

**SUPPORTED MODIFIED ZIEGLER-METALLOCENE CATALYST
FOR OLEFIN POLYMERIZATION**

The invention relates to a mixed or bimetallic catalyst. It also relates to a synthesis for the catalyst which results in improved properties, that are manifested in the bimodal molecular weight distribution products which are produced in the (co)polymerization of ethylene in a single reactor in the presence of this catalyst.

Bimodal molecular weight distribution products and broad molecular weight distribution products of ethylene polymers and copolymers contain two components of different molecular weight, one component having a relatively high molecular weight compared to the second component and designated by the acronym HMW (high molecular weight); the second component being of relatively lower molecular weight than the HMW component and being designated by the acronym LMW (low molecular weight component.) In turn, HMW and the LMW components can have varying molecular weight distribution. The production of two different molecular weight components is related to the hydrogen response, and thus process conditions of polymerization or copolymerization. By comparison, the molecular weight distribution is dependent on the catalyst per se.

Depending upon the characteristics of the resin's molecular weight distribution, characterized by gel permeation chromatography (GPC), high molecular weight polyethylene and copolymers of ethylene may be suitable for film or HIC (household and industrial containers) applications. An HIC resin is also characterized by ADS (annular die swell).

The catalyst of the invention which will be more fully described below comprises two transition metals. Its method of synthesis directly affects the properties of ethylene polymer and copolymer products produced in catalytic polymerization and copolymerization in the presence of these catalysts.

- 2 -

FIG. 1 is a GPC chromatogram of the product of Example 2.
FIG. 2 is a GPC chromatogram of the product of Example 5.

A novel catalyst component can be activated by an activator which is an alkyl aluminum compound, such as trialkyl aluminum compounds, including trimethylaluminum, triethylaluminum and diisobutylaluminum hydride.

The catalyst component comprises at least two transition metals on a support. At least one of the transition metal sources is provided as a non-metallocene. The amount of alkyl aluminum compound activator relative to the non-metallocene transition metal source ranges from 0.1 to 1000 preferably 5 to 200. The transition metals may be deposited on the support simultaneously. In a preferred embodiment, the two transition metals are deposited on the support stepwise rather than simultaneously. In a preferred embodiment, at least one source of the transition metals is a metallocene, preferably a zirconocene; in a most preferred embodiment, the transition metal source provided as the metallocene is deposited on the support before the second transition metal source, a non-metallocene; the embodiments of providing the metallocene results in homogeneous distribution of metallic components.

At least one of the non-metallocene transition metals is provided as a contact product of at least three components; additional reactants may be contacted with this source of transition metal. The at least three components include a trihydrocarbylsilanol, an organomagnesium compound and a titanium compound or salt formed by contacting TiCl_4 with an alcohol. The resulting titanium component is highly active; thus, the catalyst requires less titanium loading. The relative amount of the titanium on the support ranges from 0.1 to 1 millimole/g silica, preferably 0.2 to 0.3 millimole/g silica, based on the dehydrated silica.

The relative amount of the trihydrocarbylsilanol to the amount of the titanium contacted with it ranges from 0.1 to 10 molar ratio, preferably 0.8 to 1.2 molar ratio. The relative amount of the organomagnesium to the amount of the

- 3 -

titanium contacted with it ranges from 0.1 to 10 molar ratio, preferably 0.8 to 1.2 molar ratio. The relative amount of the alcohol contacted with the titanium ranges from 0.001 to 1 molar ratio, preferably 0.2 to 0.6 molar ratio; in
5 preferred embodiments the titanium and alcohol are allowed to contact prior to addition of either the organomagnesium or trialkylsilanol.

One of the transition metals, preferably a titanium component, is a compound or a salt of Ti(IV). In the most
10 preferred embodiment, the titanium source is titanium tetrachloride TiCl_4 . This component is provided as a non-metallocene; metallocene refers to a metal compound which contains a cyclopentadienyl group.

In preferred embodiments, this at least one of the
15 transition metals is provided as a contact product of at least three components; additional reactants may be contacted with this source of transition metal and include the support, and derivatives thereof. The support may be alumina, silica, or silica/aluminum or magnesium oxide derivatives.
20 Preferably, the support is silica. In the most preferred embodiment, the silica is one in which the average pore diameter ranges from 50 to 500Å, preferably 100 to 450Å, and most preferably 300 to 400Å. Preferably, the carrier is silica, which contains [OH] groups. The carrier material
25 must have at least some active hydroxyl (OH) groups to produce the catalyst composition of this invention. The hydroxyl group concentration will be at least 0.7 mmole/gram silica. Preferably, the hydroxyl group concentration of the silica will range from 1.6 to 2.5 mmoles/gram silica. This
30 range is favored by lower drying, dehydration and/or calcination temperatures.

The silica hydroxyl (herein silanol, silica hydroxyl is used interchangeably) groups are detectable by IR spectroscopy. Quantitative determinations of the hydroxyl
35 concentration on silica are made by contacting a silica sample with methyl magnesium iodide and measuring methane evolution (by pressure determination).

- 4 -

Dehydration of silica material can be effected by heating at 100° to 600°C, preferably from 150° to 350°C and most preferably at 200° to 300°C.

By comparison, Davison 955 silica dehydrated at 600°C (for 16 hours) will have a surface hydroxyl concentration of 0.7 mmoles per gram (mmols/gm) of silica. Davison 955 silica dehydrated at 800°C will be a silica with 0.5 mmole of silica hydroxy per gram silica. The silica of the most preferred embodiment is a high surface area, amorphous silica (surface area = 300 m²/gm; pore volume of 1.65 to 3.1 cm³/gm), and it is a material marketed under the trade names of Davison 952 or Davison 955 by the Davison Chemical Division of W. R. Grace and Company or PQ MS-3030 by Philadelphia Quartz Corp. As purchased, the silicas are not dehydrated and must be dehydrated prior to use. The catalyst synthesis of the catalyst of the invention exhibiting highest activity dictates that the silica contain hydroxyl groups for contact with the solution containing aluminoxane and metallocene. The amount of hydroxyl groups, in mmoles/gram silica can be affected by the dehydration temperatures used to condition the silica. Specifically, the dehydration temperatures of 600°C reduce the amount of reactive hydroxyl groups available for contact with the solution of aluminoxane and metallocene. By comparison, the dehydration temperatures of 250°C increase the amount of reactive hydroxyl groups available for contact with the solution of aluminoxane and metallocene, relative to the silica heat treated, for dehydration purposes to 600°C. Accordingly, preferred dehydration and/or calcination temperatures are below 400°C, more preferably below 300°C, and most preferably at 250°C. Accordingly, the silica used in embodiments of the invention will contain a silanol (OH) concentration of greater than 0.7 mmoles OH per gram silica; preferably it will contain greater than 0.7 mmoles up to 2.5 mmoles OH per gram of silica. In preferred embodiments, the concentration ranges from 1.6 to 1.9 mmoles/gram silica.

The trialkylsilanol component has a formula $A_xB_yC_zSiOH$, in which each of A, B, and C is hydrocarbyl of 1 to 10 carbon

- 5 -

atoms and each is the same or different, and each of x, y, and z is a number from 1 to three and $x+y+z$ is equal to 3. The hydrocarbyl of A, B and C can be alkyl or aryl. If A, B or C is alkyl, it can contain 1 to 10 carbon atoms, and preferably it contains 1 to 6 carbon atoms, most preferably contains 2 carbon atoms. If A, B or C is aryl it can be unsubstituted phenyl or benzyl or substituted phenyl or benzyl; preferably if A, B or C is aryl, it contains 6 to 10 and preferably 6 to 8 carbon atoms. The trialkyl silanol component in the preferred embodiment is triethylsilanol. The organomagnesium compound is preferably a dialkylmagnesium which contains alkyl groups, each being the same or different and each containing 1 to 12 carbon atoms, preferably 4 to 8, and most preferably 4 carbon atoms. Examples of alkyl include ethyl butyl, methyl ethyl, dihexyl; most preferably, the alkylmagnesium is dibutylmagnesium.

The titanium component, a non-metallocene, or not a titanocene, comprises a contact product of $TiCl_4$ and an aliphatic alcohol of 1 to 12 carbon atoms, preferably 4 to 8 carbon atoms, such as butanol, pentanol, hexanol, heptanol and octanol, and analogs thereof. In Examples below pentanol was employed. The resulting titanium compound has the formula $(R'O)_a TiCl_{4-a}$, where a is a number between 0 and 4 and is neither 0 nor 4, and R is alkyl or 1 to 12 carbon atoms.

Contact of the reagents is usually undertaken under inert conditions, free of moisture and air. The contact can be undertaken at temperatures in the range of 0° to 100°C. Generally, in the synthesis reported herein the contact temperatures are in the range of 20° to 60°C. Preferably, the temperature is in the range of from 25° to 45°C. All stages are undertaken at more or less the same temperature, except the reaction of DBM with Et_3SiOH which sometimes takes place at 45°C to improve component solubility.

Preferably, the first supported transition metal source is contacted with a second source of a transition metal which is a metallocene; as noted below a metallocene is a metal compound and containing at least one cyclopentadienyl group.

- 6 -

More preferably, the metallocene is activated. In the most preferred embodiments the metallocene is converted to ionic form. Preferably, this conversion is undertaken with an alumoxane as a cocatalyst. The amount of alumoxane ranges from 50 to 500 molar ratio, preferably 100 to 300 molar ratio. To form catalysts of the invention, all catalyst components can be dissolved with alumoxane and impregnated into the carrier. Catalyst preparation is undertaken under anhydrous conditions and in the absence of oxygen. In a unique process, the carrier material is impregnated with alumoxane, preferably methylalumoxane, in a process described below. The class of alumoxanes comprises oligomeric linear and/or cyclic alkylalumoxanes represented by the formula:
 $R-(Al(R)-O)_n-AlR_2$ for oligomeric, linear alumoxanes and
 $(-Al(R)-O-)_m$ for oligomeric cyclic alumoxane
wherein n is 1-40, preferably 10-20, m is 3-40, preferably 3-20 and R is a C_1-C_8 alkyl group and preferably methyl. Methaluminoxane (MAO) is a mixture of oligomers with a very wide distribution of molecular weights and usually with an average molecular weight of 1200. MAO is typically kept in solution in toluene. The volume of the solution comprising an alumoxane and a solvent therefor can vary, depending on the catalyst sought to be produced.

The metallocene compounds can be selected from a large variety of compounds. The amount of this transition metal provided as a metallocene ranges from 0.1 molar ratio to 0.5 molar ratio based on the other transition metal source.

In a preferred embodiment, the metallocene is added to the solution of the alumoxane prior to impregnating the carrier with the solution. The mole ratio of aluminum provided by aluminoxane, expressed as Al, to metallocene metal expressed as M (e.g. Zr), ranges from 50 to 500, preferably 75 to 400, and most preferably 100 to 300. An added advantage of the present invention is that this Al:Zr ratio can be directly controlled. In a preferred embodiment the alumoxane and metallocene compound are mixed together at ambient temperature for 0.1 to 6.0 hours, prior to use in the

- 7 -

infusion step. The solvent for the metallocene and alumoxane can be appropriate solvents, such as aromatic hydrocarbons, halogenated aromatic hydrocarbons, ethers, cyclic ethers or esters; preferably it is toluene.

5 The metallocene compound has the formula $Cp_mMA_nB_p$ in which Cp is an unsubstituted or substituted cyclopentadienyl group and unbridged or bridged indenyl, M is zirconium or hafnium and A and B belong to the group including a halogen atom, hydrogen or an alkyl group. In the above formula of the
10 metallocene compound, the preferred transition metal atom M is zirconium. In the above formula of the metallocene compound, the Cp group is an unsubstituted, a mono- or a polysubstituted cyclopentadienyl group. The substituents on the cyclopentadienyl group can be preferably straight or
15 branched chain C_1 - C_6 alkyl groups. The cyclopentadienyl group can be also a part of a bicyclic or a tricyclic moiety such as indenyl, tetrahydroindenyl, fluorenyl or a partially hydrogenated fluorenyl group, as well as a part of a substituted bicyclic or tricyclic moiety. In the case when m
20 in the above formula of the metallocene compound is equal to 2, the cyclopentadienyl groups can be also bridged by polymethylene or dialkylsilane groups, such as $-CH_2-$, $-CH_2-CH_2-$, $-CR'R''-$ and $-CR'R''-CR'R''-$ where R' and R'' are short alkyl groups or hydrogen, $-Si(CH_3)_2-$, $Si(CH_3)_2-CH_2-CH_2-$
25 $Si(CH_3)_2-$ and similar bridge groups. If the A and B substituents in the above formula of the metallocene compound are halogen atoms, they belong to the group of fluorine, chlorine, bromine or iodine. If the substituents A and B in the above formula of the metallocene compound are alkyl
30 groups, they are preferably straight-chain or branched C_1 - C_8 alkyl groups, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, n-pentyl, n-hexyl or n-octyl.

Suitable metallocene compounds include
bis(cyclopentadienyl)metal dihalides,
35 bis(cyclopentadienyl)metal hydridohalides,
bis(cyclopentadienyl)metal monoalkyl monohalides,
bis(cyclopentadienyl)metal dialkyls and bis(indenyl)metal

- 8 -

dihalides wherein the metal is zirconium or hafnium, halide groups are preferably chlorine and the alkyl groups are C_1 - C_6 alkyls. Illustrative, but non-limiting examples of metallocenes include bis(cyclopentadienyl)zirconium dichloride, bis(cyclopentadienyl)hafnium dichloride, bis(cyclopentadienyl)zirconium dimethyl, bis(cyclopentadienyl)hafnium dimethyl, bis(cyclopentadienyl)zirconium hydridochloride, bis(cyclopentadienyl)hafnium hydridochloride, bis(n-butylcyclopentadienyl)zirconium dichloride, bis(n-butylcyclopentadienyl)hafnium dichloride, bis(n-butylcyclopentadienyl)zirconium dimethyl, bis(n-butylcyclopentadienyl)hafnium dimethyl, bis(n-butylcyclopentadienyl)zirconium hydridochloride, bis(n-butylcyclopentadienyl)hafnium hydridochloride, bis(pentamethylcyclopentadienyl)zirconium dichloride, bis(pentamethylcyclopentadienyl)hafnium dichloride, bis(n-butylcyclopentadienyl)zirconium dichloride, cyclopentadienyl-zirconium trichloride, bis(indenyl)zirconium dichloride, bis(4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride, and ethylene-[bis(4,5,6,7-tetrahydro-1-indenyl)] zirconium dichloride, ethylene bridged- or silane bridged- bis(indenyl) zirconium dichloride. The metallocene compounds utilized within the embodiment of this art can be used as crystalline solids, as solutions in aromatic hydrocarbons or in a supported form.

Use of the catalyst in polymerization and copolymerization can be in the solution, slurry, or gas phase. [In an embodiment described in another copending application, the catalyst is treated with hexene before being introduced into the polymerization.] Preferably the conditions include a pressure of less than 1000 psi and generally no greater than 350 psi. Temperatures may range from 30° to 120°C. Generally, the polymerization temperature ranges from 50° to 120°C. The ethylene partial pressures range from 50 to 500 psia. Hydrogen is used as a chain terminator. The partial pressure of hydrogen ranges from 0.1 to 10 psia. The process

- 9 -

conditions include solution, slurry or gas phase polymerization conditions in which the partial pressure of ethylene is within 180 to 400 psia ranges.

5 The products produced in the polymerization or copolymerization are characterized by a density of 0.89 to 0.97, preferably 0.918 to 0.958; by an I₂₁ [ASTM D-1238] of 1 to 100, preferably 5 to 65; and by a molecular weight distribution expressed as MFR (I₂₁/I₂) of 30 to 300, preferably 50 to 150 [ASTM D-1238]. In the HIC products
10 produced by the slurry, particularly desirable properties obtainable hereby include Annular Die Swell (ADS) by a rheometer of 0.5 to 0.9, preferably 0.65 to 0.75.

Annular die swell is measured by weighing 252 centimeters (cm) of a tube extruded at shear rate of 2000 1/sec through
15 an annular die having a tapered entrance angle of 24.4°; die lend length of 3.05 mm; die gap of 0.505 mm and average die diameter of 5.16 mm.

EXAMPLES ILLUSTRATING ESSENCE OF INVENTION

Example 1 - Preparation of Bimetallic Catalyst

20 a. Component A

Davison 955 silica was dehydrated at 250°C for 16 hours. In a flask, 0.1 g of Bis(n-butylcyclopentadienyl) Zirconium Dichloride (from Boulder Scientific Company) was mixed with 10 ml of methylaluminoxane (MAO) solution (4.76M, from
25 Witco/Schering Company). In another flask, 7.4 ml of this reaction product solution was mixed with 5 g of the 250°C dehydrated silica and dried to remove toluene under nitrogen purge at 55° to 60°C at least 4 hours.

b. Component B

30 In a flask, 0.14 ml of triethylsilanol was dissolved in approximately 20 ml heptane and heated to 55° to 60°C. Then 1.23 ml of 0.736 M dibutylmagnesium (DBM) in heptane solution was added rapidly and stirred for one hour. This reaction product could be used to prepare a high activity Ti catalyst
35 if it was reacted with titanium chloride compounds.

- 10 -

c. Final Catalyst

In a flask, 3 grams of Component A was slurried in 20 ml heptane. It was heated to 55°C, and the component B solution was added. The slurry was stirred for 4 hours.

5 In another flask, 1.00 ml of 0.884M TiCl₄ in heptane solution was diluted in approximately 15 ml heptane. Then 0.54 ml of 0.829 M pentanol/heptane solution was added slowly with stirring at room temperature to give a 0.5 pentanol/Ti molar ratio. This modification will allow us to adjust the
10 MW of Ti-catalyzed polymer for optimized product performance. This solution was added to the slurry of component A/B. A new brownish slurry mixture was formed. The slurry was dried to solid by nitrogen purging at 55°C for 5½ hours. 3.15 g of light brown solid was obtained.

15 Comparative Example 1**Preparation of Ti-Base Type Bimetallic Catalyst**

In a flask, 2 g of 600°C-dehydrated Davison 955 silica was slurried with approximately 16 ml heptane. 1.96 ml of dibutylmagnesium in heptane solution (0.736 M) was added. It
20 was stirred for 1 hour at room temperature. 0.16 ml of n-butanol was then added and stirred for another hour. Under agitation, 0.39 ml of 0.927 M TiCl₄/heptane solution was added to this slurry. The slurry was stirred for one hour before drying under vacuum at 45° to 55°C. 2.19 g of Ti-base
25 catalyst was obtained.

In a small vial, 10 ml of the above-mentioned MAO solution was mixed with 0.2006 gram of (n-BuCp)₂ZrCl₂ to form a complex solution. 3.91 ml of this solution was mixed with 2.19 g of Ti-base catalyst, and dried at 45° to 55°C under
30 vacuum. 2.96 grams of catalyst was obtained.

Example 2**Preparation of 1,1'-Ethylene Bis(Indenyl) Zirconium Dichloride - Type of Example 1 Catalyst**

The preparation is identical to Example 1, except (n-BuCp)₂ZrCl₂ was replaced by 1,1-C₂H₄ bis(indenyl)₂ZrCl₂ at same
35 level of Zr content, Davison 955-250 silica was replaced by PQ's 988-200 silica, and 4 ml heptane/g silica was added

- 11 -

immediately after the Zr/MAO impregnation. The uniformity of MAO distribution among particles is quite good as indicated by Scanning Electron Microscopy Analysis; this precursor showed that 95% of particles have similar amount of Al and only 5% of the particles have higher levels of Al.

Example 3**Ethylene Polymerization in Slurry Using Example 1 Catalyst.**

3 liters of heptane were transferred to a 2.5-gallon reactor and 0.5 ml of 15 wt% solution of triethylaluminum (TEAL) in heptane was injected into the reactor under agitation (900 RPM). 30 ml of 1-hexene was then transferred to the reactor. The reactor was heated to 90°C and 3.7 psia of hydrogen was fed into the reactor to obtain a H₂/C₂ molar ratio of 0.02. The reactor was saturated with 200 psig ethylene to maintain the ethylene partial pressure of 182 psia. 0.24 gram of Example 1 catalyst and 300 ml heptane were fed into the reactor, using ethylene pressure slightly above the reactor pressure, to start the polymerization.

The polymerization was maintained at 90°C for 1 hour.

The polymer slurry was stabilized with an antioxidant package and dried over night at room temperature. The solid product was placed in a vacuum oven for 1 hour. The polymer was weighed and a productivity of 1000 g/g cat/hr was calculated. The dry granular product was extruded through a Randcastle mini-extruder. The following melt flow properties were determined: I₂ (melt index) or I₅ and I₂₁ (flow index or FI) [ASTM D-1238]. The melt flow properties of this product were: I₂₁ = 1.27, I₅ = 0.046 and FR (I₂₁/I₅) = 27.6. GPC analysis on the extrudate shows a HMW-film type bimodal was obtained (Figure 1).

Comparative Example 2**Ethylene Polymerization in Slurry using the Comparative Example 1 Catalyst**

The polymerization conditions are identical to that of Example 3, except 7 ml of Trimethylaluminum alkyl (TMA, the preferred cocatalyst by this system) co-catalyst solution (2.42M) and the comparative Example 1 catalyst were used.

- 12 -

preferred cocatalyst by this system) co-catalyst solution (2.42M) and the comparative Example 1 catalyst were used. The H_2/C_2 ratio was adjusted to 0.03 to raise the FI. The stabilized, dry polymer was weighed and a productivity of 1850 g/g cat/hr was calculated. The properties of the product extrudate were: $I_{21} = 1.3$ and MFR (I_{21}/I_2) = 40. GPC analysis showed a MWD with a low molecular weight shoulder, not suitable for premium HIC or film applications.

Example 4

Ethylene Polymerization in Slurry using Example 2 Catalyst and TMA Cocatalyst

The polymerization conditions are identical to that of Comparative Example 2, except the Example 2 catalyst was used and the polymerization time was shortened to $\frac{1}{2}$ hour to avoid hydrogen starvation during the second half hour. The hydrogen/ethylene ratio was 0.02. The stabilized, dry polymers were weighed and a productivity of 2300 g/g cat/hr was calculated. The granular product was extruded through a Randcastle mini-extruder. The properties of this product were: $I_{21} = 0.9$ and MFR (I_{21}/I_2) = 57. GPC analysis on the extrudate showed that a HIC type bimodal MWD was obtained.

Example 5

Ethylene Polymerization in Slurry Using Example 2 Catalyst and DIBAH Cocatalyst.

The polymerization conditions are identical to that of Example 3, except 1 ml of DIBAH cocatalyst solution (1.258M) and Example 2 catalyst were used, and the polymerization time was shortened to $\frac{1}{2}$ hour to avoid hydrogen starvation during the second half hour. The hydrogen/ethylene ratio of this experiment was adjusted to 0.04 to raise the FI. The stabilized, dry polymer was weighed and a productivity of 2700 g/g cat/hr was calculated. The granular product was extruded through a Randcastle mini-extruder. We found the properties of this product were: $I_{21} = 16$ and MFR (I_{21}/I_2) = 104. GPC analysis on the extrudate showed that a bimodal MWD suitable for HIC type applications was obtained (Figure 2).

CLAIMS:

1. A catalyst composition comprising two transition metals and a support, wherein at least one of said two transition metals is provided as a non-metallocene and is a contact product of at least (a) and (b),
5 wherein (a) is a contact product of trihydrocarbylsilanol and dialkyl magnesium, wherein trihydrocarbylsilanol has a formula $A_xB_yC_zSiOH$ in which each of A, B, and C is hydrocarbyl of 1 to 10 carbon atoms and each is the same or different
10 and each of x, y, and z is a number from 1 to 3 and $x+y+z=3$
 wherein said dialkyl magnesium is a compound in which each alkyl is the same or different and contains 1 to 8 carbon atoms;
15 wherein (b) is the contact product of titanium tetrachloride and an alcohol containing 1 to 12 carbon atoms, to form a compound of the empirical formula $(R'O)_aTiCl_{(4-a)}$, where a is a number greater than 0 and less than 4 .
2. The catalyst composition of claim 1, wherein the support is silica which is dehydrated at temperatures in the range of 200° to 300°C.
3. The catalyst composition of claim 1, wherein a second source of transition metal is provided as an activated metallocene.
4. The catalyst composition of claim 1, wherein at least one of A, B, or C is alkyl which contains 1 to 6 carbon atoms.
5. The catalyst of claim 1, where at least one of A, B, and C is an aryl group which contains 6 to 10 carbon atoms.



6. The catalyst composition of claim 3, wherein at least one of A, B, or C is alkyl which contains 1 to 6 carbon atoms.

7. The catalyst of claim 6 wherein the activated metallocene is contacted with the support prior to contact with said non-metallocene.

8. The catalyst composition of claim 7 wherein the alcohol is pentanol.

