[0008] The molecular weight distribution is one of the most important properties of a polymer. By changing this parameter, the crystalline structure and the crystallization rate of a polymer is dramatically influenced, which has impact on the convertability and usability of a certain polymer for a certain application. As an example, for extrusion applications like sheet, pipe, film, raffia, or thermoforming, a broader molecular weight distribution is advantageous, while for applications like fiber or injection molding a narrower molecular weight distribution would be advantageous. As used to processing polymers produced using phthalate based Ziegler-Natta catalysts, the converters insist in molecular weight distributions typically produced by such catalysts and expect that phthalate free Ziegler-Natta catalysts deliver a similar molecular weight distribution. Unfortunately, state of the art diether based catalysts deliver polymers where the molecular weight distribution is too narrow while succinate based catalysts deliver polymers where the molecular weight distribution is far too broad.

SUMMARY OF THE DISCLOSURE

[0008a] In an aspect, there is provided a supported Ziegler-Natta catalyst system comprising a support, titanium, magnesium, and a diether internal electron donor as the only internal electron donor, wherein the support consists of oxides of silicon, aluminum, titanium, zirconium, metals from Groups I or II of the Periodic Table, or mixtures or chemical combinations of these oxides, and having an activity and hydrogen response suitable for the production of propylene polymers having a molecular weight distribution (PI(GPC)) in the range from about 5.75 to about 9.

[0008b] In another aspect, there is provided a method for making a solid catalyst component for use in a Ziegler-Natta catalyst system, the method including:

(a) combining a porous particulate support in an inert solvent with a hydrocarbon soluble organomagnesium compound to form a slurry mixture, wherein the support consists of oxides of silicon, aluminum, titanium, zirconium, metals from Groups I or II of the Periodic Table, or mixtures or chemical combinations of these oxides;

(b) halogenating the organomagnesium compound and contacting the halogenated reaction product with a C1 to C8 alkanol;

(c) reacting the slurry mixture with a titanium compound, followed by reacting the

slurry mixture with an internal donor consisting essentially of at least one diether compound;

(d) extracting the solid intermediate with a mixture of a titanium compound and a hydrocarbon solvent to form the solid catalyst component; and

(e) recovering the solid catalyst component;

wherein the diether compound is selected such that the resulting solid catalyst component has an activity and hydrogen response suitable for the production of propylene polymers having a molecular weight distribution in the range from about 5.75 to about 9.

[0008c] In an aspect, there is provided a catalyst produced by the process as defined above.

[0008d] In an aspect, there is provided a process for the polymerization of olefins of formula $CH2=CHR^1$, in which R^1 is hydrogen or a hydrocarbon radical having 1-12 carbon atoms carried out in the presence of a catalyst as defined above.

[0008e] In another embodiment, there is provided a propylene polymer having a molecular weight distribution (PI(GPC)) in the range from about 5.75 to about 9 produced using a supported Ziegler-Natta catalyst system comprising a diether internal electron donor.

[0009] Embodiments disclosed herein provide a non-phthalate Ziegler-Natta catalyst system for the polymerization and copolymerization of olefins that overcome the above shortcomings in the prior art and provide a Ziegler-Natta catalyst system with a unique selection, combination, and treatment of the three essential components of a Ziegler-Natta catalyst, the support, the transition metal component and the internal donor, as described below. The resulting Ziegler-Natta catalyst has unusually high activity, excellent hydrogen response and stereoselectivity, while the molecular weight distribution is comparable to phthalate containing Ziegler-Natta catalysts.

[0010] Embodiments disclosed herein relate to a method for making a solid catalyst component for use in a Ziegler-Natta catalyst system. The method may include the steps of: (a) combining a porous particulate support in an inert solvent with a hydrocarbon soluble organomagnesium compound to form a slurry mixture; (b) halogenating the organomagnesium compound; (c) reacting the slurry mixture with a titanium compound, followed by reacting the slurry mixture with at least one diether compound (internal donor); (d) extracting the solid intermediate with a mixture of a

CLAIMS

What is claimed:

1. A supported Ziegler-Natta catalyst system comprising a support, titanium, magnesium, and a diether internal electron donor as the only internal electron donor, wherein the support consists of oxides of silicon, aluminum, titanium, zirconium, metals from Groups I or II of the Periodic Table, or mixtures or chemical combinations of these oxides, and having an activity and hydrogen response suitable for the production of propylene polymers having a molecular weight distribution (PI(GPC)) in the range from about 5.75 to about 9.

2. A method for making a solid catalyst component for use in a Ziegler-Natta catalyst system, the method including:

   (a) combining a porous particulate support in an inert solvent with a hydrocarbon soluble organomagnesium compound to form a slurry mixture, wherein the support consists of oxides of silicon, aluminum, titanium, zirconium, metals from Groups I or II of the Periodic Table, or mixtures or chemical combinations of these oxides;

   (b) halogenating the organomagnesium compound and contacting the halogenated reaction product with a C1 to C8 alkanol;

   (c) reacting the slurry mixture with a titanium compound, followed by reacting the slurry mixture with an internal donor consisting essentially of at least one diether compound;

   (d) extracting the solid intermediate with a mixture of a titanium compound and a hydrocarbon solvent to form the solid catalyst component; and

   (e) recovering the solid catalyst component;

   wherein the diether compound is selected such that the resulting solid catalyst component has an activity and hydrogen response suitable for the production of propylene polymers having a molecular weight distribution in the range from about 5.75 to about 9.

3. The process of claim 2, wherein, in step (b), the alkanol is used at a molar ratio to the organomagnesium compound in the range from 1.5:1 to 3.5:1

4. The process of claim 2, wherein, in step (b), the alkanol is used at a molar ratio to the organomagnesium compound of 2.5:1.

5. The process of claim 2, wherein, in step (c), the titanium compound is used in an amount of 1 to 15 moles for each mole of the magnesium compound.

6. The process of claim 2, wherein, in step (c), the titanium compound is used in an amount of 2 to 10 moles for each mole of the magnesium compound.

~~3.~~ 7. The process of claim 2, wherein the diether compound has the general structure (I):

$$R^1O - (C\,R^5R^6)_n - CR^3R^4 - (C\,R^7R^8)_m - OR^2 \quad \textbf{(I)}$$

where

R^1 and R^2 are the same or different and are selected from the group consisting of a saturated or unsaturated aliphatic group of from 1 to about 20 carbon atoms or an aryl group of from 6 to about 20 carbon atoms,

$n + m = 2$ to 4,

R^3, R^4, R^5, R^6, R^7 and R^8 are identical or different and are each a hydrogen atom, a linear, cyclic or branched hydrocarbon group, for example an alkyl group of from 1 to about 20 carbon atoms, an alkenyl group of from 2 to about 20 carbon atoms, an aryl group of from 6 to about 20 carbon atoms, an arylalkyl group of from 7 to about 40 carbon atoms, an alkylaryl group of from 7 to about 40 carbon atoms or an arylalkenyl

group of from 8 to about 40 carbon atoms and may contain one or more hetero atoms like Si, B, Al, O, S, N or P, and/or may contain halogen atoms like F, Cl or Br, and/or the two radicals R^3 and R^4 may form a hydrocarbon ring system, and R^3 and/or R^4 are different from hydrogen.

~~4.~~ 8. The process of claim 2, wherein the diether compound has the general structure (II):

$$R^1O - CH_2 - CR^3R^4 - CH_2 - OR^2 \quad \textbf{(II)}$$

where

R^1 and R^2 are the same or different and are selected from the group consisting of a saturated or unsaturated aliphatic group of from 1 to about 20 carbon atoms, more preferably an alkyl group of from 1 to about 10 carbon atoms, even more preferably an alkyl group of from 1 to 4 carbon atoms, ideally a methyl or ethyl group, most ideally a methyl group,

R^3 and R^4 are identical or different and are each a linear, cyclic or branched hydrocarbon group, for example an alkyl group of from 1 to about 20 carbon atoms, an alkenyl group of from 2 to about 20 carbon atoms, an aryl group of from 6 to about 20 carbon atoms, an arylalkyl group of from 7 to about 40 carbon atoms, an alkylaryl group of from 7 to about 40 carbon atoms or an arylalkenyl group of from 8 to about 40 carbon atoms and may contain one or more hetero atoms like Si, B, Al, O, S, N or P, and/or may contain halogen atoms like F, Cl or Br, and/or the two radicals R^3 and R^4 may form a hydrocarbon ring system.

~~5.~~ 9. The process of claim 2, wherein the diether compound has the general structure (III):

$$R^1O - CH_2 - CR^3R^4 - CH_2 - OR^2 \quad \textbf{(III)}$$

where

R^1 and R^2 are identical and are selected from the group consisting of an alkyl group of from 1 to about 10 carbon atoms, even more preferably an alkyl group of from 1 to 4 carbon atoms, ideally a methyl or ethyl group, most ideally a methyl group,

R^3 and R^4 are identical or different and are each a linear, cyclic or branched hydrocarbon group, for example an alkyl group of from 1 to about 10 carbon atoms, an alkenyl group of from 2 to about 10 carbon atoms, an aryl group of from 6 to about 10 carbon atoms, an arylalkyl group of from 7 to about 40 carbon atoms, an alkylaryl group of from 7 to about 40 carbon atoms or an arylalkenyl group of from 8 to about 40 carbon atoms, and/or the two radicals R^3 and R^4 may form a hydrocarbon ring system, which may contain one or more hetero atoms like Si, O, S, N or P.

~~6.~~ 10. The process of claim 2, wherein the diether compound comprises at least one of 2,2 di-cyclopentyl-1,3-dimethoxypropane; 2,2 di-(cyclopentylmethyl)-1,3-dimethoxypropane; 2,2-di-cylohexyl-1,3-dimethoxypropane; 2,2-di-(cylohexylmethyl)-1,3-dimethoxypropane; 2,2- di-norbornyl-1,3-dimethoxypropane; 2,2-di-phenyl-1,3-dimethoxypropane; 2,2-di-phenylmethyl-1,3-dimethoxypropane; 2,2-di-n-propyl-1,3-dimethoxypropane; 2,2-di-isopropyl-1,3-dimethoxypropane; 2,2-di-n-butyl-1,3-dimethoxypropane; 2,2-di-secbutyl-1,3-dimethoxypropane; 2,2-di-isobutyl-1,3-dimethoxypropane; 2,2-di-n-pentyl-1,3-dimethoxypropane; 2,2-di-(2-pentyl)-1,3-dimethoxypropane; 2,2-di-(3-pentyl)-1,3-dimethoxypropane; 2,2-di-(methylbutyl)-1,3-dimethoxypropane; 2,2-di-(3-methylbut-2-yl)-1,3-dimethoxypropane; 2,2-di-isopentyl-1,3-dimethoxypropane; 2,2-di-n-hexyl-1,3-dimethoxypropane; 2,2-di-2-hexyl-1,3-dimethoxypropane; 2,2-di-3-hexyl-1,3-dimethoxypropane; 2,2-di-(2-methylpentyl)-1,3-dimethoxypropane; 2,2-di-(3-methylpentyl)-1,3-dimethoxypropane; 2,2-di-(4-methylpentyl)-1,3-dimethoxypropane; 2-tertbutyl-1,3-dimethoxypropane; 2-ethyl-2-tertbutyl-1,3-dimethoxypropane; 2-n-propyl-2-tertbutyl-1,3-dimethoxypropane; 2-n-butyl-2-tertbutyl-1,3-dimethoxypropane; 2-isobutyl-2-tertbutyl-1,3-dimethoxypropane; 2-n-pentyl-2-tertbutyl-1,3-dimethoxypropane; 2-isopentyl-2-tertbutyl-1,3-dimethoxypropane; 2-n-hexyl-2-tertbutyl-1,3-dimethoxypropane; 2-ethyl-2-isopropyl-1,3-dimethoxypropane; 2-n-propyl-2-isopropyl-1,3-dimethoxypropane; 2-n-butyl-2-isopropyl-1,3-dimethoxypropane; 2-secbutyl-2-isopropyl-1,3-dimethoxypropane; 2-isobutyl-2-isopropyl-1,3-dimethoxypropane; 2-n-pentyl-2-isopropyl-1,3-dimethoxypropane; 2-(2-pentyl)-2-isopropyl-1,3-dimethoxypropane; 2-(3-pentyl)-2-isopropyl-1,3-dimethoxypropane; 2-methylbutyl-2-isopropyl-1,3-dimethoxypropane; 2-(3-methylbut-2-yl)-2-isopropyl-1,3-dimethoxypropane; 2-isopentyl-2-isopropyl-1,3-dimethoxypropane; 2-n-hexyl-2-isopropyl-1,3-dimethoxypropane; 2-(2-hexyl)-2-

isopropyl-1,3-dimethoxypropane; 2-(3-hexyl)-2-isopropyl-1,3-dimethoxypropane; 2-(2-methylpentyl)-2-isopropyl-1,3-dimethoxypropane; 2-(3-methylpentyl)-2-isopropyl-1,3-dimethoxypropane; 2-(4-methylpentyl)-2-isopropyl-1,3-dimethoxypropane; 2-ethyl-2-cyclopentyl-1,3-dimethoxypropane; 2-n-propyl-2-cyclopentyl-1,3-dimethoxypropane; 2-isopropyl-2-cyclopentyl-1,3-dimethoxypropane; 2-n-butyl-2-cyclopentyl-1,3-dimethoxypropane; 2-isobutyl-2-cyclopentyl-1,3-dimethoxypropane; 2-secbutyl-2-cyclopentyl-1,3-dimethoxypropane; 2-n-pentyl-2-cyclopentyl-1,3-dimethoxypropane; 2-(2-pentyl)-2-cyclopentyl-1,3-dimethoxypropane; 2-(3-pentyl)-2-cyclopentyl-1,3-dimethoxypropane; 2-methylbutyl-2-cyclopentyl-1,3-dimethoxypropane; 2-(3-methylbut-2-yl)-2-cyclopentyl-1,3-dimethoxypropane; 2-ethyl-2-cyclohexyl-1,3-dimethoxypropane; 2-n-propyl-2-cyclohexyl-1,3-dimethoxypropane; 2-isopropyl-2-cyclohexyl-1,3-dimethoxypropane; 2-n-butyl-2-cyclohexyl-1,3-dimethoxypropane; 2-isobutyl-2-cyclohexyl-1,3-dimethoxypropane; 2-secbutyl-2-cyclohexyl-1,3-dimethoxypropane; 2-n-pentyl-2-cyclohexyl-1,3-dimethoxypropane; 2-(2-pentyl)-2-cyclohexyl-1,3-dimethoxypropane; 2-(3-pentyl)-2-cyclohexyl-1,3-dimethoxypropane; 2-methylbutyl-2-cyclohexyl-1,3-dimethoxypropane; 2-(3-methylbut-2-yl)-2-cyclohexyl-1,3-dimethoxypropane; and the corresponding 1,3-diethoxypropane analogues.

~~7.~~ 11. The process of claim 2, wherein the diether compound comprises at least one of 9,9-bis(methoxymethyl)fluorene; 9,9-bis(methoxymethyl)-2,3,6,7-tetramethylfluorene; 9,9-bis(methoxymethyl)-2,7-dimethylfluorene; 9,9-bis(methoxymethyl)-2,7-diisoproylfluorene; 9,9-bis(methoxymethyl)-2,7-ditertbutylfluorene; 9,9-bis(methoxymethyl)-2,8-dimethylfluorene; 9,9-bis(methoxymethyl)-3,6-dimethylfluorene; 9,9-bis(methoxymethyl)-3,6-ditertbutylfluorene; 9,9-bis(methoxymethyl)-3,6-diisopropylfluorene; 9,9-bis(methoxymethyl)-4,5-dimethylfluorene; 9,9-bis(methoxymethyl)-2-methylfluorene; 9,9-bis(methoxymethyl)-4-methylfluorene; 9,10-dihydro-9,9-dimethoxyanthracene; 9,10-dihydro-9,9-diethoxyanthracene; 9,9-Dimethoxyxanthene; 9,9-Diethoxyxanthene; and the corresponding 9,9-bis(ethoxymethyl)- ananalogues.

~~8.~~ 12. The process of claim 2, wherein the diether compound comprises at least one of 2,2-di-isobutyl-1,3-dimethoxypropane; 2,2-di-isopropyl-1,3-dimethoxypropane; 2,2-di-cyclopentyl-1,3-dimethoxypropane; 2-isopropyl-2-isopentyl-1,3-dimethoxypropane; 2-isopropyl-2-isobutyl-1,3-dimethoxypropane; 2-isopropyl-2-cyclopentyl-

dimethoxypropane; 2-ethyl-2-tert-butyl-1,3-dimethoxypropane or the corresponding 1,3-diethoxypropane analogues or 9,9-bis(methoxymethyl)fluorene or 9,9-bis(ethoxymethyl)fluorene.

~~9.~~ 13. The process of claim 2, wherein the diether donor compound is used in an amount of from about 0.01 to about 2 mole for each mole of the magnesium halide compound

~~10.~~ 14. A catalyst produced by the process of any one of claims 2-13~~2-9~~.

~~11.~~ 15. The catalyst of claim 14~~10~~, wherein the catalyst has an activity and hydrogen response resulting in the production of propylene polymers having a molecular weight distribution (PI(GPC)) in the range from about 5.75 to about 9.

~~12.~~ 16. A process for the polymerization of olefins of formula $CH2=CHR^1$, in which R^1 is hydrogen or a hydrocarbon radical having 1-12 carbon atoms carried out in the presence of a catalyst according to any one of claims 1 and 14-15~~10-11~~.