins having from 2-8 carbon atoms, said catalyst system comprising a Group 6b metal-alkali metal compound wherein said Group 6b metal is a cyclopentadienyl Group 6b metal trialkaryl complex anion in which the Group 6b metal has an oxidation state +3 and wherein said complex anion is balanced by an alkali metal cation selected from lithium, sodium, potassium and cesium and wherein said alkali metal cation is, optionally, coordinately linked to a neutral hydrocarbyl based ligand containing a heteroatom selected from oxygen, nitrogen, phosphorus and sulphur, said Group 6b-alkali metal compound being supported on an inorganic support.

2. A catalyst system for the homopolymerization of alpha-olefins having from 2-8 carbon atoms, said catalyst system comprising a Group 6b metal-alkali metal compound wherein said Group 6b metal is a cyclopentadienyl Group 6b metal trialkaryl complex anion in which the Group 6b metal has an oxidation state +3 and wherein said complex anion is balanced by an alkali metal cation selected from lithium, sodium, potassium and cesium said Group 6b-alkali metal compound being supported on an inorganic support.

3. The catalyst system of claim 2 wherein the Group 6b metal is chromium.

4. The catalyst system of claim 1 wherein the Group 6b alkali metal compound has the

formula:

$$[A]^{+} - [Q]_{c}\,[(C_5(R')_5)_aMX_b]^{-}$$

wherein M is a Group 6b metal such as chromium, molybdenum and tungsten; $(C_5(R')_5)$ is a cyclopentadienyl or substituted cyclopentadienyl ring; R′ is at each independent occurrence hydrogen, a hydrocarbyl radical having from 1-20 carbon atoms, or adjacent R′ groups may together form one or more rings; X is an alkaryl radical having from 7-20 carbon atoms; a is 1 or 2; b is an integer from 1-3 inclusive; and a+b is 4; A is an alkali metal cation selected from lithium, sodium, potassium or cesium; Q is at each occurrence a neutral hydrocarbyl based ligand containing a heteroatom selected from the group consisting of oxygen, nitrogen, phosphorus and sulphur and coordinately linked to the alkali metal cation and c is 0-3 inclusive.

5. The catalyst system of claim 4 wherein M is chromium; $C_5(R')_5$ is pentamethylcyclopentadienyl and c is zero.

6. The catalyst system of claim 5 wherein A is lithium and X is benzyl.

7. The catalyst system of claim 2 wherein the support is an inorganic metal oxide or inorganic metal phosphate.

8. The catalyst system of claim 7 wherein the support is selected from the group

consisting of silica and aluminum phosphate.

9. A catalyst system for the homopolymerization of alpha-olefins having from 2-8 carbon atoms, said catalyst system comprising a Group 6b metal-alkali metal compound wherein said Group 6b metal is a cyclopentadienyl Group 6b metal trialkaryl complex anion in which the Group 6b metal has an oxidation state +3 and wherein said complex anion is balanced by an alkali metal cation selected from lithium, sodium, potassium and cesium and wherein said alkali metal cation is coordinately linked to a neutral hydrocarbyl based ligand containing a heteroatom selected from oxygen, nitrogen, phosphorus and sulphur, said Group 6b-alkali metal compound being supported on an inorganic support.

10. The catalyst system of claim 9 wherein Group 6b metal is chromium.

11. The catalyst system of claim 4 wherein c is 1, 2, or 3.

12. The catalyst system of claim 11 wherein $C_5(R')_5$ is pentamethylcyclopentadienyl and M is chromium.

13. The catalyst system of claim 12 wherein A is lithium and X is benzyl.

14. The catalyst system of claim 10 wherein the support is an inorganic metal oxide

or inorganic metal phosphate.

15. The catalyst system of claim 14 wherein the support is selected from silica and aluminum phosphate.

16. A catalyst system for the homopolymerization of alpha-olefins having from 2-8 carbon atoms, said catalyst system comprising a Group 6b metal-alkali metal compound wherein said Group 6b metal is a cyclopentadienyl Group 6b metal trialkaryl complex anion in which the Group 6b metal has an oxidation state +3 and wherein said complex anion is balanced by an alkali metal cation selected from lithium, sodium and cesium and wherein said alkali metal cation is, optionally, coordinately linked to a neutral hydrocarbyl based ligand containing a heteroatom selected from oxygen, nitrogen, phosphorus and sulphur, said Group 6b-alkali metal compound being supported on an inorganic support, and a Group 2 or 3 metal alkyl compound.

17. A catalyst system for the homopolymerization of alpha-olefins having from 2-8 carbon atoms, said catalyst system comprising a Group 6b metal-alkali metal compound wherein said Group 6b metal is a cyclopentadienyl Group 6b metal trialkaryl complex anion in which the Group 6b metal has an oxidation state +3 and wherein said complex anion is balanced by an alkali metal cation selected from lithium, sodium and cesium said Group 6b-alkali metal compound being

supported on an inorganic support, and a Group 2 or 3 metal alkyl compound.

18. The catalyst system of claim 17 wherein the Group 6b metal is chromium.

19. The catalyst system of claim 16 wherein the Group 6b alkali metal compound has the formula:

$$[A]^+ - [Q]_c\ [(C_5(R')_5)_aMX_b]^-$$

wherein M is a Group 6b metal such as chromium, molybdenum and tungsten; $(C_5(R')_5)$ is a cyclopentadienyl or substituted cyclopentadienyl ring; R′ is at each independent occurrence hydrogen, a hydrocarbyl radical having from 1-20 carbon atoms, or adjacent R′ groups may together form one or more rings; X is an alkaryl radical having from 7-20 carbon atoms; a is 1 or 2; b is 1, 2, or 3; and a+b is 4; A is an alkali metal cation selected from lithium, sodium, potassium or cesium; Q is at each independent occurrence a neutral hydrocarbyl based ligand containing a heteroatom selected from the group consisting of oxygen, nitrogen, phosphorus and sulphur and coordinately linked to the alkali metal cation; and c is 0-3 inclusive.

20. The catalyst system of claim 19 wherein M is chromium; $C_5(R')_5$ is pentamethylcyclopentadienyl and c is zero.

21. The catalyst system of claim 20 wherein A is lithium and X is benzyl.

22. A catalyst system for the homopolymerization of alpha-olefins having from 2-8 carbon atoms, said catalyst system comprising a Group 6b metal-alkali metal compound wherein said Group 6b metal is a cyclopentadienyl Group 6b metal trialkaryl complex anion in which the Group 6b metal has an oxidation state +3 and wherein said complex anion is balanced by an alkali metal cation selected from lithium, sodium, potassium and cesium and wherein said alkali metal cation is coordinately linked to a neutral hydrocarbyl based ligand containing a heteroatom selected from oxygen, nitrogen, phosphorus and sulphur, said Group 6b-alkali metal compound being supported on an inorganic support, and a Group 2 or 3 metal alkyl compound.

23. The catalyst system of claim 22 wherein the Group 6b metal is chromium.

24. The catalyst system of claim 23 wherein c is 1, 2 or 3.

25. The catalyst system of claim 24 wherein M is chromium; $C_5(R')_5$ is pentamethylcyclopentadienyl and c is 2.

26. The catalyst system of claim 25 wherein A is lithium; X is benzyl and the support is selected from silica and aluminum phosphate.

27. The catalyst system of claim 16 wherein the Group 2 metal alkyl compound is an

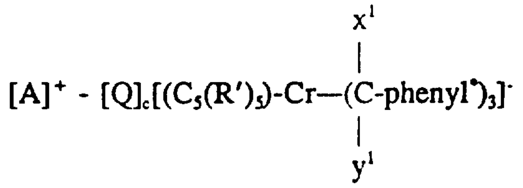
alkyl aluminum compound.

28. The catalyst system of claim 27 wherein the alkyl aluminum compound is selected from the group consisting of trialkylaluminum compounds, alkyl aluminum alkoxides, alkyl aluminum halides and aluminoxanes.

29. The catalyst system of claim 17 wherein the Group 2 metal alkyl compound is an alkyl aluminum compound.

30. The catalyst system of claim 29 wherein the alkyl aluminum compound is an aluminoxane or trialkylaluminum compound.

31. The catalyst system of claim 4 wherein the Group 6 b-alkali metal compound has the formula:



$$[A]^+ - [Q]_c[(C_5(R')_5)\text{-Cr}—(\overset{\overset{x^1}{|}}{\underset{\underset{y^1}{|}}{C}}\text{-phenyl}^{*})_3]^-$$

wherein Cr is chromium; $(C_5(R')_5)$ is a cyclopentadienyl or substituted cyclopentadienyl ring; R' at each independent occurrence is hydrogen, a hydrocarbyl radical having from 1-20 carbon atoms, or adjacent R' groups may together form one or more rings; x^1 and y^1 are the same or different and are selected from hydrogen or hydrocarbyl radicals having from 1-6 carbon atoms; phenyl* is phenyl or a substituted phenyl ring where the substituents at each independent occurrence can be hydrogen or a hydrocarbyl radical having from 1-6 carbon atoms; A is an alkali metal cation selected from lithium, sodium, potassium or cesium; Q is at each independent occurrence a neutral hydrocarbyl based ligand containing a heteroatom selected from the group consisting of oxygen, nitrogen, phosphorus and sulphur and coordinately linked to the alkali metal cation; and c is 0-3 inclusive.

32. The catalyst system of claim 31 wherein $C_5(R')_5$ is pentamethylcyclopentadienyl and c is zero.

33. The catalyst system of claim 32 wherein x^1 and y^1 are hydrogen and $phenyl^*$ is phenyl.

34. The catalyst system of claim 33 wherein A is lithium.

35. The catalyst system of claim 34 wherein the support is an inorganic metal oxide or an inorganic metal phosphate.

36. The catalyst system of claim 35 wherein the support is selected from silica and aluminum phosphate.

37. The catalyst system of claim 36 wherein $C_5(R')_5$ is pentamethylcyclopentadienyl

and c is 1, 2, or 3.

38. The catalyst system of claim 37 wherein x^1 and y^1 are hydrogen; phenyl* is phenyl; A is lithium and wherein the support is an inorganic metal oxide or an inorganic metal phosphate.

39. The catalyst system of claim 38 wherein the support is selected from silica and aluminum phosphate.

40. The catalyst system of claim 31 which contains in addition a group 2 or 3 metal alkyl compound.

41. The catalyst system of claim 40 wherein $C_5(R')_5$ is pentamethylcyclopentadienyl and c is zero.

42. The catalyst system of claim 41 wherein x^1 and y^1 are hydrogen; phenyl* is phenyl; A is lithium and wherein the support is an inorganic metal oxide or an inorganic metal phosphate.

43. The catalyst system of claim 42 wherein the support is selected from silica and aluminum phosphate.

44. The catalyst system of claim 41 wherein the Group 2 or 3 metal alkyl compound is an alkyl aluminum compound.

45. The catalyst system of claim 44 wherein the alkyl aluminum compound is an aluminoxane or trialkylaluminum compound.

46. A process for the polymerization of alpha-olefins having from 2-8 carbon atoms which comprises contacting said alpha-olefins under polymerization reaction conditions in the contact presence of a catalyst system according to any of claims 1 to 45.

47. A process according to claim 46 wherein the alpha-olefin is ethylene.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/01224

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :CO8F 4/622,10/00
US CL : 502/117; 526/155,134
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 502/103,113,117; 526/114,160,155,134

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X ___ Y	Acc. Chem, Res.,Volume 23, Published 1990,Theopold,"Organochromium (III) Chemistry, A Neglected Oxidation State", pages 263-270, particularly, page 264.	1-6 ___ 7-47
	US, A, 5,183,868 (Nordquest) 2 February 1993, col. 2, lines 23-24	
Y	EP,A, 0,509,294 (Carney et al), 21 October 1992, See page 3, lines 14-16, See also page 5, lines 5-20.	7-47
T	US, A 5,418,200 (CARNEY ET AL) 23 MAY 1995	1-47

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search
24 APRIL 1996

Date of mailing of the international search report
21 MAY 1996

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