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] Polymer produced by a Ziegler−Natta catalyst contains a copolymer fraction where most of comonomer in the polymer resides and a high density fraction (HDF) where there is basically no or very low level of comonomer. The molecular weight of the HDF is typically higher than that of the copolymer fraction. The molecular weight of the polymer can be increased by reducing the fraction of the copolymer and/or increasing the HDF.

[0006] Electron donors, including conventional small organic molecule electron donors or metal compounds that contains alkoxide or carboxylate ligands, in addition to Ziegler−Natta catalysts increase the HDF. However, electron donors usually decrease the efficiency of a catalyst.

[0007] 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

[0008] 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).

[0009] Examples of this disclosure include catalyst systems. The catalyst system includes a heterogeneous procatalyst, an electron donor, and a hydrogenation procatalyst. The heterogeneous procatalyst includes a titanium species, an aluminum species, and a magnesium chloride component. The hydrogenation procatalyst has the formula Cp_2TiX_2. In formula Cp_2TiX_2, each Cp is a cyclopentadienyl substituted with at least one R^1, wherein R^1 is $(C_1−C_{10})$alkyl; and each X is independently a halogen atom.

[0009a] In one aspect, there is provided a catalyst system comprising: a heterogeneous procatalyst comprising a titanium species, an aluminum species, and a magnesium chloride component, wherein the heterogeneous procatalyst comprises particles having an average particle size from 0.1 micron to 10 microns; and an electron donor; and a hydrogenation procatalyst having the formula $Cp_2TiX_nTiCp_2$ or Cp_2TiX_n where: each Cp is cyclopentadienyl 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.

[0010] Examples of this disclosure includes polymerize preprocess. 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.

[0010a] In another aspect, there is provided a polymerization process comprising reacting (C_2-C_{12})α-olefins in solution in the presence of a catalyst system in a reactor at a reaction temperature from 150 °C to 350 °C, the catalyst system comprising: a heterogeneous procatalyst comprising a titanium species, an aluminum species, and a magnesium chloride component, wherein the heterogeneous procatalyst comprises particles having an average particle size from 0.1 micron to 10 microns; an electron donor; and a hydrogenation procatalyst having the formula $Cp_2TiX_nTiCp_2$ or Cp_2TiX_n where: each Cp is cyclopentadienyl 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.

DETAILED DESCRIPTION

[0011] Embodiments of this disclosure include catalyst systems. The catalyst system includes a heterogeneous procatalyst and a hydrogenation procatalyst. The heterogeneous procatalyst includes a titanium species, an aluminum species, and a magnesium chloride component. The hydrogenation procatalyst has the formula Cp_2TiX_2. In formula Cp_2TiX_2, each Cp is a cyclopentadienyl substituted with at least one R^1, wherein R^1 is (C_1-C_{10})alkyl; and each X is independently a halogen atom.

[0012] In embodiments of the catalyst system, the heterogeneous procatalyst includes a titanium species. In some embodiments, the titanium species of the heterogeneous procatalyst may have catalytic activity. In some embodiments, the titanium species may include $TiCl_{4-c}(OR)_c$

or $TiCl_{3-d}(OR)_d$, wherein R is (C_1-C_{20})hydrocarbyl, subscript c is 0, 1, 2, 3, or 4, and subscript d is 0, 1, 2, or 3. In some embodiments, the titanium species may include, for example, titanium (IV) tetrachloride, titanium (III) trichloride, tris(2,2,6,6-tetramethyl-3,5-heptanedionato)titanium(III), trichlorotris(tetrahydrofuran) titanium(III), di-n-butoxytitanium(IV) dichloride, diethoxytitanium(IV) dichloride, diisopropoxytitanium(IV) dichloride, diisobutoxytitanium(IV) dichloride, triisopropoxytitanium(IV) chloride, tri-n-butoxytitanium(IV) chloride, triisobutoxytitanium(IV) chloride, titanium(IV) tetraisopropoxide ($Ti(O^iPr)_4$), titanium(IV) ethoxide, titanium(IV) *n*-butoxide, titanium(IV) isobutoxide, titanium(IV) 2-ethylhexoxide, dichlorobis(2,2,6,6-tetramethyl-3,5-heptanedionato)titanium(IV), tetrachlorobis(tetrahydrofuran) titanium(IV), methyltitanium (IV) trichloride, or combinations thereof. In some embodiments, the titanium species may be titanium (IV) tetrachloride or titanium(IV) tetraisopropoxide ($Ti(O^iPr)_4$). For example, in some embodiments, the titanium species may include a titanium halide, a titanium alkoxide, or combinations thereof. For example, in some embodiments, the titanium species may include, but is not limited to, titanium tetrachloride ($TiCl_4$), titanium(IV) tetraisopropoxide (Ti(OiPr)4), other titanium halide or titanium alkoxide, or combinations of these.

[0013] In embodiments of the catalyst system, the heterogeneous procatalyst includes an aluminum species. In one or more embodiments, the aluminum species is chosen from

CLAIMS

1. A catalyst system comprising:

a heterogeneous procatalyst comprising a titanium species, an aluminum species, and a magnesium chloride component, wherein the heterogeneous procatalyst comprises particles having an average particle size from 0.1 micron to 10 microns; and

an electron donor; and

a hydrogenation procatalyst having the formula $Cp_2TiX_nTiCp_2$ or Cp_2TiX_n

where:

each Cp is cyclopentadienyl 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.

2. The catalyst system of claim 1, wherein the electron donor is a vanadium compound chosen from VOX_3 or $VO(OR^3)_3$, where each X is independently a halogen atom or (C_1-C_{40})heterohydrocarbyl anion; and each R^3 is independently (C_1-C_{20})hydrocarbyl or $-C(O)R^{11}$, where R^{11} is (C_1-C_{30})hydrocarbyl.

3. The catalyst system of claim 1, wherein the heterogeneous procatalyst is an unsupported bulk catalyst.

4. The catalyst system of any one of claims 1 to 3, wherein the heterogeneous procatalyst comprises heterogeneous procatalyst particles with a non-controlled morphology.

5. The catalyst system of any one of claims 1 to 4, wherein the heterogeneous procatalyst comprises heterogeneous procatalyst particles, wherein greater than or equal to 10% of the particles have a particle size less than or equal to 1 micron.

6. The catalyst system of any one of claims 1 to 5, further comprising an alkyl aluminum cocatalyst having a structure $Al(R^2)_3$, where each R^2 is independently (C_1-C_{20})alkyl or halogen atom.

7. The catalyst system of any one of claims 1 to 6, further comprising an alkyl aluminum cocatalyst selected from the group consisting of trialkylaluminum compounds, dialkylaluminum chlorides, alkylalumnium dichlorides, alkylaluminum alkoxides, and alkylaluminoxanes.

8. A polymerization process comprising reacting $(C_2-C_{12})\alpha$-olefins in solution in the presence of a catalyst system in a reactor at a reaction temperature from 150 °C to 350 °C, the catalyst system comprising:

a heterogeneous procatalyst comprising a titanium species, an aluminum species, and a magnesium chloride component, wherein the heterogeneous procatalyst comprises particles having an average particle size from 0.1 micron to 10 microns;

an electron donor; and

a hydrogenation procatalyst having the formula $Cp_2TiX_nTiCp_2$ or Cp_2TiX_n

where:

each Cp is cyclopentadienyl 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.

9. The polymerization process of claim 8, further comprising an alkylaluminum cocatalyst having a structure $Al(R^2)_3$, where each R^2 is independently (C_1-C_{20})alkyl or halogen atom.

10. The polymerization process of claim 8 or claim 9, further comprising trialkylaluminum, dialkylaluminum chloride, alkylalumnium dichloride, alkylaluminum alkoxide, or alkylaluminoxane.

11. The polymerization process of claim 8, wherein the electron donor is a vanadium compound chosen from VOX_3 or $VO(OR^3)_3$, where each X is independently a halogen atom or (C_1-C_{40})heterohydrocarbyl anion; and R^3 is (C_1-C_{20})hydocarbyl or $-C(O)R^{11}$, where R^{11} is(C_1-C_{30})hydrocarbyl.

12. The polymerization process of any one of claims 8 to 11, wherein the heterogeneous procatalyst is a bulk catalyst.

13. The polymerization process of any one of claims 8 to 12, wherein the heterogeneous procatalyst comprises heterogeneous procatalyst particles, wherein greater than or equal to 10% of the particles have a particle size less than or equal to 1 micron.

14. The polymerization process of any one of claims 8 to 13, wherein the proheterogeneous catalyst comprises heterogeneous procatalyst particles with a non-controlled particle morphology.