



Description

Background of the invention Field of the invention

- 5 This invention relates to an improved catalyst used in ethylene polymerization, and more particularly, to vanadium containing catalyst compositions having high activity and providing an improved process in the gas phase for producing polyethylenes having a desirable balance of properties useful in certain applications.

10 Description of the prior art

- Polyethylene having a relatively broad molecular weight distribution possess wide utility in the areas of wire and cable insulation, blow molding and pipe fabrication. Such broad molecular weight distribution polyethylenes, produced for example by the process disclosed in U.S. Patent 3,324,095 (Carrick et al.), possess instability through the presence of a relatively high level of unsaturation. Relatively narrow molecular weight distribution polyethylenes can be made in the gas phase as described in for example U.S. Patent 4,302,565 (Goeke et al.) and U.S. Patent 4,302,566 (Karol et al.). Such gas phase polymerization procedures use catalysts with high activity to produce polyethylene low in unsaturation and possessing high utility in various film applications. Such polyethylenes, however, have limited utility in other areas requiring the properties of increased melt flow and extrudability as well as lower melt fracture found in broad molecular weight distribution polyethylenes. It would therefore be desirable to develop a high activity catalyst composition and process for producing a highly saturated polyethylene in the gas phase having a broad molecular weight distribution.

- Vanadium catalysts have been used to produce polyethylenes. U.S. Patent 3,956,255 (Ort) discloses an ethylene polymerization catalyst composition consisting essentially of a vanadium compound combined with an alkylaluminum alkoxide and a trialkylaluminum. This catalytic composition is deposited on silica which has been reacted with an alkylaluminum or an alkylaluminum alkoxide. Optionally, a halogenated alkane may be used as promoter.

- U.S. Patent 4,173,698 (Kano et al.) describes an ethylene polymerization catalyst which is the unsupported product of a vanadium trichloride-ether complex combined with an aluminum trihalide. An organoaluminum compound is used as cocatalyst.

- U.S. Patent 4,202,958 (Yamaguchi et al.) pertains to an ethylene polymerization process using an unsupported, solid catalyst obtained by reducing a vanadium halide with an organic aluminum compound in the presence of an ether compound. An organic aluminum cocatalyst is also provided.

- U.S. Patent 4,263,171 (Shida et al.) is representative of disclosures of olefin polymerization catalysts using magnesium containing compounds. The patent discloses a silica supported catalyst of a magnesium-aluminum alkyl complex and halogen-containing transition metal compound (including vanadium).

- U.S. Patent 4,294,947 (Doerk et al.) describes an ethylene/butene-1 copolymerization in a liquid butene-1 solvent using an unsupported catalyst comprising the reaction product of a vanadyl chloride and/or alkoxide with alkylaluminum chloride and organoaluminum cocatalysts.

- Many of these references, representative of the prior art, are directed towards providing catalyst with high activity or towards select improvements in particular polymerization procedures or polyethylene properties. Because of the complexity, it has not been possible, prior to the present invention, to provide a commercially useful, optimized process in the gas phase using a vanadium catalyst to produce polyethylenes having a desirable balance of properties. In order to provide such a process, the catalyst must be one that can, simultaneously: provide a superior hydrogen response in order to achieve very low levels of unsaturation in the polyethylene; provide a high degree of productivity such that the catalyst residues in the polyethylene are so small, preferably less than about 10 ppm of vanadium, so as to allow them to remain therein thereby avoiding catalyst removal steps; provide a polyethylene which can be readily molded in a variety of molding applications, i.e. provide a polyethylene having relatively broad molecular weight distribution and wide melt index range; provide enhanced copolymerization of ethylene with other alpha olefins to enable a wide range in density control of the polyethylene as well as a broader range of comonomers which can be used; provide a polyethylene possessing a high bulk density in order to be commercially acceptable in handling and transportation costs; provide a polyethylene having a particle size which can be readily fluidized in a fluid-bed reactor, and which is low in fines content; and provide freely-flowing particulate polyethylene free of fused or chunk-like agglomerations; while preferably using the simplest catalyst composition possible consisting essentially of a minimum number of components.

60 Summary of the invention

- The present invention concerns a catalyst composition and process for producing polyethylene. The process comprises polymerizing ethylene with or without at least one C₃ to C₁₀ alpha-olefin monomer in the gas phase at a temperature between about 10° to about 115°C. The monomers are contacted with a catalyst composition comprising a specific supported precursor, cocatalyst and promoter. The supported precursor

consists essentially of a particular class of vanadium compounds and modifiers which are impregnated on a solid, inert carrier.

Detailed description of the invention

- 5 The invention relates to a high activity, catalyst composition and process for producing polyethylene. The polyethylene so produced possesses a superior balance of properties in fluidity, molecular weight distribution, bulk density, and saturation. Such polymers have a density and melt index which can be selected from among a broad range of densities and melt indices.

10 Polyethylene

The polyethylene prepared in the process of the present invention is ethylene homopolymer or copolymers of a major mole percent, i.e., at least about 50%, of ethylene, and a minor mole percent, i.e., no more than about 50%, of one or more C_3 to C_{10} alpha-olefins. Preferred alpha-olefins are propylene, butene-1, hexene-1, 4-methylpentene-1 and octene-1. Additional monomers may be provided, including

- 15 conjugated or nonconjugated dienes such as butadiene, 1,4 hexadiene and ethylidene norbornene. The polyethylenes possess a desirable balance of properties. The polyethylenes can range in density from about 0.86 to about 0.96 g/cc. They can possess a melt index of between a no-flow value up to about 300 dg/min, and preferably from about 0.1 up to about 50 dg/min. These polymers possess a broad molecular weight distribution, defined as a weight average molecular weight/number average molecular weight ratio (M_w/M_n), of greater than about 10, and preferably between about 14 to about 22. These
- 20 polymers also possess a high bulk density of at least about 0.32 g/cc (20 lbs/ft³), and preferably between about 0.38 (24) to about 0.51 g/cc (32 lbs/ft³). The unsaturation level is very low, being much less than 1 carbon-carbon double bond per thousand carbon atoms ($C=C/1000C$), preferably less than about 0.2 $C=C/1000C$, and most preferably less than about 0.1 $C=C/1000C$. The copolymers have a residual catalyst
- 25 content, in terms of parts per million of vanadium metal, of less than about 10 ppm, and preferably less than about 6 ppm. The preferred polymers produced by the gas phase process of the present invention are freely-flowing, particulate solids, substantially free of fused or chunk-like agglomerations.

The polyethylenes of the present invention are useful in a wide variety of applications including blow molding, film and pipe manufacture, extrusion coating, as well as wire and cable applications.

30 Catalyst

The catalyst composition of the present invention comprises a supported precursor, a cocatalyst and a promoter. The supported precursor consists essentially of a vanadium compound and modifier impregnated on a solid, inert carrier. The vanadium compound in the precursor is the reaction product of a

35 vanadium trihalide and an electron donor. The halogen in the vanadium trihalide is chlorine, bromine or iodine, or mixtures thereof. A particularly preferred vanadium trihalide is vanadium trichloride, VCl_3 .

The electron donor is a liquid, organic Lewis base in which the vanadium trihalide is soluble. The electron donor is selected from the group consisting of alkyl esters of aliphatic and aromatic carboxylic acids, aliphatic esters, aliphatic ketones, aliphatic amines, aliphatic alcohols, alkyl and cycloalkyl ethers, and mixtures thereof. Preferred electron donors are alkyl and cycloalkyl ethers, including particularly

40 tetrahydrofuran. Between about 1 to about 20, preferably between about 1 to about 10, and most preferably about 3 moles of the electron donor are complexed with each mole of vanadium used.

The modifier used in the precursor has the formula:



wherein:

M is either boron or $AlR_{(3-a)}$ and wherein each R is independently alkyl, provided that the total number of aliphatic carbon atoms in any one R group may not exceed 14;

- 50 X is chlorine, bromine or iodine; and

a is 0, 1 or 2, with the provision that when M is boron a is 3.

Preferred modifiers include C_1 to C_6 alkylaluminum mono- and di- chlorides and boron trichloride. A particularly preferred modifier is diethyl aluminum chloride. About 0.1 to about 10, and preferably about 0.2 to about 2.5, moles of modifier are used per mole of electron donor.

- 55 The carrier is a solid, particulate porous material inert to the polymerization. The carrier consists essentially of silica or alumina, i.e., oxides of silicon or aluminum or mixtures thereof. Optionally, the carrier may contain additional materials such as zirconia, thoria or other compounds chemically inert to the polymerization or mixtures thereof.

- The carrier is used as a dry powder having an average particle size of between about 10 to about 250, preferably about 20 to about 200, and most preferably about 30 to about 100, μm . The porous carrier has a surface area of greater than or equal to about 3, and preferably greater than or equal to about 50, m^2/g . A preferred carrier is silica having pore sizes of greater than or equal to about 80, and preferably greater than or equal to about 100, angstroms. The carrier is predried by heating to remove water, preferably at a temperature of greater than or equal to about 600°C.

- 65 The amount of carrier used is that which will provide a vanadium content of between about 0.05 to

about 0.5 mmole of vanadium per gram (mmole V/g), and preferably between about 0.2 to about 0.35 mmole V/g, and most preferably about 0.25 mmole V/g.

The carrier is ordinarily free of preparative chemical treatment by reaction with an alkylaluminum compound prior to the formation of the supported precursor. Such treatment results in the formation of aluminum alkoxides chemically bonded to the carrier molecules. We have discovered that the use of such a treated carrier in the catalyst composition and process of the present invention is not only nonessential, but instead results in undesirable agglomeration when used in the preparation of high density polyethylene (>0.94 g/cc), resulting in a chunk-like, non-freely flowing product.

In addition, we have also discovered that the presence of a magnesium compound in the supported precursor does not significantly raise catalyst activity, and is therefore a nonessential component.

The cocatalyst has the formula:



wherein R is as previously defined in the definition of M in equation I. Preferred cocatalysts include C_2 to C_8 trialkylaluminum compounds. A particularly preferred cocatalyst is triisobutyl aluminum. Between about 5 to about 500, and preferably between about 10 to about 50, moles of cocatalyst are used per mole of vanadium.

The promoter has the formula:



wherein:

R' is hydrogen or unsubstituted or halosubstituted lower, i.e., up to about C_6 containing, alkyl;

X' is halogen; and

b is 0, 1 or 2.

Preferred promoters include fluoro, chloro or bromo substituted ethane or methane having at least 2 halogens attached to a carbon atom. Preferred promoters include CCl_4 , CHCl_3 , CH_2Cl_2 , CBr_4 , CFCl_3 , CH_3CCl_3 , and $\text{CF}_2\text{ClCCl}_3$. Particularly preferred promoters are methylene dichloride (CH_2Cl_2), 1,1,1-trichloroethane, (CH_3CCl_3), and chloroform (CHCl_3). Between about 0.1 to about 10, and preferably between about 0.2 to about 2, moles of promoter are used per mole of cocatalyst.

Catalyst preparation

The catalyst composition of the present invention is produced by first preparing the supported precursor. In one embodiment, the vanadium compound is prepared by dissolving the vanadium trihalide in the electron donor at a temperature between about 20°C up to the boiling point of the electron donor for a few hours. Preferably, mixing occurs at about 65°C for about 3 hours or more. The vanadium compound so produced is then impregnated onto the carrier. Impregnation may be effected by adding the carrier as a dry powder or as a slurry in the electron donor or other inert solvent. The liquid is removed by drying at less than about 100°C for a few hours, preferably between about 45° to about 90°C for about 3 to 6 hours. The modifier, dissolved in an inert solvent, such as a hydrocarbon, is then mixed with the vanadium impregnated carrier. The liquid is removed by drying at temperatures of less than about 70°C for a few hours, preferably between about 45° to about 65°C for about 3 hours.

The cocatalyst and promoter are added to the supported precursor either before and/or during the polymerization reaction. The cocatalyst and promoter are added either together or separately, and either simultaneously or sequentially during polymerization. The cocatalyst and promoter are preferably added separately as solutions in inert solvent, such as isopentane, during polymerization.

Polymerization

The ethylene polymerization is conducted in the gas phase using those procedures well established in the art. It is preferred that the polymerization occur using a continuous, fluidized bed process. Using such a procedure, portions of the catalyst composition and monomers are fed to a reactor vessel from which polyethylene product is continuously removed. The density of the ethylene copolymer produced may be varied over a wide range depending upon the amount of alpha-olefin comonomer addition and upon the particular comonomer employed. The greater the mole percent of alpha-olefin added the lower the density.

The polymerization is conducted at a temperature below the sintering of the polyethylene. The operating temperature will range from between about 10° to about 115°C . Preferred operating temperatures will vary depending upon the polyethylene density which is desired. High density polyethylenes of greater than about 0.94 g/cc are produced at operating temperatures of between about 85° to about 115°C , and preferably at about 90° to about 100°C . Low density polyethylenes ranging in density from about 0.91 to about 0.94 g/cc are preferably produced at an operating temperature of between about 75° to about 90°C . Very low density polyethylenes of less than about 0.91 g/cc are preferably produced at an operating temperature of between about 10° to about 80°C . In the case of such very low density polyethylenes, it is necessary to dilute the reaction mixture with a large quantity of a diluent gas in order to prevent the formation of polymer agglomerates and sustain polymerization on a continuous basis.

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The fluid bed reactor is operated at pressures of up to about $6895 \cdot 10^3$ (1000) and preferably between about $345 \cdot 10^3$ (50) to about $2413 \cdot 10^3$ Pa (350 psi).

A chain transfer agent, such as hydrogen, may be used to terminate the polymer chain. Usually the ratio of hydrogen to ethylene will vary between about 0.001 up to about 2.0 moles of hydrogen per mole of ethylene. We have discovered that hydrogen response is improved utilizing the catalyst composition of the present invention such that less hydrogen is required to produce polyethylene having extremely low unsaturation content.

Examples

The following examples are designed to illustrate the catalyst composition and process of the invention and are not intended as a limitation of the scope thereof.

The properties of the polymers produced in the examples were determined, unless otherwise indicated, by following the test procedures:

Property	Test procedure
Ash content	Polyethylene is ashed and weighed; productivity can be calculated in pounds of polyethylene produced per pound of total catalyst.
Bulk density (g/cc)	ASTM-D-1895 (Method B).
Density (g/cc)	ASTM-1505, based on ASTM-D-1928 (Procedure C) plaque preparation.
Fines (wt.%)	Amount of polymer particles which pass through a 200 mesh screen.
Flow index (dg/min)	ASTM D-1238-Condition F
Melt flow ratio	Flow Index/Melt Index; with melt index measured using ASTM D-1238, Condition E.
Particle agglomeration	Based on visual observation of polyethylene product exiting from the reactor.
Unsaturation ($C=C/1000C$) ^a	Based on infrared spectrophotometric measurements of absorbance (at $10.35 \mu m$ for transvinylidene, $11.0 \mu m$ for terminal vinyl and $11.25 \mu m$ for pendant vinyl unsaturations) of $635 \mu m$ (25 mil) thickness pressings of polymer. Unsaturation concentration is proportional to absorbance per $25.4 \mu m$ (mil) divided by absorptivity (as taken from absorptivity values published by R. J. deKock et al., in <i>J. Polymer Science</i> , Part B, 2, 339, 1964).

^a—Number of carbon-carbon double bonds per 1000 carbon atoms

Shorthand designations used in the Examples are defined as follows:

Designation	Description
DEAC	Diethylaluminum chloride
ED	Electron donor compound
FI	Flow index
MFR	Melt flow ratio
STY	Space time yield
TEAL	Triethylaluminum
THF	Tetrahydrofuran
TIBA	Triisobutylaluminum
TnHAL	Tri- <i>n</i> -hexylaluminum
EADC	Ethylaluminum dichloride

Catalyst preparation

The catalyst compositions used in the Examples were prepared using the following standard procedures. To a flask containing 4 liters of anhydrous THF is added 34 g VCl_3 (.216 moles). The mixture is stirred for 5 hrs. at $65^\circ C$ under a nitrogen blanket until the VCl_3 has dissolved. To this solution is added 800 g of silica (dehydrated by heating to $600^\circ C$) and stirring is continued for 4 hrs. at $65^\circ C$. In Comparative Examples A to D the silica had been chemically treated with 5.5 wt.% TEAL. The flask is vented and the solution is dried to the mud stage at $70^\circ C$. The temperature is dropped to $45^\circ C$ and a nitrogen purge is used for 6 hrs. or until a 4—10% by weight THF level is reached in the resulting product. The impregnated silica so produced is a free-flowing solid which has 0.25 mmoles of vanadium per gram. The solid is removed from the flask and stored under nitrogen.

Then, except in Comparative Example C, the modifier was introduced using the following procedure. To a flask containing 4 liters of anhydrous isopentane is added 500 g of the impregnated silica described

above. To this mixture is added, with stirring, a 25 weight percent solution of diethylaluminum chloride, as modifier, in anhydrous hexane. The amount of modifier was employed in an amount sufficient to provide the number of moles of modifier per mole of THF in the vanadium compound as set forth in the Examples. This mixture is heated to 45°C and purged with nitrogen for three hours or until the product is a free-flowing powder. The vanadium precursor so produced is then removed from the flask and stored under nitrogen.

Polymerization

The polyethylene was produced in a fluid bed reactor using the following standard procedure, under the operating conditions set forth in Table I. Ethylene was copolymerized with the comonomer set forth in the Examples. TIBA cocatalyst was added during polymerization as a 5 weight percent solution in isopentane. Chloroform, CHCl_3 , was added, except in Comparative Example D, as a 5 weight percent solution in isopentane unless otherwise indicated, in proportion to the cocatalyst as set forth in the Examples.

Each polymerization was continuously conducted for greater than one hour after equilibrium was reached under a pressure of about $2170 \cdot 10^3$ Pa (300 psig) and at a gas velocity, a nitrogen gas concentration and temperature set forth in Table I.

Examples 1—8 and Comparative Examples A—D

Using the procedures set forth above, and based on the parameters set forth in Table I, these examples were conducted using a variety of catalyst compositions to prepare high density ethylene copolymers. Examples 1—6 present embodiments of the present invention using butene-1 copolymerization. Examples 7 and 8 pertain to additional embodiments of the present invention using hexene-1 copolymerization. Comparative Examples A to D were conducted using an inert carrier which had been chemically treated with an alkylaluminum prior to impregnation. Comparative Example C was conducted using a catalyst composition without a modifier. Comparative Example D was conducted using a catalyst composition without a promoter.

An analysis of the polyethylene, using the above-described testing procedures, is set forth in Table I.

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TABLE I
Use of claimed catalyst and comparative data
preparation of high density ethylene copolymers

Example	1	2	3	4	5	6
Catalyst:						
Modifier	DEAC	DEAC	DEAC	DEAC	DEAC	DEAC
Promoter	CHCl ₃ ^a	CHCl ₃ ^a	CHCl ₃	CHCl ₃	CHCl ₃	CHCl ₃
Modifier/THF ratio	0.9	0.9	0.9	0.9	0.9	0.9
Carrier pretreatment	Untreated	Untreated	Untreated	Untreated	Untreated	Untreated
Cocatalyst	TIBA	TIBA	TIBA	TIBA	TIBA	TIBA
Promoter/cocatalyst ratio	2.0-2.22	2.0-2.22	2	2	2	2
A/V ratio	20-25	20-25	20-25	20-25	20-25	20-25
Polymerization:						
Temperature (°C)	100°	100°	100°	100°	90°	100°
Gas velocity m/s (ft/sec)	0.61 (2)	0.61 (2)	0.61 (2)	0.61 (2)	0.61 (2)	0.61 (2)
N ₂ pressure (mole %)	10	10	10	10	10	10
Comonomer	Butene-1	Butene-1	Butene-1	Butene-1	Butene-1	Butene-1
Comonomer/C ₂ H ₄ ratio	0.006	0.006	0.002	0.002	0.006	0.002
H ₂ /C ₂ H ₄ ratio	0.061	0.05	0.051	0.046	0.045	0.028
STY kg/h-m ³ (lb/hr-ft ³)	105.4 (6.6)	102.2 (6.4)	89.4 (5.6)	102.2 (6.4)	115.0 (7.2)	127.8 (8.0)
Polyethylene:						
Density (g/cc)	0.957	0.958	0.958	0.958	0.956	0.954
FI (dg/min)	33-38	23-27	34-38	23-27	35-38	23-25
MFR	70-75	70-75	70-75	70-75	90-95	70-75
Bulk density g/cc (lb/ft ³)	0.424 (26.5)	0.424 (26.5)	0.448 (28)	0.448 (28)	0.432 (27)	0.440 (27.5)
Fines (wt.%)	0.01	0.01	0.01	0.01	0.01	0.01
Ash (wt.%)	0.05	0.05	0.052	0.052	0.050	0.048
Particle agglomeration	Minor to none	Minor to none	Minor to none	Minor to none	Minor to none	Minor to none
Comments:	All Examples 1-8 produced polyethylene with high bulk density, low fines content, low ash content (i.e. high catalyst activity), good particle fluidity (no agglomeration problem) and had good hydrogen response (shown by low H ₂ /Monomer Ratios)					

^ausing 1 wt% (instead of 5 wt%) solution in isopentane.

TABLE I (Continued)
Use of claimed catalyst and comparative data
preparation of high density ethylene copolymers

Example	7	8	A	B	C	D
Catalyst:						
Modifier	DEAC	DEAC	DEAC	DEAC	None	DEAC
Promoter	CHCl ₃	CHCl ₃	CHCl ₃	CHCl ₃	CHCl ₃	None
Modifier/THF ratio	0.9	0.9	0.25	0.95	—	0.95
Carrier pretreatment	Untreated	Untreated	Treated	Treated	Treated	Treated
Cocatalyst	TIBA	TIBA	TIBA	TIBA	TIBA	TIBA
Promoter/cocatalyst ratio	1.33	1.33	1	2	2	—
A/V ratio	20—25	20—25	20	20	25	12
Polymerization:						
Temperature (°C)	100°	90°	100°	100°	100°	100°
Gas velocity m/s (ft/sec)	0.61 (2)	0.61 (2)	0.58 (1.9)	0.58 (1.9)	0.34 (1.1)	0.58 (1.9)
N ₂ pressure (mole %)	16.5	20	15	15	15	15
Comonomer	Hexene-1	Hexene-1	Butene-1	Butene-1	Butene-1	Butene-1
Comonomer/C ₂ H ₄ ratio	0.010	0.011	0.002	0.002	0.002	0.009
H ₂ /C ₂ H ₄ ratio	0.022	0.038	0.043	0.03	0.07*	0.14*
STY kg/h-m ³ (lb/hr-ft ³)	59.1 (3.7)	60.7 (3.8)	87.8 (5.5)	63.9 (4)	63.9 (4)	63.9 (4)
Polyethylene:						
Density (g/cc)	0.945	0.943	0.956—8	0.956—8	0.956—8	0.956
FI (dg/min)	5—6	5—6	20—22	20—22	20—22	20—22
MFR	70—75	90—95	70—75	70—75	70—75	75
Bulk density g/cc (lb/ft ³)	0.424 (26.5)	0.440 (27.5)	0.416—0.432 (26—27)	0.448—0.464 (28—29)	0.320—0.336 (20—21)*	0.512 (32)
Fines (wt.%)	0.01	0.01	0.08	0.05	8*	6*
Ash (wt.%)	0.036	0.036	0.036	0.025—0.030	0.040—0.045	0.062*
Particle agglomeration	Minor to none	Minor to none	Severe*	Severe*	None	None
Comments:			*Examples A & B demonstrated severe agglomeration problems	*Inferior hydrogen response, bulk density and fines	*Inferior hydrogen response, bulk density and fines	*Inferior hydrogen response, fines and activity

The results set forth in Table I indicate that the catalyst composition of the present invention provides high activity as demonstrated by the low ash values, as well as a desirable balance of product properties, demonstrated by lower H₂/monomer ratios (improved hydrogen response), higher bulk densities, improved particle fluidity, and lower fines content. In contrast, the particle agglomeration in Comparative Examples A and B was discovered to be particularly severe involving catalyst compositions similar to those of the present invention, but which utilized carrier which had been pretreated with alkylaluminum compounds. In addition, without the presence of a modifier as in Comparative Example C, hydrogen response decreases (as shown by an increase in H₂/monomer ratio), bulk density is lowered and the fines content is greater, all at less desirable values. Similarly, in the absence of the promoter as in Comparative Example D, the hydrogen response is less, the fines content is greater and the catalyst activity is lowered, all to less desirable values.

Example 9 and Comparative Examples E and F

These examples set forth and compare the superior saturation properties of polyethylene produced using the catalyst composition and process of the present invention, with the results set forth in Table II. Using those procedures set forth above, Example 9 was conducted to produce an ethylene/butene copolymer having the designated level of unsaturation. Comparative Example E was conducted under similar procedures using TEAL as cocatalyst, but without DEAC modifier. The polyethylene produced by the present invention contains superior low unsaturation levels even when compared with a highly similar catalyst composition as in Example E.

For comparative purposes, Example F sets forth the saturation content of polyethylene produced by an alternative process of the prior art, and is shown to possess a significantly higher level of unsaturation leading to instability of the polymer which degrades over time. In contrast, polyethylene produced by the catalyst composition and the process of the present invention has been shown to exhibit superior stability due to the very low saturation content in the polymer.

TABLE II
Polyethylene unsaturation comparison

Example	9	Comparative	
		E	F
Catalyst	Modified ^a V	Unmodified ^b V	Silyl- chromate ^c
Unsaturation: (C=C/1000C)			
Trans vinyl	0.0108	0.0197	0.038
Terminal vinyl	0.0104	0.0508	1.148
Pendant vinylidene	0.0619	0.0812	0.106
Total	0.0831	0.1517	1.292

^a—using VCl₃/THF/SiO₂/DEAC/TIBA/CHCl₃ catalyst of the present invention

^b—using VCl₃/THF/SiO₂/TEAL/CHCl₃ catalyst; at 90°C polymerization temperature

^c—using polymerization process of U.S. Patent 3,324,095 (Carrick et al.)

Examples 10—13

Using the procedures set forth above, and based on the parameters set forth in Table III, these examples were conducted to prepare low density ethylene copolymers. Examples 10—12 illustrate the copolymerization of ethylene with butene-1. Example 13 illustrates the copolymerization of ethylene with propylene. TEAL was employed as the cocatalyst in each of these examples. The results set forth in Table III indicate that the catalyst composition of the present invention provides high activity and a desirable balance of product properties in the preparation of low density ethylene copolymers as well as high density ethylene copolymers.

TABLE III
Preparation of low density ethylene copolymers

Example	10	11	12	13
Catalyst:				
Modifier	DEAC	DEAC	DEAC	DEAC
Promoter	CHCl ₃	CHCl ₃	CHCl ₃	CHCl ₃
Modifier/THF ratio	1.0	1.0	1.0	1.0
Carrier pretreatment	Untreated	Untreated	Untreated	Untreated
Cocatalyst	TEAL	TEAL	TEAL	TEAL
Promoter/cocatalyst ratio	1.54	1.31	1.22	1.0
Al/V ratio	40	40	40	35
Polymerization:				
Temperature (°C)	85°	85°	85°	90°
Comonomer	Butene-1	Butene-1	Butene-1	Propylene
Comonomer/C ₂ H ₄ ratio	0.139	0.086	0.054	0.13
H ₂ /C ₂ H ₄ ratio	0.026	0.016	0.014	0.02
STY kg/h-m ³ (lb/hr-ft ³)	83.0 (5.2)	81.4 (5.1)	81.4 (5.1)	67.1 (4.2)
Polyethylene:				
Density (g/cc)	0.915	0.922	0.927	0.922
FI (dg/min)	459	9.5	3.4	19
MFR	49	—	—	—
Bulk density g/cc (lb/ft ³)	0.378 (23.6)	0.374 (23.4)	0.378 (23.6)	0.448 (28)
Fines (wt.%)	0	0	0	0
Ash (wt.%)	0.039	0.071	0.082	0.10
Particle agglomeration	Minor to none	Minor to none	Minor to none	Minor to none

Examples 14—19

Using the procedures set forth above, and based on the parameters set forth in Table IV, these examples were conducted to prepare very low density copolymers of ethylene and propylene. TEAL was substituted for TIBA as the cocatalyst in Example 14. The results set forth in Table IV indicate that the catalyst composition of the present invention may also be used to provide very low density ethylene copolymers having a desirable balance of product properties at high activity.

TABLE IV
Preparation of very low density ethylene copolymers

Example	14	15	16	17	18	19
Catalyst:						
Modifier	DEAC	DEAC	DEAC	DEAC	DEAC	DEAC
Promoter	CHCl ₃	CHCl ₃	CHCl ₃	CHCl ₃	CHCl ₃	CHCl ₃
Modifier/THF ratio	1.7	1.7	1.7	1.7	1.7	1.7
Carrier pretreatment	Untreated	Untreated	Untreated	Untreated	Untreated	Untreated
Cocatalyst	TEAL	TIBA	TIBA	TIBA	TIBA	TIBA
Promoter/cocatalyst ratio	1.0	1.0	1.0	1.0	1.0	1.0
Al/V ratio	40	40	40	40	43	45
Polymerization:						
Temperature (°C)	75°	70°	65°	50°	40°	36°
Gas velocity m/s (ft/sec)	0.46 (1.5)	0.46 (1.5)	0.46 (1.5)	0.46 (1.5)	0.46 (1.5)	0.46 (1.5)
N ₂ pressure (mole %)	45	50	59	57	60	60
Comonomer	Propylene	Propylene	Propylene	Propylene	Propylene	Propylene
Comonomer/C ₂ H ₄ ratio	0.22	0.24	0.26	0.35	0.31	0.34
H ₂ /C ₂ H ₄ ratio	0.01	0.007	0.006	0.006	0.002	trace
STY kg/h-m ³ (lb/hr-ft ³)	65.4 (4.1)	75.1 (4.7)	60.7 (3.8)	43.1 (2.7)	68.7 (4.3)	67.1 (4.2)
Polyethylene:						
Density (g/cc)	0.906	0.895	0.894	0.882	0.871	0.865
FI (dg/min)	27	9	6	20	3	1
MFR	41	53	64	51	—	—
Bulk density g/cc (lb/ft ³)	0.432 (27)	0.384 (24)	0.368 (23)	0.320 (20)	0.368 (23)	0.368 (23)
Fines (wt.%)	—	—	0.05	0	0	0
Ash (wt.%)	0.10	0.082	0.11	—	0.14	0.07

Examples 20—22

Using the procedures set forth above, and based on the parameters set forth in Table V, ethylene was copolymerized with hexene-1 using catalyst compositions employing tri-*n*-hexylaluminum, ethylaluminum dichloride and triethylaluminum as modifiers. The modifiers were used to treat VCl₃-impregnated silica containing 0.2 mmoles of vanadium per gram of combined weight of the VCl₃ and silica. TEAL was employed as the cocatalyst in each of these examples. The results set forth in Table V indicate that various modifiers may be used in the catalyst compositions of the present invention.

TABLE V
Use of catalysts with various modifiers

Example	20	21	22
Catalyst:			
Modifier	TnHAL	EADC	TEAL
Promoter	CHCl ₃	CHCl ₃	CHCl ₃
Modifier/THF ratio	0.84	0.84	0.84
Carrier pretreatment	Untreated	Untreated	Untreated
Cocatalyst	TEAL	TEAL	TEAL
Promoter/cocatalyst ratio	1.1	1.1	1.0
Al/V ratio	102	37	38
Polymerization:			
Temperature (°C)	90°	90°	90°
Gas velocity m/s (ft/sec)	0.55 (1.8)	0.55 (1.8)	0.55 (1.8)
N ₂ pressure (mole %)	4	10	11.3
Comonomer	Hexene-1	Hexene-1	Hexene-1
Comonomer/C ₂ H ₄ ratio	0.0018	0.0018	0.003
H ₂ /C ₂ H ₄ ratio	0.068	0.067	0.076
STY kg/h-m ³ (lb/ft ³)	68.7 (4.3)	127.8 (8.0)	102.2 (6.4)
Polyethylene:			
Density (g/cc)	0.957	0.955	0.957
FI (dg/min)	28—30	27—29	23—24
MFR	90—95	95—100	90—100
Bulk density g/cc (lb/ft ³)	0.464 (29.0)	0.451 (28.2)	0.467 (29.2)
Fines (wt.%)	3.4 ^a	3.3 ^a	1.6 ^a
Ash (wt.%)	0.041	0.056	0.054
Particle agglomeration	Minor to none	Minor to none	Minor to none

^athrough 120 mesh screen (instead of 200)

Claims

1. A process for producing polyethylene which comprises polymerizing ethylene with or without at least one C₃ to C₁₀ alpha-olefin monomer in the gas phase at a temperature between about 10°C to about 115°C, by contacting the monomers with a catalyst composition comprising:

(A) a supported precursor consisting essentially of:

(1) a vanadium compound which is the reaction product of:

(a) a vanadium trihalide of chlorine, bromine or iodine; and

(b) an electron donor which is a liquid, organic Lewis base in which said vanadium trihalide is soluble;

(2) a modifier having the formula:



wherein:

M is either boron or AlR_(3-a) and wherein each R is independently alkyl, provided that the total number of aliphatic carbon atoms in any one R group may not exceed 14;

X is chlorine, bromine or iodine; and

a is 0, 1 or 2, with the provision that when M is boron a is 3; and

(3) wherein said vanadium compound and said modifier are on a solid, inert carrier which consists

essentially of silica or alumina;

Examples 20—22

Using the procedures set forth above, and based on the parameters set forth in Table V, ethylene was copolymerized with hexene-1 using catalyst compositions employing tri-*n*-hexylaluminum, ethylaluminum dichloride and triethylaluminum as modifiers. The modifiers were used to treat VCl_3 -impregnated silica containing 0.2 mmoles of vanadium per gram of combined weight of the VCl_3 and silica. TEAL was employed as the cocatalyst in each of these examples. The results set forth in Table V indicate that various modifiers may be used in the catalyst compositions of the present invention.

TABLE V
Use of catalysts with various modifiers

Example	20	21	22
Catalyst:			
Modifier	TnHAL	EADC	TEAL
Promoter	CHCl_3	CHCl_3	CHCl_3
Modifier/THF ratio	0.84	0.84	0.84
Carrier pretreatment	Untreated	Untreated	Untreated
Cocatalyst	TEAL	TEAL	TEAL
Promoter/cocatalyst ratio	1.1	1.1	1.0
Al/V ratio	102	37	38
Polymerization:			
Temperature ($^{\circ}\text{C}$)	90°	90°	90°
Gas velocity m/s (ft/sec)	0.55 (1.8)	0.55 (1.8)	0.55 (1.8)
N_2 pressure (mole %)	4	10	11.3
Comonomer	Hexene-1	Hexene-1	Hexene-1
Comonomer/ C_2H_4 ratio	0.0018	0.0018	0.003
$\text{H}_2/\text{C}_2\text{H}_4$ ratio	0.068	0.067	0.076
STY kg/h- m^3 (lb/ft 3)	68.7 (4.3)	127.8 (8.0)	102.2 (6.4)
Polyethylene:			
Density (g/cc)	0.957	0.955	0.957
FI (dg/min)	28—30	27—29	23—24
MFR	90—95	95—100	90—100
Bulk density g/cc (lb/ft 3)	0.464 (29.0)	0.451 (28.2)	0.467 (29.2)
Fines (wt.%)	3.4 ^a	3.3 ^a	1.6 ^a
Ash (wt.%)	0.041	0.056	0.054
Particle agglomeration	Minor to none	Minor to none	Minor to none

^athrough 120 mesh screen (instead of 200)

Claims

1. A process for producing polyethylene which comprises polymerizing ethylene with or without at least one C_3 to C_{10} alpha-olefin monomer in the gas phase at a temperature between about 10°C to about 115°C , by contacting the monomers with a catalyst composition comprising:

(A) a supported precursor consisting essentially of:

(1) a vanadium compound which is the reaction product of:

(a) a vanadium trihalide of chlorine, bromine or iodine; and

(b) an electron donor which is a liquid, organic Lewis base in which said vanadium trihalide is soluble;

(2) a modifier having the formula:



wherein:

M is either boron or $\text{AlR}_{(3-a)}$ and wherein each R is independently alkyl, provided that the total number of aliphatic carbon atoms in any one R group may not exceed 14;

X is chlorine, bromine or iodine; and

a is 0, 1 or 2, with the provision that when M is boron a is 3; and

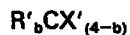
(3) wherein said vanadium compound and said modifier are on a solid, inert carrier which consists essentially of silica or alumina;



(B) a cocatalyst having the formula



- 5 wherein R is as previously defined; and
(C) a promoter having the formula:



10 wherein:

R' is hydrogen or unsubstituted or halosubstituted lower alkyl;
X' is halogen; and
b is 0, 1 or 2.

2. The process of claim 1 wherein the electron donor is selected from the group consisting of alkyl
15 esters of aliphatic and aromatic carboxylic acids, aliphatic esters, aliphatic ketones, aliphatic amines, aliphatic alcohols, alkyl and cycloalkyl ethers, and mixtures thereof.

3. The process of claim 1, wherein said vanadium trihalide contains chlorine; said electron donor is an alkyl or cycloalkyl ether; said modifier is a C₁ to C₆ alkylaluminum mono- or di- chloride, or boron trichloride; said carrier is silica; said cocatalyst is a C₂ to C₈ trialkylaluminum; and said promoter is a fluoro,
20 chloro or bromo substituted ethane or methane.

4. The process of claim 1 wherein said vanadium trihalide is vanadium trichloride; said electron donor is tetrahydrofuran; said modifier is diethylaluminum chloride; said carrier is silica; said cocatalyst is triisobutylaluminum or triethylaluminum; and said promoter is chloroform.

5. The process of any one of claims 1 to 4 wherein polyethylene having a density of greater than about
25 0.94 g/cc is produced at a temperature of between about 85°C to about 115°C.

6. The process of claim 5 wherein said polyethylene is an ethylene homopolymer, propylene/ethylene, butene-1/ethylene or hexene-1/ethylene copolymer.

7. The process of any one of claims 1 to 4 wherein polyethylene having a density of from about 0.91 g/cc to about 0.94 g/cc is produced at a temperature of between about 75°C to about 90°C.

30 8. The process of any one of claims 1 to 4 wherein polyethylene having a density of less than about 0.91 g/cc is produced at a temperature of between about 10°C to about 80°C.

9. The process of claim 7 or 8 wherein said polyethylene is propylene/ethylene, butene-1/ethylene or hexene-1/ethylene copolymer.

10. A supported catalyst precursor for producing polyethylene consisting essentially of:

35 (1) a vanadium compound which is the reaction product of:

(a) a vanadium trihalide of chlorine, bromine or iodine; and

(b) an electron donor which is a liquid, organic Lewis base in which said vanadium trihalide is soluble;
(2) a modifier having the formula:



wherein:

M is either boron or AlR_(3-a) and wherein each R is independently alkyl, provided that the total number of aliphatic carbon atoms in any one R group may not exceed 14;

45 X is chlorine, bromine or iodine; and

a is 0, 1 or 2, with the provision that when M is boron a is 3; and

(3) wherein said vanadium compound and said modifier are on a solid, inert carrier which consists essentially of silica or alumina.

11. The precursor of claim 10 wherein the electron donor is selected from the group consisting of alkyl
50 esters of aliphatic and aromatic carboxylic acids, aliphatic esters, aliphatic ketones, aliphatic amines, aliphatic alcohols, alkyl and cycloalkyl ethers, and mixtures thereof.

12. The precursor of claim 10 wherein said vanadium trihalide contains chlorine; said electron donor is an alkyl or cycloalkyl ether; said modifier is a C₁ to C₆ alkylaluminum mono- or di- chloride, or boron trichloride; and said carrier is silica.

55 13. The precursor of claim 10 wherein said vanadium trihalide is vanadium trichloride; said electron donor is tetrahydrofuran; said modifier is diethylaluminum chloride; and said carrier is silica.

14. A catalyst composition comprising:

(a) the supported precursor of any one of claims 10—13;

(b) a cocatalyst having the formula:



wherein R is as previously defined; and

(c) a promoter having the formula:



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wherein:

R' is hydrogen or unsubstituted or halosubstituted lower alkyl;

X' is halogen; and

b is 0, 1 or 2.

5 15. The catalyst composition of claim 14 wherein said cocatalyst is a C₂ to C₈ trialkylaluminum; and said promoter is a fluoro, chloro or bromo substituted ethane or methane.

16. The catalyst composition of 14 wherein said cocatalyst is triisobutylaluminum or triethylaluminum; and said promoter is chloroform.

10 Patentansprüche

1. Verfahren zur Herstellung von Polyethylen, das umfaßt; das Polymerisieren von Ethylen mit oder ohne mindestens einem C₃- bis C₁₀ - α - Olefinmonomer in der Gasphase bei einer Temperatur zwischen etwa 10 bis etwa 115°C durch In - Berührung - bringen der Monomeren mit einer Katalysatorzusammen-

15 setzung, die

(A) auf einem Träger einen Vorläufer, der im wesentlichen aus

(1) einer Vanadiumverbindung, die das Reaktionsprodukt aus

(a) einem Vanadiumtrihalogenid von Chlor, Brom oder Jod und

20 (b) einem Elektronendonator, der eine flüssige organische Lewis-Base ist, in welcher das Vanadiumtrihalogenid löslich ist; ist;

(2) einem Modifizierungsmittel mit der Formel



25 worin

M Bor oder AlR_(3-a) ist und jedes R unabhängig Alkyl ist, unter der Bedingung, daß die Gesamtzahl der aliphatischen Kohlenstoffatome in irgendeiner Gruppe R 14 nicht übersteigt;

X Chlor, Brom oder Jod ist, und

a=0, 1 oder 2 ist, unter der Bedingung, daß, wenn M Bor ist, a=3 ist; besteht, und

30 (3) worin die Vanadiumverbindung und das Modifizierungsmittel sich auf einem festen, inerten Träger befinden, der im wesentlichen aus Siliciumdioxid oder Aluminiumoxid besteht,

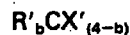
(B) einen Kokatalysator der Formel



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worin R wie oben definiert ist, und

(C) einen Beschleuniger der Formel



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worin

R' Wasserstoff oder unsubstituiertes oder halogensubstituiertes Niederalkyl ist;

X' Halogen ist und

b=0, 1 oder 2 ist, umfaßt.

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2. Verfahren nach Anspruch 1, worin der Elektronendonator ausgewählt ist aus der aus Alkylestern aliphatischer und aromatischer Carbonsäuren, aliphatischen Estern, aliphatischen Ketonen, aliphatischen Aminen, aliphatischen Alkoholen, Alkyl- und Cycloalkylethern und Mischungen derselben bestehenden Gruppe.

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3. Verfahren nach Anspruch 1, worin das Vanadiumtrihalogenid Chlor enthält, der Elektronendonator ein Alkyl- oder Cycloalkylether ist, das Modifizierungsmittel ein C₁- bis C₆ - Alkylaluminium - mono - oder -dichlorid oder Bortrichlorid ist, der Träger Siliciumdioxid ist, der Kokatalysator ein C₂- bis C₈ - Trialkylaluminium ist und der Beschleuniger ein fluor-, chlor- oder brom - substituiertes Ethan oder Methan ist.

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4. Verfahren nach Anspruch 1, worin das Vanadiumtrihalogenid Vanadiumtrichlorid ist, der Elektronendonator Tetrahydrofuran ist, das Modifizierungsmittel Diethylaluminiumchlorid ist, der Träger Siliciumdioxid ist, der Kokatalysator Triisobutylaluminium oder Triethylaluminium ist und der Beschleuniger Chloroform ist.

5. Verfahren nach irgendeinem der Ansprüche 1 bis 4, worin Polyethylen mit einer Dichte über etwa 0,94 g/cm³ bei einer Temperatur zwischen etwa 85 bis etwa 115°C hergestellt wird.

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6. Verfahren nach Anspruch 5, worin das Polyethylen ein Ethylenhomopolymer, Propylen/Ethylen-, Buten - 1/Ethylen - oder Hexen - 1/Ethylen - Copolymer ist.

7. Verfahren nach irgendeinem der Ansprüche 1 bis 4, worin Polyethylen mit einer Dichte von etwa 0,91 g/cm³ bis etwa 0,94 g/cm³ bei einer Temperatur zwischen etwa 75 bis etwa 90°C hergestellt wird.

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8. Verfahren nach irgendeinem der Ansprüche 1 bis 4, worin Polyethylen mit einer Dichte von weniger als etwa 0,91 g/cm³ bei einer Temperatur zwischen etwa 10 bis etwa 80°C hergestellt wird.



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9. Verfahren nach Anspruch 7 oder 8, worin das Polyethylen Propylen/Ethylen-, Buten - 1/Ethylen - oder Hexen - 1/Ethylen - Copolymer ist.

10. Trägerkatalysatorvorläufer zur Herstellung von Polyethylen, der im wesentlichen besteht aus:

(1) einer Vanadiumverbindung, die das Reaktionsprodukt aus

(a) einem Vanadiumtrihalogenid von Chlor, Brom oder Jod und

(b) einem Elektronendonator, der eine flüssige, organische Lewis-base ist, in welcher das Vanadiumtrihalogenid löslich ist, ist

(2) einem Modifizierungsmittel der Formel



worin

M Bor oder $AlR_{(3-a)}$ ist und jedes R unabhängig Alkyl ist, unter der Bedingung, daß die Gesamtzahl der aliphatischen Kohlenstoffatome in irgendeiner Gruppe R 14 nicht übersteigt;

X Chlor, Brom oder Jod ist, und

a=0, 1 oder 2 ist, unter der Bedingung, daß, wenn M Bor ist, a=3 ist; und

(3) worin die Vanadiumverbindung und das Modifizierungsmittel sich auf einem festen, inerten Träger befinden, der im wesentlichen aus Siliciumdioxid oder Aluminiumoxid besteht.

11. Vorläufer nach Anspruch 10, worin der Elektronendonator ausgewählt ist aus der aus Alkylestern aliphatischer und aromatischer Carbonsäuren, aliphatischen Estern, aliphatischen Ketonen, aliphatischen Aminen, aliphatischen Alkoholen, Alkyl- und Cycloalkylethern und Mischungen derselben bestehenden Gruppe.

12. Vorläufer nach Anspruch 10, worin das Vanadiumtrihalogenid Chlor enthält, der Elektronendonator ein Alkyl- oder Cycloalkylether ist, das Modifizierungsmittel ein C_1 - bis C_6 - Alkylaluminiummono - oder -dichlorid oder Bortrichlorid ist und der Träger Siliciumdioxid ist.

13. Vorläufer nach Anspruch 10, worin das Vanadiumtrihalogenid Vanadiumtrichlorid ist, der Elektronendonator Tetrahydrofuran ist, das Modifizierungsmittel Diethylaluminiumchlorid ist und der Träger Siliciumdioxid ist.

14. Katalysatorzusammensetzung, die umfaßt:

(a) einen Trägervorläufer nach irgendeinem der Ansprüche 10 bis 13,

(b) einen Cokatalysator der Formel



worin R wie oben definiert ist, und

(c) einen Beschleuniger der Formel



worin

R' Wasserstoff oder unsubstituiertes oder halogensubstituiertes Niederalkyl ist,

X' Halogen ist und

b=0, 1 oder 2 ist.

15. Katalysatorzusammensetzung nach Anspruch 14, worin der Cokatalysator ein C_2 - bis C_8 - Trialkylaluminium ist und der Beschleuniger ein fluor-, chlor- oder brom - substituiertes Ethan oder Methan ist.

16. Katalysatorzusammensetzung nach Anspruch 14, worin der Cokatalysator Triisobutylaluminium oder Triethylaluminium ist und der Beschleuniger Chloroform ist.

Revendications

1. Procédé de production de polyéthylène, qui consiste à polymériser de l'éthylène en présence ou en l'absence d'au moins un monomère alpha - oléfinique en C_3 à C_{10} en phase gazeuse à une température comprise entre environ 10°C et environ 115°C par mise en contact des monomères avec une composition de catalyseur comprenant:

(A) un précurseur fixé sur un support essentiellement constitué:

(1) d'un composé de vanadium qui est le produit de réaction:

(a) d'un trihalogénure de vanadium comprenant du chlore, du brome ou de l'iode; et

(b) d'un donneur d'électrons qui est une base de Lewis organique liquide dans laquelle ledit trihalogénure de vanadium est soluble;

(2) d'un modificateur de formule



dans laquelle:

M représente le bore ou un composé $AlR_{(3-a)}$ dans lequel chaque R représente, indépendamment, un



groupe alkyle, sous réserve que le nombre total d'atomes aliphatiques de carbone dans tout groupe R ne puisse pas dépasser 14; et

X est le chlore, le brome ou l'iode; et

a a la valeur 0, 1 ou 2, sous réserve que lorsque M représente le bore, a soit égal à 3; et

- 5 (3) le composé de vanadium et le modificateur étant fixés sur un support inerte solide qui est essentiellement constitué de silice ou d'alumine;

(B) un cocatalyseur de formule



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dans laquelle R est tel que défini ci-dessus; et

(C) un promoteur de formule:



15

dans laquelle:

R' est l'hydrogène ou un groupe alkyle inférieur non substitué ou à substituant halogéno;

X' est un halogène; et

b a la valeur 0, 1 ou 2.

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2. Procédé suivant la revendication 1, dans lequel le donneur d'électrons est choisi dans le groupe comprenant des esters alkyliques d'acides carboxyliques aliphatiques et aromatiques, des esters aliphatiques, des cétones aliphatiques, des amines aliphatiques, des alcools aliphatiques, des éthers d'alkyle et de cycloalkyle et leurs mélanges.

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3. Procédé suivant la revendication 1, dans lequel le trihalogénure de vanadium contient du chlore; le donneur d'électrons est un éther d'alkyle ou de cycloalkyle; le modificateur est un monochlorure ou un dichlorure de (alkyle en C₁ à C₆)-aluminium ou le trichlorure de bore; le support est la silice; le cocatalyseur est un tri-(alkyle en C₂ à C₆)-aluminium; et le promoteur est un éthane ou un méthane à substituant fluoro, chloro ou bromo.

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4. Procédé suivant la revendication 1, dans lequel le trihalogénure de vanadium est le trichlorure de vanadium; le donneur d'électrons est le tétrahydrofurane; le modificateur est le chlorure de diéthyl-aluminium; le support est la silice; le cocatalyseur est le triisobutylaluminium ou le triéthylaluminium; et le promoteur est le chloroforme.

35

5. Procédé suivant l'une quelconque des revendications 1 à 4, dans lequel le polyéthylène ayant une masse volumique supérieure à environ 0,94 g/cm³ est produit à une température comprise entre environ 85°C et environ 115°C.

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6. Procédé suivant la revendication 5, dans lequel le polyéthylène est un homopolymère d'éthylène, un copolymère propylène/éthylène, un copolymère butène-1/éthylène ou un copolymère hexène-1/éthylène.

45

7. Procédé suivant l'une quelconque des revendications 1 à 4, dans lequel du polyéthylène ayant une masse volumique d'environ 0,91 g/cm³ à environ 0,94 g/cm³ est produit à une température comprise entre environ 75°C et environ 90°C.

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8. Procédé suivant l'une quelconque des revendications 1 à 4, dans lequel du polyéthylène ayant une masse volumique inférieure à environ 0,91 g/cm³ est produit à une température comprise entre environ 10°C et environ 80°C.

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9. Procédé suivant la revendication 7 ou 8, dans lequel le polyéthylène est un copolymère propylène/éthylène, butène-1/éthylène ou hexène-1/éthylène.

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10. Précurseur de catalyseur fixé sur un support pour la production de polyéthylène, essentiellement constitué:

(1) d'un composé de vanadium qui est le produit de réaction:

(a) d'un trihalogénure de vanadium contenant du chlore, du brome ou de l'iode; et

50

(b) d'un donneur d'électrons qui est une base de Lewis organique liquide dans laquelle le trihalogénure de vanadium est soluble;

(2) d'un modificateur de formule:



55

dans laquelle:

M représente le bore ou un composé $\text{AlR}_{(3-a)}$ dans lequel chaque R représente, indépendamment, un groupe alkyle, sous réserve que le nombre total d'atomes aliphatiques de carbone dans tout groupe R ne puisse pas dépasser 14;

60

X est le chlore, le brome ou l'iode; et

a est égal à 0, 1 ou 2, dans réserve que lorsque M est le bore, a soit égal à 3; et

(3) le composé de vanadium et le modificateur étant fixés sur un support inerte solide qui est essentiellement constitué de silice ou d'alumine.

65

11. Précurseur suivant la revendication 10, dans lequel le donneur d'électrons est choisi dans le groupe comprenant des esters d'alkyle d'acides carboxyliques aliphatiques et aromatiques, des esters



aliphatiques, des cétones aliphatiques, des amines aliphatiques, des alcools aliphatiques, des éthers d'alkyle et de cycloalkyle et leurs mélanges.

12. Précurseur suivant la revendication 10, dans lequel le trihalogénure de vanadium contient du chlore; le donneur d'électrons est un éther d'alkyle ou de cycloalkyle; le modificateur est un monochlorure ou un dichlorure de (alkyle en C₁ à C₆)-aluminium ou le trichlorure de bore; et le support est la silice.

13. Précurseur suivant la revendication 10, dans lequel le trihalogénure de vanadium est le trichlorure de vanadium; le donneur d'électrons est le tétrahydrofuranne; le modificateur est le chlorure de diéthylaluminium; et le support est la silice.

14. Composition de catalyseur, comprenant:

- (a) le précurseur fixé sur un support suivant l'une quelconque des revendications 10 à 13;
- (b) un cocatalyseur de formule:



15 dans laquelle R est tel que défini ci-dessus; et

- (c) un promoteur de formule:



20 dans laquelle:

R' est l'hydrogène ou un groupe alkyle inférieur non substitué ou à substituant halogéno;

X' est un halogène; et

b a la valeur 0, 1 ou 2.

15. Composition de catalyseur suivant la revendication 14, dans laquelle le cocatalyseur est un tri(alkyle en C₂ à C₈ - aluminium et le promoteur est un éthane ou un méthane à substituant fluoro, chloro ou bromo.

16. Composition de catalyseur suivant la revendication 14, dans laquelle le cocatalyseur est le triisobutylaluminium ou le triéthylaluminium; et le promoteur est le chloroforme.

