the reactor. The reaction mixture, when removed from the reactor, may be processed to remove 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 catalysts 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. 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] Examples 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.

[0007a] 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 heterogeneous procatalyst particles having an average particle size from 0.1 micron to 10 microns as measured by light scattering; and a hydrogenation procatalyst having the formula $Cp_2TiX_2TiCp_2$ 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.

[0008] 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.

[0008a] 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 heterogeneous procatalyst particles having an average particle size from 0.1 micron to 10 microns as measured by light scattering; 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.

BRIEF DESCRIPTIONS OF THE FIGURES

[0009] The FIGURE is a graph of the gel permeation chromatography.

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 heterogeneous procatalyst particles having an average particle size from 0.1 micron to 10 microns as measured by light scattering; and

a hydrogenation procatalyst having the formula $Cp_2TiX_2TiCp_2$ 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 heterogeneous catalyst is an unsupported bulk catalyst.

3. The catalyst system of claim 1 or claim 2, wherein the heterogeneous procatalyst comprises heterogeneous procatalyst particles with a non-controlled morphology.

4. The catalyst system of any one of claims 1 to 3, wherein the heterogeneous procatalyst comprises heterogeneous procatalyst particles, wherein greater than or equal to 10% of the heterogeneous procatalyst particles have a particle size less than or equal to 1 micron as measured by light scattering.

5. The catalyst system of any one of claims 1 to 4, wherein the ratio of moles titanium in the hydrogenation procatalyst to moles titanium in the heterogeneous procatalyst is greater than 1:2.

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

7. The catalyst system of any one of claims 1 to 5, further comprising an alkyl aluminum cocatalyst selected from the group consisting of trialkylaluminum compounds, dialkylaluminum chlorides, alkylaluminum dichlorides, alkylaluminum alkoxides, and alkylaluminoxanes.

8. The catalyst system of claim 6 or claim 7, wherein the ratio of moles titanium in the heterogeneous procatalyst to moles aluminum in the cocatalyst is greater than 2:1.

9. The catalyst system of claim 6 or claim 7, wherein the ratio of moles titanium in the heterogeneous procatalyst to moles aluminum in the cocatalyst is from 1000:1 to 2:1.

10. 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 heterogeneous procatalyst particles having an average particle size from 0.1 micron to 10 microns as measured by light scattering; 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.

11. The polymerization process of claim 10, wherein the catalyst system further comprises a trialkylaluminum cocatalyst $Al(R^2)_3$, where each R^2 is independently (C_1–C_{20})alkyl.

12. The polymerization process of claim 10 or claim 11, wherein the heterogeneous catalyst is a bulk catalyst.

13. The polymerization process of any one of claims 10 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 as measured by light scattering.

14. The polymerization process of any one of claims 10 to 13, wherein the heterogeneous catalyst comprises heterogeneous procatalyst particles with a non-controlled particle morphology.