succinate based catalysts deliver polymers where the molecular weight distribution is far too broad.

SUMMARY OF THE DISCLOSURE

[0011a] The disclosure provides a $MgCl_2$-based catalyst system comprising a diether internal electron donor as the only internal electron donor 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.

[0011b] In another aspect, there is provided a process for producing a Ziegler-Natta catalyst for the polymerization of olefins comprising the steps of:

a. combining a spherical spray-cooled $MgCl_2$-xROH support, wherein x is in the range of from about 1.5 to about 6.0 and ROH is an alcohol or a mixture of alcohols where R is a linear, cyclic, or branched hydrocarbon unit with 1-10 carbon atoms, with a transition metal compound in a reactor at a temperature of between about -30°C and +40°C;

b. heating the mixture in the reactor to a temperature of between about 30°C to about 100°C;

c. concurrent with the heating in step (b), or following reaching the temperature of step (b), adding an internal electron donor consisting essentially of a diether compound to the mixture in the reactor;

d. heating the resulting mixture to at least about 80°C, if necessary, and holding the resulting mixture at that temperature for about 1 to 3 hours to produce a pre-catalyst;

e. filtering the mixture containing the pre-catalyst while still hot to obtain the solid pre-catalyst component;

f. extracting the pre-catalyst with a mixture of an organic solvent and a transition metal at a temperature of at least 100°C for 1-5 hours to form a catalyst; and

g. washing the catalyst with a hydrocarbon solvent and drying the catalyst under vacuum and/or elevated temperature of 30-100°C;

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.

[0011c] There is also provided a catalyst produced by the process as defined above.

[0011d] There is also 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.

[0011e] There is also provided a propylene polymer having a molecular weight distribution (PI(GPC)) in the range from about 5.75 to about 9 produced using an $MgCl_2$-based catalyst system comprising a diether internal electron donor as the only internal electron donor.

[0012] Embodiments disclosed herein provide non-phthalate Ziegler-Natta catalyst systems for the polymerization and copolymerization of olefins that overcome the above shortcomings in the prior art and provide Ziegler-Natta catalyst systems with a unique method of selecting and combining 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.

[0013] Improved Ziegler-Natta catalyst may be formed according to embodiments herein using a spherical $MgCl_2$-xROH support, where R is a linear, cyclic or branched hydrocarbon unit with 1-10 carbon atoms and where ROH is an alcohol or a mixture of at least two different alcohols, preferably where the ROH is ethanol or a mixture of

ethanol and a higher alcohol with R being a linear, cyclic or branched hydrocarbon unit with 3-10 carbon atoms, preferably 4-10 carbon atoms; and where x has a range of about 1.5 to 6.0, preferably about 2.0 to 4.0, more preferably about 2.5 to 3.5 and even more preferably 2.95 to 3.35.

[0014] The catalyst includes a Group 4-8 transition metal, such as Ti, and a diether compound as internal donor. The catalysts described herein have an improved activity performance in olefin polymerization reactions as well as good stereoregularity and hydrogen sensitivity while the molecular weight distribution is comparable to phthalate containing Ziegler-Natta catalysts.

[0015] Embodiments herein are also directed to methods of making the improved Ziegler-Natta catalyst. Generally, spherical $MgCl_2$-xROH (x = 3.0 - 3.3) is treated with a transition metal halide, such as $TiCl_4$, at a low temperature (-10°C to +10°C). The reaction product is heated to approximately 80°C and contacted with the diether

CLAIMS

What is claimed:

1. A process for producing a Ziegler-Natta catalyst for the polymerization of olefins comprising the steps of:

a. combining a spherical spray-cooled $MgCl_2$-xROH support, wherein x is in the range of from about 1.5 to about 6.0 and ROH is an alcohol or a mixture of alcohols where R is a linear, cyclic, or branched hydrocarbon unit with 1-10 carbon atoms, with a transition metal compound in a reactor at a temperature of between about -30°C and +40°C;

b. heating the mixture in the reactor to a temperature of between about 30°C to about 100°C;

c. concurrent with the heating in step (b), or following reaching the temperature of step (b), adding an internal electron donor consisting essentially of a diether compound to the mixture in the reactor;

d. heating the resulting mixture to at least about 80°C, if necessary, and holding the resulting mixture at that temperature for about 1 to 3 hours to produce a pre-catalyst;

e. filtering the mixture containing the pre-catalyst while still hot to obtain the solid pre-catalyst component;

f. extracting the pre-catalyst with a mixture of an organic solvent and a transition metal at a temperature of at least 100°C for 1-5 hours to form a catalyst; and

g. washing the catalyst with a hydrocarbon solvent and drying the catalyst under vacuum and/or elevated temperature of 30-100°C;

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.

2. The process of claim 1, 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.

3. The process of claim 1, 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.

4. The process of claim 1, wherein the diether compound has the general structure (III):

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

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.

5. The process of claim 1, 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.

6. The process of claim 1, 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.

7. The process of claim 1, 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.

8. The process of claim 1, 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