the polyethylene product from the diluent and the unreacted reactants, with the diluent and unreacted reactants typically being recycled back into the reactor. Alternatively, the reaction mixture may be sent to a second reactor, serially connected to the first reactor, where a second polyethylene fraction may be produced.

[0005] Titanocene hydrogenation procatalysts have been used in (1) metallocene-catalyzed polymerization reactions, for removing H_2 generated by the metallocene polymerization catalysts; and (2) in one reactor of a linked reactor system, for removing H_2 carried over from a prior reactor. By removing the H_2 from a catalyst system, the H_2 cannot terminate the polymerization chain, thereby allowing an increase in molecular weight of the produced polymer. However, these applications of the titanocene catalysts for removing H_2 are limited to gas-phase and slurry-phase polymerization reactions in which reaction temperatures typically range from 60 °C to 120 °C.

SUMMARY

[0006] There is an ongoing need to create catalyst systems or procatalysts that produce high molecular weight polymers at high polymerization temperatures (temperatures from 120 °C to 250 °C). Additionally, the catalyst system should have high efficiency, high reactivity, and ability to produce polymers with a high molecular weight (greater than 100,000 g/mol).

[0007] This disclosure includes catalyst systems. The catalyst system includes a non-hydrogen-generating post-metallocene procatalyst; a co-catalyst; and a hydrogenation procatalyst having the formula Cp_2TiX_2 or $Cp_2TiX_nTiCp_2$. In the formulas, Cp_2TiX_2 and $Cp_2TiX_nTiCp_2$, each Cp is cyclopentadienyl optionally substituted with at least one $(C_1{-}C_{10})$alkyl; and each X is independently a halogen atom.

[0007a] In one aspect, there is provided a catalyst system comprising:

a non-hydrogen-generating post-metallocene procatalyst;

a co-catalyst; and

a hydrogenation procatalyst having the formula $Cp_2TiX_2TiCp_2$ or Cp_2TiX_n

where:

each Cp is cyclopentadienyl optionally substituted with at least one $(C_1{-}C_{10})$alkyl;

each X is independently monoanionic or neutral, wherein each X is independently $(C_1{-}C_{40})$hydrocarbon, $(C_1{-}C_{40})$heterohydrocarbon,

(C_1-C_{40})hydrocarbyl, (C_1-C_{40})heterohydrocarbyl, or a halogen atom; and

n is 1 or 2,

wherein the non-hydrogen-generating post-metallocene procatalyst is a bis(phenylphenoxy) Group IV procatalyst.

[0007b] In another aspect, there is provided a catalyst system comprising:

a non-hydrogen-generating post-metallocene procatalyst; and

Cp_2TiX_2 treated with an aluminum alkyl species, where:

each Cp is cyclopentadienyl substituted with at least one (C_1−C_{10})alkyl; and

each X is independently monoanionic or neutral, wherein each X is independently (C_1−C_{40})hydrocarbon, (C_1−C_{40})heterohydrocarbon, (C_1-C_{40})hydrocarbon anion, (C_1-C_{40})heterohydrocarbon anion, or a halogen atom,

wherein the non-hydrogen-generating post-metallocene procatalyst is a bis(phenylphenoxy) Group IV procatalyst.

[0008] This disclosure includes polymerization processes. The polymerization process for producing polyolefin polymers includes reacting (C_2−C_{12})α-olefins in solution in the presence of a catalyst system of this disclosure.

DETAILED DESCRIPTION

[0009] Embodiments of this disclosure include catalyst systems. In one or more embodiments, the catalyst system includes a non-hydrogen-generating post-metallocene procatalyst; a co-catalyst; and a hydrogenation procatalyst having the formula $Cp_2TiX_nTiCp_2$ or Cp_2TiX_2. In the formulas Cp_2TiX_2 and $Cp_2TiX_nTiCp_2$, each Cp is cyclopentadienyl substitute

CLAIMS

1. A catalyst system comprising:

a non-hydrogen-generating post-metallocene procatalyst;

a co-catalyst; and

a hydrogenation procatalyst having the formula $Cp_2TiX_2TiCp_2$ or Cp_2TiX_n

where:

each Cp is cyclopentadienyl optionally substituted with at least one (C_1-C_{10})alkyl;

each X is independently monoanionic or neutral, wherein each X is independently (C_1-C_{40})hydrocarbon, (C_1-C_{40})heterohydrocarbon, (C_1-C_{40})hydrocarbyl, (C_1-C_{40})heterohydrocarbyl, or a halogen atom; and

n is 1 or 2,

wherein the non-hydrogen-generating post-metallocene procatalyst is a bis(phenylphenoxy) Group IV procatalyst.

2. A catalyst system comprising:

a non-hydrogen-generating post-metallocene procatalyst; and

Cp_2TiX_2 treated with an aluminum alkyl species, where:

each Cp is cyclopentadienyl substituted with at least one (C_1-C_{10})alkyl; and

each X is independently monoanionic or neutral, wherein each X is independently (C_1-C_{40})hydrocarbon, (C_1-C_{40})heterohydrocarbon, (C_1-C_{40})hydrocarbon anion, (C_1-C_{40})heterohydrocarbon anion, or a halogen atom,

wherein the non-hydrogen-generating post-metallocene procatalyst is a bis(phenylphenoxy) Group IV procatalyst.

3. The catalyst system of claim 2, wherein the aluminum species comprises alkylaluminoxane, modified alkylaluminoxane, or an aluminum alkyl having the formula AlR_3 wherein each R is independently (C_1-C_{40})hydrocarbon (C_1-C_{40})heterohydrocarbon, (C_1-C_{40})hydrocarbyl, (C_1-C_{40})heterohydrocarbyl, or a halogen atom.

4. The catalyst system of claim 2, wherein the aluminum species is the reaction product of AlR_3 and water, alcohol, silanol, or a Lewis basic.

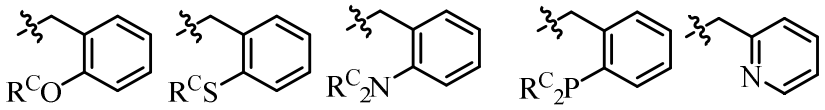
5. The catalyst system of claim 4, wherein the Lewis base is pyridine or mono-substituted alkylamine, disubstituted alkylamine,or tri-substituted alkylamine.

6. The catalyst system of claim 2, wherein the aluminum species is diisobutylaluminum oxide (DIBAO or DIBAL-O) or Isobutylaluminoxane (IBAO).

7. The catalyst system of claim 1, wherein the catalyst system further comprises an impurity scavenger.

8. The catalyst system of claim 1, wherein each X is a substituted benzyl or substituted heteroarylbenzyl.

9. The catalyst system of claim 1, wherein X is selected from the group consisting of:

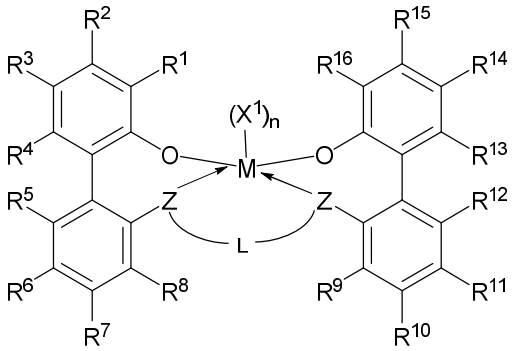


, wherein R^C is independently a $(C_1–C_{18})$hydrocarbon or $(C_5–C_{18})$aryl.

10. The catalyst system of claim 1, wherein the non-hydrogen-generating post metallocene procatalyst produces less than or equal to 1 ppm of hydrogen under polymerization conditions.

11. The catalyst system of claim 1, wherein the non-hydrogen-generating post metallocene procatalyst is unsupported and the hydrogenating catalyst is unsupported.

12. The catalyst system of claim 1, wherein the non-hydrogen-generating post metallocene procatalyst is a metal–ligand complex according to formula (I):



(I)

where:

M is a metal chosen from titanium, zirconium, or hafnium, the metal being in a formal oxidation state of +2, +3, or +4;

n is 0, 1, or 2;

when n is 1, X^1 is a monodentate ligand or a bidentate ligand;

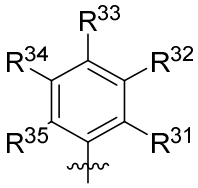
when n is 2, each X^1 is independently a monodentate ligand;

each X^1 that is a monodentate ligand is independently halogen, unsubstituted $(C_1–C_{20})$hydrocarbyl, unsubstituted $(C_1–C_{20})$hydrocarbylC(O)O–, or $R^KR^LN–$, where each of R^K and R^L is independently an unsubstituted $(C_1–C_{20})$hydrocarbyl;

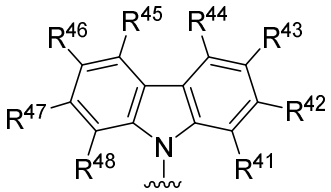
L is a diradical selected from the group consisting of $(C_1–C_{40})$hydrocarbylene, $(C_1–C_{40})$heterohydrocarbylene, $–Si(R^C)_2–$, $–Si(R^C)_2OSi(R^C)_2–$, $–Si(R^C)_2C(R^C)_2–$, $–Si(R^C)_2Si(R^C)_2–$, $–Si(R^C)_2C(R^C)_2Si(R^C)_2–$, $–C(R^C)_2Si(R^C)_2C(R^C)_2–$, $–Ge(R^C)_2–$, –O–, –S–, –S(O)–, $–S(O)_2–$, $–N=C(R^C)–$, –C(O)O–, –OC(O)–, –C(O)N(R)–, and $–N(R^C)C(O)–$;

each Z is independently chosen from –O–, or –S–;

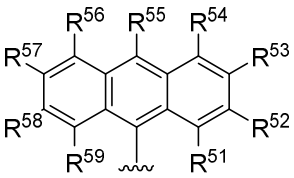
R^1, R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13}, R^{14}, R^{15}, and R^{16} are independently selected from the group consisting of –H, $(C_1–C_{40})$hydrocarbyl, $(C_1–C_{40})$heterohydrocarbyl, $–Si(R^C)_3$, $–Ge(R^C)_3$, $–OR^C$, $–SR^C$, $–NO_2$, –CN, $–CF_3$, $R^CS(O)–$, $R^CS(O)_2–$, $–N=C(R^C)_2$, $R^CC(O)O–$, $R^COC(O)–$, $R^CC(O)N(R)–$, $(R^C)_2NC(O)–$, halogen, radicals having formula (XI), radicals having formula (XII), and radicals having formula (XIII):



(XI)



(XII)



(XIII)

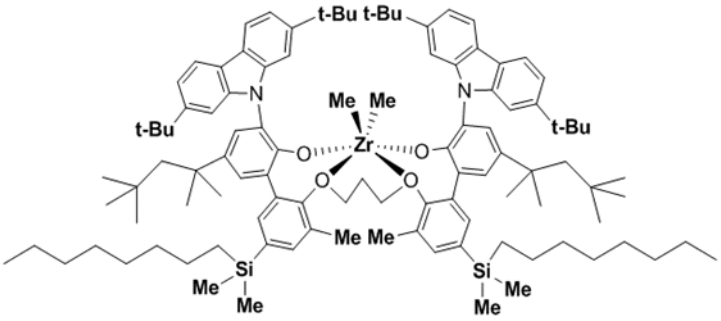
where:

each of R^{31} – R^{35}, R^{41} – R^{48}, and R^{51} – R^{59} is independently chosen from –H, (C_1–C_{40})hydrocarbyl, (C_1–C_{40})heterohydrocarbyl, –Si(R^C)$_3$, –Ge(R^C)$_3$, –OR^C, –SR^C, –NO_2, –CN, –CF_3, R^CS(O)–, R^CS(O)$_2$–, (R^C)$_2$C=N–, R^CC(O)O–, R^COC(O)–, (R^C)$_2$NC(O)–, or halogen;

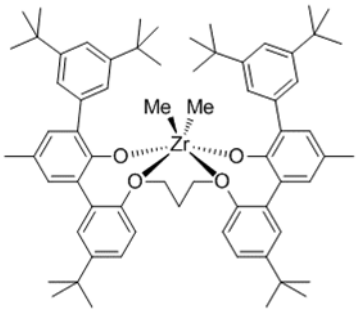
each R^C is independently a (C_1–C_{18})hydrocarbon or (C_5–C_{18})aryl; and

each R is independently (C_1–C_{40})hydrocarbon (C_1–C_{40})heterohydrocarbon, (C_1–C_{40})hydrocarbyl, (C_1–C_{40})heterohydrocarbyl, or a halogen atom.

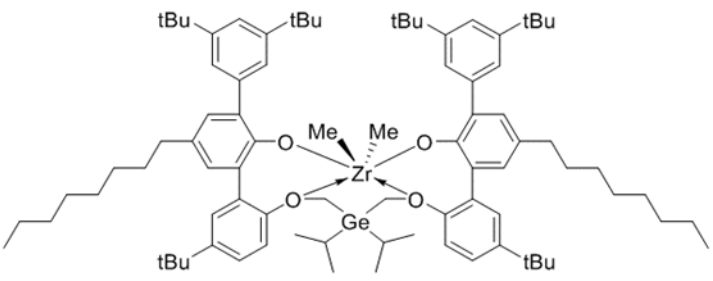
13. The catalyst system of claim 1, wherein the non-hydrogen-generating post metallocene procatalyst is:



(PCAT-1),



(PCAT-2),



(PCAT-3),

(2',2"-(propane-l,3-diylbis(oxy))bis(5'-chloro-3-(3,6-di-tert-octyl-9H-carbazol-9-yl)-3'-methyl-5-(2,4,4-trimethylpentan-2-yl)biphenyl-2-ol)dimethyl-hafnium (Procatalyst 1A),

(2',2"-(propane-l,3-diylbis(oxy))bis(3-(3,6-di-tert-butyl-9H-carbazol-9-yl)-3'-chloro-5-(2,4,4-trimethylpentan-2-yl)biphenyl-2-ol)dimethyl-hafnium (Procatalyst 2A),

(2',2"-(propane-l,3-diylbis(oxy))bis(3'-chloro-3-(3,6-di-tert-butyl-9H-carbazol-9-yl)-5'-fluoro-5-(2,4,4-trimethylpentan-2-yl)biphenyl-2-ol)dimethyl-hafnium (Procatalyst 3A),

(2',2"-(propane-l,3-diylbis(oxy))bis(3-(3,6-di-tert-butyl-9H-carbazol-9-yl)-3'-methyl-5-(2,4,4-trimethylpentan-2-yl)biphenyl-2-ol)dimethyl-hafnium (Procatalyst 4A),

(2',2"-(propane-l,3-diylbis(oxy))bis(5'-cyano-3-(3,6-di-tert-butyl-9H-carbazol-9-yl)-3'-methyl-5-(2,4,4-trimethylpentan-2-yl)biphenyl-2-ol)dimethyl-hafnium (Procatalyst 5A),

(2',2"-(propane-l,3-diylbis(oxy))bis(5'-dimethylamino-3-(3,6-di-tert-butyl-9H-carbazol-9-yl)-3'- methyl-5-(2,4,4-trimethylpentan-2-yl)biphenyl-2-ol)dimethyl-hafnium (Procatalyst 6A),

(2',2"-(propane-l,3-diylbis(oxy))bis(3',5'-dimethyl-3-(3,6-di-tert-butyl-9H-carbazol-9-yl)-5-(2,4,4-trimethylpentan-2-yl)biphenyl-2-ol)dimethyl-hafnium (Procatalyst 7A),

(2',2"-(propane-l,3-diylbis(oxy))bis(5'-chloro-3-(3,6-di-tert-butyl-9H-carbazol-9-yl)-3'-ethyl-5-(2,4,4-trimethylpentan-2-yl)biphenyl-2-ol)dimethyl-hafnium (Procatalyst 8A),

(2',2"-(propane-l,3-diylbis(oxy))bis(3-(3,6-di-tert-butyl-9H-carbazol-9-yl)-3'-methyl-5'-tert-butyl-5-(2,4,4-trimethylpentan-2-yl)biphenyl-2-ol)dimethyl-hafnium (Procatalyst 9A),

(2',2"-(propane-l,3-diylbis(oxy))bis(3-(3,6-di-tert-butyl-9H-carbazol-9-yl)-5'-fluoro-3'-methyl-5-(2,4,4-trimethylpentan-2-yl)biphenyl-2-ol)dimethyl-hafnium (Procatalyst 10A),

(2',2"-(propane-l,3-diylbis(oxy))bis(3-(9H-carbazol-9-yl)-5'-chloro-3'-methyl-5-(2,4,4-trimethylpentan-2-yl)biphenyl-2-ol)dimethyl-hafnium (Procatalyst 11A),

(2',2"-(propane-l,3-diylbis(oxy))bis(3-(3,6-di-tert-butyl-9H-carbazol-9-yl)-3'-methyl-5'-trifluoromethyl-5-(2,4,4-trimethylpentan-2-yl)biphenyl-2-ol)dimethyl-hafnium (Procatalyst 12A),

(2',2"-(2,2-dimethyl-2-silapropane-l,3-diylbis(oxy))bis(3',5'-dichloro-3-(3,6-di-tert-butyl-9H-carbazol-9-yl)-5-(2,4,4-trimethylpentan-2-yl)biphenyl-2-ol)dimethyl-hafnium (Procatalyst 13A),

(2'2"-(2,2-dimethyl-2-silapropane-1-diylbis(oxy))bis(5'-chloro-3-(3,6-di-tert-butyl-9H-carbazol-9-yl)-3'-methyl-5-(2,4,4-trimethylpentan-2-yl)biphenyl-2-ol)dimethyl-hafnium (Procatalyst 14A),

(2',2"-(propane-l,3-diylbis(oxy))bis(3'-bromo-5'-chloro-3-(3,6-di-tert-butyl-9H-carbazol-9-yl)-5-(2,4,4-trimethylpentan-2-yl)biphenyl-2-ol)dimethyl-hafnium (Procatalyst 15A),

(2',2"-(propane-l,3-diylbis(oxy))-(5'-chloro-3-(3,6-di-tert-butyl-9H-carbazol-9-yl)-3'-fluoro-5-(2,4,4-trimethylpentan-2-yl)biphenyl-2-ol)-(3",5"-dichloro-3-(3,6-di-tert-butyl-9H-carbazol-9-yl)-5-(2,4,4-trimethylpentan-2-yl)biphenyl-2-ol)dimethyl-hafnium (Procatalyst 16A),

(2',2"-(propane-l,3-diylbis(oxy))bis(3-(3,6-di-tert-butyl-9H-carbazol-9-yl)-5'-fluoro-3'-trifluoromethyl-5-(2,4,4-trimethylpentan-2-yl)biphenyl-2-ol)dimethyl-hafnium (Procatalyst 17A),

(2',2"-(butane-l,4-diylbis(oxy))bis(5'-chloro-3-(3,6-di-tert-butyl-9H-carbazol-9-yl)-3'-methyl-5-(2,4,4-trimethylpentan-2-yl)biphenyl-2-ol)dimethyl-hafnium (Procatalyst 18A),

(2',2"-(ethane-l,2-diylbis(oxy))bis(5'-chloro-3-(3,6-di-tert-butyl-9H-carbazol-9-yl)-3'-methyl-5-(2,4,4-trimethylpentan-2-yl)biphenyl-2-ol)dimethyl-hafnium (Procatalyst 19A),

(2',2"-(propane-l,3-diylbis(oxy))bis(5'-chloro-3-(3,6-di-tert-butyl-9H-carbazol-9-yl)-3'-methyl-5-(2,4,4-trimethylpentan-2-yl)biphenyl-2-ol)dimethyl-zirconium (Procatalyst 20A),

(2',2"-(propane-l,3-diylbis(oxy))bis(3-(3,6-di-tert-butyl-9H-carbazol-9-yl)-3',5'-dichloro-5-(2,4,4-trimethylpentan-2-yl)biphenyl-2-ol)dimethyl-titanium (Procatalyst 24); or

(2',2"-(propane-l,3-diylbis(oxy))bis(5'-chloro-3-(3,6-di-tert-butyl-9H-carbazol-9-yl)-3'-methyl-5-(2,4,4-trimethylpentan-2-yl)biphenyl-2-ol)dimethyl-titanium (Procatalyst 21A).