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(54) Title: CATALYST COMPOSITION

(57) **Abstract:** A method for the preparation of a polymerisation catalyst composition comprises combining a catalyst component solid comprising a first monoeyclopentadienyl metallocene compound with a catalyst component solution comprising a second monocyclopentadienyl metallocene compound. The monocyclopentadienyl metallocene complexes may be the same or different and by combining the first catalyst component in solid form with the second catalyst component in solution, the control of the resultant polymer properties may be improved by independently controlling the concentration of each of the catalyst components.

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CATALYST COMPOSITION

The present invention relates to a catalyst composition comprising a solid catalyst component and a catalyst component in solution, said catalyst composition is particularly suitable for use in the polymerisation of olefins in the gas phase.

In recent years there have been many advances in the production of polyolefin homopolymers and copolymers due to the introduction of metallocene catalysts. Metallocene catalysts offer the advantage of generally a higher activity than traditional Ziegler catalysts and are usually described as catalysts which are single site in nature. There have been developed several different families of metallocene complexes. In earlier years catalysts based on bis (cyclopentadienyl) metal complexes were developed, examples of which may be found in EP 129368 or EP 206794. More recently complexes having a single or mono cyclopentadienyl ring have been developed. Such complexes have been referred to as 'constrained geometry' complexes and examples of these complexes may be found in EP 416815 or EP 420436. In both of these complexes the metal atom eg. zirconium is in the highest oxidation state.

Other complexes however have been developed in which the metal atom may be in a reduced oxidation state. Examples of both the bis (cyclopentadienyl) and mono (cyclopentadienyl) complexes have been described in WO 96/04290 and WO 95/00526 respectively.

The above metallocene complexes are utilised for polymerisation in the presence of a cocatalyst or activator. Typically activators are aluminoxanes, in particular methyl aluminoxane or alternatively may be compounds based on boron compounds. Examples of the latter are borates such as trialkyl-substituted ammonium tetraphenyl- or tetrafluorophenyl-borates or triarylboranes such as tris(pentafluorophenyl) borane. Catalyst systems incorporating borate activators are described in EP 561479, EP 418044 and EP 551277.

The above metallocene complexes may be used for the polymerisation of olefins in solution, slurry or gas phase. When used in the slurry or gas phase the metallocene complex and/or the activator are suitably supported. Typical supports include inorganic oxides eg. silica or polymeric supports may alternatively be used.

Examples of the preparation of supported metallocene catalysts for the polymerisation of olefins may be found in WO 94/26793, WO 95/07939, WO 96/00245, WO 96/04318, WO 97/02297 and EP 642536.

WO 0246246 describes a process for polymerising olefins comprising continuously combining a catalyst component slurry with a catalyst component solution to form a catalyst composition and then polymerising olefins in a reactor. For example the catalyst component slurry may be a slurry of silica supported methyl aluminoxane and the catalyst component solution may be a solution of a metallocene complex. Other examples disclosed are those wherein a solution of a metallocene component is activated with a slurry comprising a silica supported aluminoxane and a second catalyst compound.

US 5786291 describes the preparation of supported metallocene catalysts comprising the combination of a silica supported metallocene in solid form with a solution of a different metallocene. The metallocenes disclosed comprise bridged bis(indenyl) complexes.

US2002/0103310 describes catalysts comprisng the combination of a solid or a slurry of one or more bulky ligand metallocene catalysts, a support and one or more activators with a solution comprising one or more phenoxide catalyst compounds.

WO 03/047751 describes the preparation of bimetallic compounds comprising the combination of a slurry of a non-metallocene catalyst with a solution of a metallocene compound.

We have now surprisingly found that by combining a first catalyst component comprising a monocyclopentadienyl metallocene compound in solid form with a second catalyst component comprising a monocyclopentadienyl metallocene compound in solution, the control of the resultant polymer properties may be improved by independently controlling the concentration of each of the catalyst components.

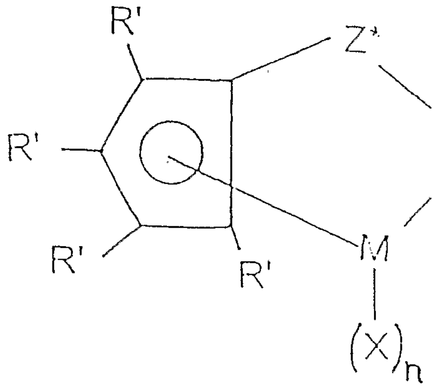
Thus according to a first aspect of the present invention there is provided a method for the preparation of a polymerisation catalyst composition comprising

(a) combining a catalyst component solid comprising a first monocyclopentadienyl metallocene compound with

(b) a catalyst component solution comprising a second monocyclopentadienyl metallocene compound to form a catalyst composition.

The first and second monocylcopentadienyl metallocene compounds may be the same or different. Preferably the first and the second monocyclopentadienyl metallocene compounds are the same.

Suitable monocyclopentadienyl metallocene compounds comprise the general formula:



wherein:-

R' each occurrence is independently selected from hydrogen, hydrocarbyl, silyl, germyl, halo, cyano, and combinations thereof, said R' having up to 20 nonhydrogen atoms, and optionally, two R' groups (where R' is not hydrogen, halo or cyano) together form a divalent derivative thereof connected to adjacent positions of the cyclopentadienyl ring to form a fused ring structure;

X is hydride or a moiety selected from the group consisting of halo, alkyl, aryl, aryloxy, alkoxy, alkoxyalkyl, amidoalkyl, siloxyalkyl etc. having up to 20 non-hydrogen atoms and neutral Lewis base ligands having up to 20 non-hydrogen atoms,

Y is -O-, -S-, -NR*-, -PR*-,

M is hafnium, titanium or zirconium,

Z* is $SiR*_2$, $CR*_2$, $SiR*_2SIR*_2$, $CR*_2CR*_2$, CR*=CR*, $CR*_2SIR*_2$, or $GeR*_2$, wherein:

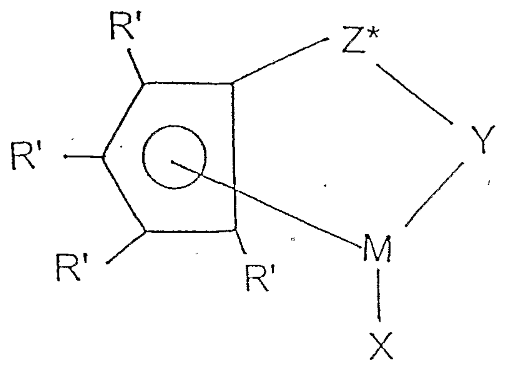
R* each occurrence is independently hydrogen, or a member selected from hydrocarbyl, silyl, halogenated alkyl, halogenated aryl, and combinations thereof, said

R* having up to 10 non-hydrogen atoms, and optionally, two R* groups from Z* (when R* is not hydrogen), or an R* group from Z* and an R* group from Y form a ring system.,

and n is 1 or 2 depending on the valence of M.

Examples of suitable monocyclopentadienyl compounds are (tert-butylamido) dimethyl (tetramethyl-η^5- cyclopentadienyl) silanetitanium dichloride and (2-methoxyphenylamido) dimethyl (tetramethyl--η^5- cyclopentadienyl) silanetitanium dichloride.

Particularly preferred monocyclopentadienyl metallocene compounds for use in the preparation of the supported catalysts of the present invention may be represented by the general formula:



wherein:-

R' each occurrence is independently selected from hydrogen, hydrocarbyl, silyl, germyl, halo, cyano, and combinations thereof, said R' having up to

20 nonhydrogen atoms, and optionally, two R' groups (where R' is not hydrogen, halo or cyano) together form a divalent derivative thereof connected to adjacent positions of the cyclopentadienyl ring to form a fused ring structure;

X is a neutral η^4 bonded diene group having up to 30 non-hydrogen atoms, which forms a π-complex with M;

Y is -O-, -S-, -NR*-, -PR*-,

M is titanium or zirconium in the + 2 formal oxidation state;

Z* is SiR^*_2, CR^*_2, $SiR^*_2SIR^*_2$, $CR^*_2CR^*_2$, $CR^*=CR^*$, $CR^*_2SIR^*_2$, or GeR^*_2, wherein:

R* each occurrence is independently hydrogen, or a member selected from hydrocarbyl, silyl, halogenated alkyl, halogenated aryl, and combinations thereof, said

R* having up to 10 non-hydrogen atoms, and optionally, two R* groups from Z* (when R* is not hydrogen), or an R* group from Z* and an R* group from Y form a ring system.

Examples of suitable X groups include s-trans-η^4-1,4-diphenyl-1,3-butadiene, s-trans-η^4-3-methyl-1,3-pentadiene; s-trans-η^4-2,4-hexadiene; s-trans-η^4-1,3-pentadiene; s-trans-η^4-1,4-ditolyl-1,3-butadiene; s-trans-η^4-1,4-bis(trimethylsilyl)-1,3-butadiene; s-cis-η^4-3-methyl-1,3-pentadiene; s-cis-η^4-1,4-dibenzyl-1,3-butadiene; s-cis-η^4-1,3-pentadiene; s-cis-η^4-1,4-bis(trimethylsilyl)-1,3-butadiene, said s-cis diene group forming a π-complex as defined herein with the metal.

Most preferably R' is hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, benzyl, or phenyl or 2 R' groups (except hydrogen) are linked together, the entire $C_5R'_4$ group thereby being, for example, an indenyl, tetrahydroindenyl, fluorenyl, terahydrofluorenyl, or octahydrofluorenyl group.

Highly preferred Y groups are nitrogen or phosphorus containing groups containing a group corresponding to the formula -N($R^{//}$)- or -P($R^{//}$)- wherein $R^{//}$ is C_{1-10} hydrocarbyl.

Most preferred compounds are amidosilane - or amidoalkanediyl compounds

Most preferred compounds are those wherein M is titanium.

Specific compounds suitable for use in the present invention are those disclosed in WO 95/00526 and are incorporated herein by reference.

A particularly preferred compound for use in the method of the present invention is (t-butylamido) (tetramethyl-η^5- cyclopentadienyl) dimethyl silanetitanium -η^4-1.3 -pentadiene.

Other suitable monocyclopentadienyl metallocene compounds are phosphinimine complexes having the general formula

(Cp)mM(PI)nLq

wherein Cp is a ligand from the group consisting of cyclopentadienyl, substituted cyclopentadienyl, indenyl, substituted indenyl, fluorenyl and substituted fluorenyl,

M is a Group 4 metal selected from hafnium, titanium or zirconium,

PI is a phosphinimine ligand,

L is an actvatable ligand,

m is 1 and n is 1 or 2, q is 1 or 2, and

m = n = q equals the valence of said metal.

The preferred Group 4 metal is titanium.

The phospinimine ligands are defined by the formula:

$R_3P=N-$

wherein each R is independently selected from the group consisting of a hydrogen atom, a halogen atom, a C_{1-20} hydrocarbyl radical, a C_{1-8} alkoxy radical, a C_{6-10} aryl or aryloxy radical, an amido radical, a silyl radical and a germanyl radical. Preferred phosphinimine ligands are those wherein each R is a hydrocarbyl radical and a particularly preferred phosphinimine ligand is tri-(tertiary butyl) phosphinimine.

The activatable ligands are those which may be activated by a cocatalyst for polymerisation. Suitable ligands are independently selected from the group consisting of a hydrogen atom, a halogen atom, a C_{1-10} hydrocarbyl radical, a C_{1-10} alkoxy radical and similar.

The preferred phosphinimine complexes for use in the present invention are those wherein the Cp is cyclopentadienyl and the activatable ligand is halide for example chloride. Particularly preferred complexes have the formula $(Cp)(t\text{-}Bu_3P=N)TiCl_2$ or $(Cp(C_6F_5)(tBu_3PN)TiCl_2$ and the dimethyl derivatives.

Suitable complexes of this type are described in WO 99/40125, WO 00/05237, WO 00/05238, WO 00/32653 and WO 01/05849, the relevant portions of which are incorporated herein by reference.

The catalyst component solid of the present invention preferably comprises a support material.

Suitable support materials include inorganic metal oxides or alternatively polymeric supports may be used for example polyethylene, polypropylene, clays, zeolites, etc.

The most preferred support material for use with the solid catalyst component of the present invention is silica. Suitable silicas include Ineos ES70 and Grace Davison 948 silicas.

The support material may be subjected to a heat treatment and/or chemical treatment to reduce the water content or the hydroxyl content of the support material. Typically chemical dehydration agents are reactive metal hydrides, aluminium alkyls and halides. Prior to its use the support material may be subjected to treatment at $100^{O}C$ to $1000^{O}C$ and preferably at 200 to $850^{O}C$ in an inert atmosphere under reduced pressure.

The supports are preferably pretreated with an organometallic compound preferably an organoaluminium compound and most preferably a trialkylaluminium compound in a dilute solvent.

The support material is pretreated with the organometallic compound at a temperature of $-20^{O}C$ to $150^{O}C$ and preferably at $20^{O}C$ to $100^{O}C$.

The catalyst component solid and the catalyst component solution may suitably also comprise a cocatalyst.

Preferably the catalyst component solid comprises a cocatalyst.

Suitable cocatalysts for use in the method of the present invention are those typically used with the aforementioned monocyclopentadienyl metallocene compounds.

Suitable cocatalysts include aluminoxanes such as methyl aluminoxane (MAO), boranes such as tris(pentafluorophenyl) borane and borates.

Aluminoxanes are well known in the art and preferably comprise oligomeric linear and/or cyclic alkyl aluminoxanes. Aluminoxanes may be prepared in a number of ways and preferably are prepare by contacting water and a trialkylaluminium compound, for example trimethylaluminium, in a suitable organic medium such as benzene or an aliphatic hydrocarbon.

A preferred aluminoxane is methyl aluminoxane (MAO).

Other suitable cocatalysts are organoboron compounds in particular triarylboron compounds. A particularly preferred triarylboron compound is tris(pentafluorophenyl) borane.

Other compounds suitable as cocatalysts are compounds which comprise a cation and an anion. The cation is typically a Bronsted acid capable of donating a proton and the anion is typically a compatible non-coordinating bulky species capable of stabilizing the cation.

Such cocatalysts may be represented by the formula:

$$(L^*\text{-}H)^+_d\ (A^{d-})$$

wherein

L^* is a neutral Lewis base

$(L^*\text{-}H)^+_d$ is a Bronsted acid

A^{d-} is a non-coordinating compatible anion having a charge of d^-, and

d is an integer from 1 to 3.

The cation of the ionic compound may be selected from the group consisting of acidic cations, carbonium cations, silylium cations, oxonium cations, organometallic cations and cationic oxidizing agents.

Suitably preferred cations include trihydrocarbyl substituted ammonium cations eg. triethylammonium, tripropylammonium, tri(n-butyl)ammonium and similar. Also suitable are N,N-dialkylanilinium cations such as N,N-dimethylanilinium cations.

The preferred ionic compounds used as cocatalysts are those wherein the cation of the ionic compound comprises a hydrocarbyl substituted ammonium salt and the anion comprises an aryl substituted borate..

Typical borates suitable as ionic compounds include:

triethylammonium tetraphenylborate
triethylammonium tetraphenylborate,
tripropylammonium tetraphenylborate,
tri(n-butyl)ammonium tetraphenylborate,
tri(t-butyl)ammonium tetraphenylborate,

N,N-dimethylanilinium tetraphenylborate,
N,N-diethylanilinium tetraphenylborate,
trimethylammonium tetrakis(pentafluorophenyl) borate,
triethylammonium tetrakis(pentafluorophenyl) borate,
tripropylammonium tetrakis(pentafluorophenyl) borate,
tri(n-butyl)ammonium tetrakis(pentafluorophenyl) borate,
N,N-dimethylanilinium tetrakis(pentafluorophenyl) borate,
N,N-diethylanilinium tetrakis(pentafluorophenyl) borate.

A preferred type of cocatalyst suitable for use with the transition metal compounds of the present invention comprise ionic compounds comprising a cation and an anion wherein the anion has at least one substituent comprising a moiety having an active hydrogen.

Suitable cocatalysts of this type are described in WO 98/27119 the relevant portions of which are incorporated herein by reference.

Examples of this type of anion include:

triphenyl(hydroxyphenyl) borate
tri (p-tolyl)(hydroxyphenyl) borate
tris (pentafluorophenyl)(hydroxyphenyl) borate
tris (pentafluorophenyl)(4-hydroxyphenyl) borate

Examples of suitable cations for this type of cocatalyst include triethylammonium, triisopropylammonium, diethylmethylammonium, dibutylethylammonium and similar.

Particularly suitable are those cations having longer alkyl chains such as dihexyldecylmethylammonium, dioctadecylmethylammonium, ditetradecylmethylammonium, bis(hydrogentated tallow alkyl) methylammonium and similar.

Particular preferred cocatalysts of this type are alkylammonium tris(pentafluorophenyl) 4-(hydroxyphenyl) borates. A particularly preferred cocatalyst is bis(hydrogenated tallow alkyl) methyl ammonium tris (pentafluorophenyl) (4-hydroxyphenyl) borate.

With respect to this type of cocatalyst, a preferred compound is the reaction product of an alkylammonium tris(pentaflurophenyl)-4-(hydroxyphenyl) borate and an organometallic compound, for example triethylaluminium.

The preferred method according to the present invention comprises

(a) combining a catalyst component solid comprising

(i) a first monocyclopentadienyl metallocene compound, and

(ii) a support with

(b) a catalyst component solution comprising a second monocyclopentadienyl metallocene compound to form a catalyst composition.

The most preferred method according to the present invention comprises

(a) combining a catalyst component solid comprising

(i) a first monocyclopentadienyl metallocene compound,

(ii) a cocatalyst, and

(iii) a support with

(b) a catalyst component solution comprising a second monocyclopentadienyl metallocene compound to form a catalyst composition.

The catalyst compositions of the present invention may be suitable for the polymerisation of olefin monomers selected from (a) ethylene, (b) propylene (c) mixtures of ethylene and propylene and (d) mixtures of (a), (b) or (c) with one or more other alpha-olefins.

Thus according to another aspect of the present invention there is provided a process for the polymerisation of olefin monomers selected from (a) ethylene, (b) propylene (c) mixtures of ethylene and propylene and (d) mixtures of (a), (b) or (c) with one or more other alpha-olefins, said process performed in the presence of a polymerisation catalyst composition as hereinbefore described

The catalyst compositions of the present invention are most suitable for use in slurry or gas phase processes.

The preferred process is a gas phase process.

A slurry process typically uses an inert hydrocarbon diluent and temperatures from about $0^{O}C$ up to a temperature just below the temperature at which the resulting polymer becomes substantially soluble in the inert polymerisation medium. Suitable diluents include toluene or alkanes such as hexane, propane or isobutane. Preferred temperatures are from about $30^{O}C$ up to about $200^{O}C$ but preferably from about $60^{O}C$ to $100^{O}C$. Loop reactors are widely used in slurry polymerisation processes.

Gas phase processes for the polymerisation of olefins, especially for the homopolymerisation and the copolymerisation of ethylene and α-olefins for example 1-butene, 1-hexene, 4-methyl-1-pentene are well known in the art.

Typical operating conditions for the gas phase are from 20°C to 100°C and most preferably from 40°C to 85°C with pressures from subatmospheric to 100 bar.

Particularly preferred gas phase processes are those operating in a fluidised bed. Examples of such processes are described in EP 89691 and EP 699213 the latter being a particularly preferred process for use with the catalyt compositions of the present invention.

Particularly preferred polymerisation processes are those comprising the polymerisation of ethylene or the copolymerisation of ethylene and α-olefins having from 3 to 10 carbon atoms.

Thus according to another aspect of the present invention there is provided a process for the polymerisation of ethylene or the copolymerisation of ethylene and α-olefins having from 3 to 10 carbon atoms, said process performed under polymerisation conditions in the presence of a polymerisation catalyt composition as hereinbefore described.

The preferred α-olefins are 1-butene, 1-hexene, 4-methyl-1-pentene and 1-octene.

By combining the first catalyst component in solid form with the second catalyst component in solution, the control of the resultant polymer properties may be improved by independently controlling the concentration of each of the catalyst components.

Thus according to another aspect of the present invention there is provided a process for the control of polymer properties comprising

(a) combining a catalyst component solid comprising a first monocyclopentadienyl metallocene compound with

(b) a catalyst component solution comprising a second monocyclopentadienyl metallocene compound to form a catalyst composition,

(c) combining the catalyst composition with one or more olefin(s) in a polymerisation reactor to form a polymer product,

(d) measuring a sample of the polymer product to obtain an initial product property, and

(e) changing a process parameter to obtain a second product property.

The present invention will be further illustrated with reference to the accompanying examples:

Abbreviations

TEA	triethylaluminium
Ionic Activator A	$[N(H)Me(C_{18}H_{37})_2][B(C_6F_5)_3(p\text{-}OHC_6H_4)]$
Complex A	$(C_5Me_4SiMe_2N^tBu)Ti(\eta^4\text{-}1,3\text{-pentadiene})$

Example 1

To 3.82 ml (0.265 mmol) of a toluene solution of Ionic Compound A (9.1 % wt) was added 1.06 ml (0.265 mmol) of a toluene solution of TEA ([Al]=0.25 mol/l). This solution was the added to 4.0 g of TEA treated silica (Grace 948, [Al]= 1.37 mmol/g) and the mixture was well agitated until non lumps were visible and was allowed to stand for 30 min.

0.795 ml (0.135 mmol) of an heptane solution of Complex A (8.58% wt) was then added (molar ratio B/Ti=2). The mixture was well agitated until no lumps were visible, was allowed to stand for 30 min and finally dried under vacuum.

[Al]=1.43 mmol/g

[Ti]=33.5 µmol/g

Example 2

To 2 g of the above supported catalyst component from Example 1 (two days after its preparation) was added 0.397ml (0.068 mmol) of an heptane solution of Complex A (8.58% wt) was then added (total molar ratio B/Ti~1). The mixture was well agitated until no lumps were visible, was allowed to stand for 30 min and finally dried under vacuum.

[Al] = 1.43 mmol/g

[Ti]= 68.6 µmol/g

Polymerisation runs

The catalysts from Example 1 (comparative) and Example 2 was tested for ethylene – 1-hexene copolymerisation as follows:

A 2.5 l double jacketed thermostatic stainless steel autoclave was purged with nitrogen at 70°C for at least one hour. 150g of PE pellets previously dried under vacuum at 80°C for 12 hours were introduced and the reactor was then purged three times with nitrogen (7 bar to atmospheric pressure). ~0.13 g of TEA treated silica (1.5 mmol TEA/g) was added under pressure and allowed to scavenge impurities for at least 15 minutes under agitation. The gas phase was then composed (addition of ethylene, 1-hexene and hydrogen) and a mixture of supported catalyst (~0.1 g) and silica/TEA (~0.1 g) was injected. A constant pressure of ethylene and a constant pressure ratio of ethylene/co-monomer were maintained during the run. The run was terminated by venting the reactor and then purging the reactor 3 times with nitrogen. The PE powder produced during the run was then separated from the PE seed bed by simple sieving.

Typical conditions are as follows:

Temperature: 70°C
Ethylene pressure: 6.5 b
C6/C2 (% vol)=0.5
H2= 90 ml
T° = 70 °C
catalyst added: 0.100 g
run length: 1h

Catalyst	Activity	PE Density	PE MI
	(g/g.h.bar)	(g/ml)	g/10 min
Example 1	76	0.922	1.5
Example 2	97	0.921	1.1

The examples clearly show that the further addition of the catalyst component in solution leads to an improvement in activity.

Claims

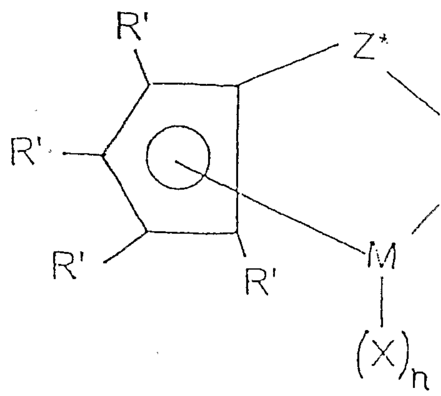
1. A method for the preparation of a polymerisation catalyst composition comprising

(a) combining a catalyst component solid comprising a first monocyclopentadienyl metallocene compound with

(b) a catalyst component solution comprising a second monocyclopentadienyl metallocene compound to form a catalyst composition.

2. A method according to claim 1 wherein the first and the second monocyclopentadienyl metallocene compounds are the same.

3. A method according to either of the preceding claims wherein the monocyclopentadienyl metallocene compounds comprise the general formula



wherein:-

R' each occurrence is independently selected from hydrogen, hydrocarbyl, silyl, germyl, halo, cyano, and combinations thereof, said R' having up to 20 nonhydrogen atoms, and optionally, two R' groups (where R' is not hydrogen, halo or cyano) together form a divalent derivative thereof connected to adjacent positions of the cyclopentadienyl ring to form a fused ring structure;

X is hydride or a moiety selected from the group consisting of halo, alkyl, aryl, aryloxy, alkoxy, alkoxyalkyl, amidoalkyl, siloxyalkyl etc. having up to 20 non-hydrogen atoms and neutral Lewis base ligands having up to 20 non-hydrogen atoms,

Y is -O-, -S-, -NR*-, -PR*-,

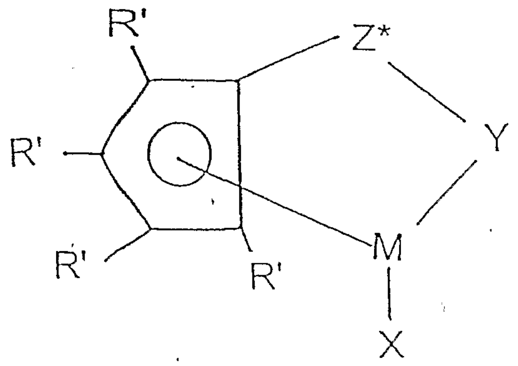
M is hafnium, titanium or zirconium,

Z* is SiR^*_2, CR^*_2, $SiR^*_2SIR^*_2$, $CR^*_2CR^*_2$, $CR^*=CR^*$, $CR^*_2SIR^*_2$, or GeR^*_2, wherein:

R* each occurrence is independently hydrogen, or a member selected from hydrocarbyl, silyl, halogenated alkyl, halogenated aryl, and combinations thereof, said R* having up to 10 non-hydrogen atoms, and optionally, two R* groups from Z* (when R* is not hydrogen), or an R* group from Z* and an R* group from Y form a ring system.,

and n is 1 or 2 depending on the valence of M.

4. A method according to claims 1 to 2 wherein the monocyclopentadienyl metallocene compounds comprise the general formula



wherein:-

R' each occurrence is independently selected from hydrogen, hydrocarbyl, silyl, germyl, halo, cyano, and combinations thereof, said R' having up to 20 nonhydrogen atoms, and optionally, two R' groups (where R' is not hydrogen, halo or cyano) together form a divalent derivative thereof connected to adjacent positions of the cyclopentadienyl ring to form a fused ring structure;

X is a neutral η^4 bonded diene group having up to 30 non-hydrogen atoms, which forms a π-complex with M;

Y is -O-, -S-, -NR*-, -PR*-,

M is titanium or zirconium in the + 2 formal oxidation state;

Z* is SiR^*_2, CR^*_2, $SiR^*_2SIR^*_2$, $CR^*_2CR^*_2$, $CR^*=CR^*$, $CR^*_2SIR^*_2$, or GeR^*_2, wherein:

R* each occurrence is independently hydrogen, or a member selected from hydrocarbyl, silyl, halogenated alkyl, halogenated aryl, and combinations thereof, said R* having up to 10 non-hydrogen atoms, and optionally, two R* groups from Z* (when R* is not hydrogen), or an R* group from Z* and an R* group from Y form a ring system.

5. A method according to claims 1 to 2 wherein the monocyclopentadienyl metallocene compounds comprise the general formula

(Cp)mM(PI)nLq

wherein Cp is a ligand from the group consisting of cyclopentadienyl, substituted cyclopentadienyl, indenyl, substituted indenyl, fluorenyl and substituted fluorenyl,

M is a Group 4 metal selected from hafnium, titanium or zirconium,

PI is a phosphinimine ligand,

L is an actvatable ligand,

m is 1 and n is 1 or 2, q is 1 or 2, and

m = n = q equals the valence of said metal.

6. A method according to claim 5 wherein the phosphinimine ligand has the formula

$R_3P=N-$

wherein each R is independently selected from the group consisting of a hydrogen atom, a halogen atom, a C_{1-20} hydrocarbyl radical, a C_{1-8} alkoxy radical, a C_{6-10} aryl or aryloxy radical, an amido radical, a silyl radical and a germanyl radical.

7. A method according to any of the preceding claims wherein the catalyst component solid additionally comprises a support.

8. A method according to claim 7 wherein the support is silica.

9. A method according to any of the preceding claims wherein the polymerisation

catalyst composition additionally comprises a cocatalyst.

10. A method according to claim 9 wherein the cocatalyst is an aluminoxane.

11. A method accoding to claim 9 wherein the cocatalyst has the formula

$$(L^*\text{-}H)^+_d\ (A^{d-})$$

wherein

L^* is a neutral Lewis base

$(L^*\text{-}H)^+_d$ is a Bronsted acid

A^{d-} is a non-coordinating compatible anion having a charge of d^-, and

d is an integer from 1 to 3.

12. A method according to claim 11 wherein the cocatalyst comprises an ionic compound comprising a cation and an anion wherein the anion has at least one substituent comprising a moiety having an active hydrogen.

13. A method according to any of the preceding claims comprising

(a) combining a catalyst component solid comprising

(i) a first monocyclopentadienyl metallocene compound,

(ii) a cocatalyst, and

(iii) a support, with

(b) a catalyst component solution comprising a second monocyclopentadienyl metallocene compound to form a catalyst composition.

14. A polymerisation catalyst composition comprising

(a) a catalyst component solid comprising a first monocyclopentadienyl metallocene compound, and

(b) a catalyst component solution comprising a second monocyclopentadienyl metallocene compound.

15. A process for the polymerisation of ethylene or the copolymerisation of ethylene and α-olefins having from 3 to 10 carbon atoms, said process perfomed under polymerisation conditions in the presence of a polymerisation catalyst composition prepared by the method of any of claims 1 to 13 or according to claim 14.

16. A processs according to claim 15 wherein the α-olefins comprise 1-butene, 1-hexene, 4-methyl-1-pentene and 1-octene.

17. A process according to claims 15 or 16 wherein the process is performed in the gas phase.

18. A process for the control of polymer properties comprising

(a) combining a catalyst component solid comprising a first monocyclopentadienyl metallocene compound with

(b) a catalyst component solution comprising a second monocyclopentadienyl

(c) metallocene compound to form a catalyst composition,combining the catalyst composition with one or more olefin(s) in a polymerisation reactor to form a polymer product,

(d) measuring a sample of the polymer product to obtain an initial product property, and

(e) changing a process parameter to obtain a second product property.

INTERNATIONAL SEARCH REPORT

PCT/GB2005/000179

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08F10/00 C08F4/64

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)

IPC 7 C08F

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 practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 538 080 B1 (SWINDOLL ROBERT D ET AL) 25 March 2003 (2003-03-25)	1-4, 7-11, 13-18
Y	example 8 column 15, line 15 - column 16, line 52 column 5, line 29 - line 45 column 5, line 59 - line 62 column 6, line 30 - line 56 -----	5,6,12
Y	US 6 486 273 B1 (MCKAY IAN ET AL) 26 November 2002 (2002-11-26) claims 1,2,4 example c; table 1 -----	5,6
Y	US 5 783 512 A (JACOBSEN ET AL) 21 July 1998 (1998-07-21) examples 11,12,17,19 -----	12

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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"O" document referring to an oral disclosure, use, exhibition or other means

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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

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"&" document member of the same patent family

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