

COMONOMER PRETREATED BIMETALLIC CATALYST
FOR BLOW MOLDING AND FILM APPLICATIONS

The invention relates to a mixed catalyst or a 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 the catalyst. The last step in the synthesis of the catalyst is contact with a monomer of alpha olefin of 3 to 10 carbon atoms. This allows for very high density ethylene polymers or copolymers to be produced.

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, the 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.

For films produced from high molecular weight polyethylene or copolymers of ethylene and for HIC (household and industrial containers) applications, the resin of ethylene preferably is characterized by gel permeation chromatography (GPC) for molecular weight distribution. Resins suitable for film applications typically show a distinctly bimodal molecular weight distribution, with the LMW and HMW components approximately equal in concentration.

A HIC resin is narrower in molecular weight distribution, and is typically characterized with an HMW shoulder.

The catalyst precursor of the invention which is 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. Prior to activation with an alkyl aluminum compound, the catalyst precursor is allowed to contact a polymerizable monomer which is an alpha olefin, under temperature conditions below 50°C. Incorporation of the alpha olefin, e.g. hexene, is detected by weight gain, after hexene contact. SEM characterization does not establish that hexene polymerizes during that contact.

The total amount of transition metals ranges from .2 to 1.0 millimole per gram support. The amount of titanium ranges from .1 to .5, preferably from .2 mmole to .4 per gram silica. The amount of Zr ranges from 0.06 to .1, preferably .07 to .087 millimoles per gram silica.

Figure 1 is a gel permeation chromatogram of a polyethylene resin of the examples.

In particular, the invention relates to a catalyst component which is a contact product of reagents comprising: silica which has a pore volume which exceeds 2.9 cc/gram and an average pore diameter which exceed 400 Angstroms; a metallocene of a first transition metal, activated by an alumoxane;

a contact product of dialkylmagnesium and trialkylsilanol;

a second transition metal source which exhibits a hydrogen response which is different from that of the metallocene; and

an olefin of 4 to 20 carbon atoms. This catalyst component is activated by an aluminum alkyl activator.

The presence of the olefin, oligomers, polymers and derivatives thereof, in the catalyst component increases the

catalyst activity and thus increases productivity associated with catalyst use. Moreover, this productivity is enhanced even under conditions for the production of very high density polyethylene, which is required for HIC product. The two
5 different transition metal sources exhibit different hydrogen responses, and thus different chain termination rates; accordingly, the two transition metal sources will produce polyethylenes of at least two different molecular weights. Although in specific embodiments herein the two different
10 transition metal sources can be characterized as a metallocene component and a non-metallocene component, the critical distinction is the fact that the two different transition metal sources exhibit different hydrogen response, under the same polymerization and hydrogen conditions. The
15 catalyst component will now be illustrated in terms of preferred embodiments.

Silica is the preferred support and has a pore volume which exceeds 2.9 cc/g, preferably greater than 3 cc/g; and most preferably a pore volume of greater than 3.1 cc/g.
20 Preferably the average pore diameter exceeds 400 Angstroms. The silica preferably has hydroxyl groups. Silica which is purchased must be dehydrated. Elevated temperatures are used to dehydrate the silica. This can be done at temperatures from 200° to 900°C, preferably from 200° to 300°C. As the
25 temperature of dehydration is increased, the number of silica silanol or hydroxy groups decreases. Accordingly, if higher hydroxyl numbers on the silica are desired, then the dehydration temperature is at the lower end of these ranges, e.g. at 200°C. Parenthetically, higher dehydration
30 temperatures reduce the hydroxyl or silanol group content of the silica. The preferred silica, PQ 988 (or PQ MS 3030), is also characterized by a very narrow pore size distribution.

A sample of the silica is impregnated with a metallocene. Preferably, the metallocene is activated with a
35 composition comprising a Group III element, e.g., with a boron compound or alumoxane prior to the impregnation.

The amount of alumoxane ranges from 1 mmol/g catalyst to 10 mmol/g catalyst, preferably 4 mmol/g cat to 7 mmol/g cat. To form catalysts of the invention, all catalyst components can be dissolved in alumoxane and impregnated into the carrier. Catalyst preparation is undertaken under anhydrous conditions and in the absence of oxygen. The class of alumoxanes comprises oligomeric linear and/or cyclic alkylalumoxanes represented by the formula: $R-(Al(R)-O)_nO/AlR_2$ 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. Methylalumoxane (MAO) is a mixture of oligomers with a very wide distribution of molecular weights and usually with an average molecular weight of about 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 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 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 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 in the above formula of the metallocene compound is equal to 2, the cyclopentadienyl groups can be also bridged by ethylene or dialkylsilane groups, such as -

CH_2- , $-\text{CH}_2-\text{CH}_2-$, $-\text{CR}'\text{R}''-$ and $-\text{CR}'\text{R}''-\text{CR}'\text{R}''-$ where R' and R'' are short alkyl groups or hydrogen, $-\text{Si}(\text{CH}_3)_2-$, $\text{Si}(\text{CH}_3)_2-\text{CH}_2-\text{CH}_2-\text{Si}(\text{CH}_3)_2-$ 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 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. The molar ratio of this transition metal provided as a metallocene to the other non-metallocene transition metal source ranges from 0.1 to 1.0. Preferably, the metallocene is 1,1-ethylene bridged bis(indenyl) zirconium dichloride.

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 alumoxane, expressed as Al, to metallocene metal expressed as M (e.g. Zr), ranges from 50 to 500, preferably 75 to 350, 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 an ambient temperature for 0.1 to 6.0 hours prior to use in the infusion step. The solvent for the metallocene and alumoxane can be appropriate solvents, such as aromatic hydrocarbons including benzene, toluene, xylene, halogenated aromatic hydrocarbons, ethers, cyclic ethers or esters. Preferably it is toluene.

As indicated above, preferably, the metallocene is introduced to the support in activated form. However, the steps of introducing the metallocene to the support and activating it can be undertaken seriatim. Temperatures of support contact can range from 20° to 50°C . In preferred embodiments herein the deposited metallocene source is subjected to contact with a liquid alkane of 5 to 10 carbon

atoms, preferably heptane, and isopentane.

Thereafter, the support containing the transition metal provided as a metallocene source is dried in nitrogen under inert conditions, at ambient temperature conditions, to
5 isolate a particulate product.

The support and transition metal provided as a metallocene are contacted with a contact product of (a) trihydrocarbyl silanol and dialkylmagnesium and (b) a mixture of alcohol and titanium, at temperatures ranging from 20° to
10 60°C. Heptane is used as a solvent for contact of (a) and (b) but any hydrocarbon solvent may be used. This contact of (a) and (b) can be conducted at temperatures ranging from 20° to 45°C. Isolation of the supported metallocene can be conducted at 20° to 60°C under inert conditions, e.g. a
15 nitrogen purge.

The trihydrocarbyl silanol of (a) trihydrocarbylsilanol and dialkylmagnesium can be represented by the empirical formula $A_xB_yC_zSiOH$. 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
20 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, preferably 6 to 8 carbon atoms. Each of x,
25 y, and z can be 1 and the sum of $x+y+z=3$.

The dialkylmagnesium contains alkyl groups. Each of the alkyl groups may be the same or different and contain 1 to 10 carbon atoms, preferably 2 to 6 carbon atoms.

The second transition metal, provided as a non-metallocene, is preferably a titanium(IV) source. The
30 titanium source is a contact mixture of an alcohol and titanium tetrachloride. The relative amounts (molar ratio) of alcohol to titanium metal (metal basis) can range from 0.1 to 1. This is then dried at 45°C and under nitrogen purge.

35 The isolated particulate intermediate containing both transition metals is then contacted with an alpha olefin of 3

to 10 carbon atoms preferably 4 to 10 carbon atoms, e.g. butene-1, pentene, methylpentene, hexene and octene. In the embodiments below, the contact of the supported two transition metals is undertaken at ambient conditions of temperature under an inert (nitrogen) atmosphere. The amount of the olefin ranges from 2 Hexene/Ti molar ratio to 60 Hexene/Ti molar ratio, when the second transition metal source is a titanium compound. Preferably, this contact is undertaken prior to activation of the titanium sites with the alkyl aluminum activator or co-catalyst. Although the olefin increases the weight of the catalyst component, SEM studies did not reveal whether the olefin had polymerized; accordingly, the olefin may be an olefin, oligomers thereof, derivatives thereof and/or polymers thereof.

The catalyst can be used in the polymerization or copolymerization of ethylene under slurry, solution or gas phase conditions (e.g. fluid bed gas phase conditions). Preferably the temperature is in the range of 35° to 120°C and the pressure is below 1000 psi, preferably below 400 psi. In preferred embodiments, the catalyst is presently run at slurry conditions. The amount of activator employed ranges from 5 to 500 Al/Ti molar ratio, based on the total Ti transition metal.

The olefin, e.g., hexene, contact step results in catalysis product of higher density, with less alpha olefin incorporation into the polymer or copolymer, when ethylene is subjected to co-polymerization with olefins of 3 to 10 carbon atoms, preferably to 8 carbon atoms. Moreover, the target FI of the resulting polymers could be reached because of this treatment. The Top Load Strength property or stiffness of bottle made is also improved.

EXAMPLES ILLUSTRATING ESSENCE OF INVENTION

The objective of these examples is to demonstrate that a modified bimetallic catalyst can polymerize ethylene with good productivity under the very high density conditions required for HIC resin production. Due to the exceptionally

high hexene incorporation of the Zr sites, a bimetallic HIC catalyst containing Zr sites produces resins with a density of around 0.946 instead of the desired >0.950 g/cc under our standard slurry HIC conditions (90°C, H₂/C₂ = 0.04, 30 ml 1-hexene). Moreover, if the 1-hexene content is lowered to 20 ml to increase the product density, the productivity decreases to less than half. Therefore, we developed a new catalyst preparation procedure to address this problem.

Example 1: A typical method for preparing the bimetallic catalyst.

a. Component A

Philadelphia Quartz 988-1M silica was dehydrated at 200°C for 16 hours. In a flask, 0.89 g of 1,1-ethylene bis(indenyl) Zirconium Dichloride (from Boulder Scientific Company) was mixed with 86.4 ml of methylalumoxane (MAO) solution (4.76M, from Witco/Schering Company). In another flask, this reaction product solution was mixed with 58.4 g of the 200°C dehydrated silica and 240 ml of heptane was added to help disperse the Zr/MAO complex. The slurry was dried to remove heptane and toluene under nitrogen purge at 41°C for 16 hours. 82.8 g of the precursor was obtained. The uniformity of MAO distribution among the 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.

b. Component B

In a flask, 30.9 ml of 0.736 M dibutylmagnesium (DBM) in heptane solution was dissolved in 450 ml heptane and heated to 45°C. Then 3.45 ml of triethylsilanol was added slowly and stirred for at least 30 minutes. The Component B solution was added to the Component A flask which contains 82.8 grams of the precursor and stirred for at least 30 minutes.

c. Final Catalyst

In another flask, 24.6 ml of 0.912 M TiCl_4 in heptane solution was diluted in 400 ml of heptane. Then 11.3 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 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 42°C for 16 hours. 69.2 g of light brown solid was obtained.

Example 2 - Preparation of hexene pretreated catalyst

1 g of Example 1 catalyst was slurried with 10 ml heptane in a flask. 1 ml of hexene was added and stirred under nitrogen purge overnight (16 hours). 1.3 g of dry powder was obtained.

Example 3 - Typical Polymerization Procedures

3 liters of heptane were transferred to a 2.5-gallon reactor and 1 ml of 1.258M solution of diisobutylaluminum hydride (DIBAH) in heptane was injected into the reactor under agitation (900 RPM). 1-hexene was then transferred to the reactor. The reactor was heated to 90°C and 7.5 psia of hydrogen was fed into the reactor to obtain a H_2/C_2 molar ratio of 0.04. The reactor was saturated with 200 psig ethylene to maintain the ethylene partial pressure of 182 psia. 0.15 gram of Example 2 catalyst and 300 ml of 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 $\frac{1}{2}$ hour. The polymer slurry was stabilized with an antioxidant package and dried overnight at room temperature. The solid product was placed in a vacuum oven for 1 hour. The polymer was weighed and a productivity of about 2000 g/g cat/hr was calculated. The dry granular product was extruded through a

Randcastle mini-extruder. The following melt flow properties were determined: I_2 (melt index) and I_{21} (flow index). GPC analysis on the extrudate was used to determine whether or not it is suitable for premium HIC or HMW film applications.

5 We conducted ethylene polymerization experiments with several levels of 1-hexene using the above-mentioned procedures with Example 2 catalyst, and compared the results with the untreated catalyst. As shown in the table below, this catalyst not only enabled us to polymerize ethylene at
10 reduced hexene levels (even homopolymerization of ethylene), but also greatly improved the catalyst activity (more than three-fold at lower level hexene concentrations).

Amount of Hexene (ml)		Productivity (g/g cat/hr)	FI (I_{21})	MFR (I_{21}/I_2)
	<u>untreated</u>			
30		1400	50	125
20		600	2	89
	<u>treated</u>			
30		2500	24	89
20		2100	15	127
10		1700	4	129
0		1100	0.5	121

90°C, $H_2/C_2 = 0.04$, heptane-slurry

The resin produced with the hexene treated bimetallic catalyst (under reduced hexene concentration, i.e. 20 ml case) showed the desired MFR and bimodal MWD required for
25 premium HIC applications (Figure 1).

Note: In the foregoing Table, I_{21} is measured according to ASTM D-1238 condition F at 190°C and I_2 is measured according to ASTM D-1238 condition E at 190°C; the ratio of I_{21}/I_2 is MFR.

THIS SHEET HAS BEEN
REPLACED

CLAIMS:

1. A catalyst component which is a contact product of reagents comprising:

5 silica which has a pore volume which exceeds 2.9 cc/gram and an average pore diameter which exceeds 400 Angstroms;

a metallocene of a first transition metal, activated by an alumoxane;

10 a contact product of dialkylmagnesium and trialkylsilanol;

a second transition metal source which exhibits a hydrogen response which is different from that of the metallocene; and

15 an olefin of 4 to 20 carbon atoms, oligomers, polymers and derivatives thereof.

2. The catalyst component of claim 1, wherein the silica is characterized by a hydroxyl group of greater than 0.7 millimoles per gram silica.

3. The catalyst component of claim 1, wherein the second source of transition metal is a contact product of titanium tetrachloride and an alcohol containing 1 to 10 carbon atoms.

4. The catalyst component of claim 1, wherein the olefin comprises hexene.

5. The catalyst component of claim 3, wherein the alcohol is pentanol.

6. The catalyst component of claim 1 wherein the metallocene is 1,1-ethylene-bis(indenyl)zirconium dichloride.



This Sheet Has Been Replaced

7. A supported catalyst comprising an alkyl aluminum compound selected from the group consisting of trialkylaluminum and dialkylaluminum hydride, and the catalyst component of claim 1.

8. The catalyst of claim 7, wherein the silica contains hydroxyl group of greater than 0.7 millimoles per gram silica.

9. The catalyst of claim 7, wherein the second source of transition metal is a contact product of titanium tetrachloride and an alcohol containing 1 to 10 carbon atoms.

10. The catalyst of claim 7, wherein the olefin comprises hexene.

11. The catalyst of claim 9, wherein the alcohol is pentanol.

12. The catalyst of claim 7, wherein the metallocene is 1,1-ethylene-bis(indenyl)zirconium dichloride.

13. A supported catalyst comprising an alkyl aluminum compound selected from the group consisting of trialkylaluminum and dialkylaluminum hydride, and a catalyst component comprising an alumoxane;

5 a contact product of dialkylmagnesium and trialkylsilanol;

 a second transition metal source which exhibits a hydrogen response which is different from that of the metallocene; and

10 an olefin of 4 to 20 carbon atoms, oligomers, polymers and derivatives thereof.



14. The catalyst component of claim 13, wherein the silica contains hydroxyl group of greater than 0.7 millimoles per gram silica.

15. The catalyst component of claim 13, wherein the second source of transition metal is a contact product of titanium tetrachloride and an alcohol containing 1 to 10 carbon atoms.

16. The catalyst component of claim 13, wherein the olefin comprises hexene.

17. The catalyst component of claim 15, wherein the alcohol is pentanol.



This Sheet Has Been Replaced

