

CLAIMS

1. A catalyst system comprising:
a heterogeneous procatalyst comprising a titanium species, an aluminum species, and a magnesium chloride component; and
a hydrogenation procatalyst having the formula $\text{Cp}_2\text{TiX}_2\text{TiCp}_2$ or Cp_2TiX_n
where:
each Cp is cyclopentadienyl substituted with at least one $(\text{C}_1\text{--}\text{C}_{10})$ alkyl;
each X is independently monoanionic or neutral, wherein each X is
independently $(\text{C}_1\text{--}\text{C}_{40})$ hydrocarbon, $(\text{C}_1\text{--}\text{C}_{40})$ heterohydrocarbon,
 $(\text{C}_1\text{--}\text{C}_{40})$ hydrocarbyl, $(\text{C}_1\text{--}\text{C}_{40})$ 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 2, wherein the heterogeneous procatalyst comprises heterogeneous procatalyst particles having an average particle size from 0.1 micron to 10 microns.
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 heterogeneous procatalyst particles have a particle size less than or equal to 1 micron.
6. The catalyst system of any one of claims 1 to 5, wherein the ratio of moles titanium in the hydrogenation procatalyst to moles titanium in the heterogeneous procatalyst is greater than 1:2.
7. The catalyst system of any one of claims 1 to 6, further comprising an alkyl aluminum cocatalyst $\text{Al}(\text{R}^2)_3$, where each R^2 is independently $(\text{C}_1\text{--}\text{C}_{20})$ alkyl or halogen atom, provided at least one R^2 is $(\text{C}_1\text{--}\text{C}_{20})$ alkyl.

8. 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, alkylaluminum dichlorides, alkylaluminum alkoxides, and alkylaluminoxanes
9. The catalyst system claim 7 or claim 8, wherein the ratio of moles titanium in the heterogeneous procatalyst to moles aluminum in the cocatalyst is greater than 2:1.
10. The catalyst system of claim 7 or claim 8, wherein the ratio of moles titanium in the heterogeneous procatalyst to moles aluminum in the cocatalyst is from 1000:1 to 2:1.
11. A polymerization process comprising:
reacting (C₂–C₁₂) α -olefins in solution in the presence of a catalyst system, the catalyst system comprising:
a heterogeneous procatalyst comprising a titanium species, an aluminum species, and a magnesium chloride component; and
a hydrogenation procatalyst having the formula Cp₂TiX_nTiCp₂ or Cp₂TiX_n
where:
each Cp is cyclopentadienyl substituted with at least one (C₁–C₁₀)alkyl;
each X is independently monoanionic or neutral, wherein
each X is independently (C₁–C₄₀)hydrocarbon, (C₁–C₄₀)heterohydrocarbon, (C₁–C₄₀)hydrocarbyl, (C₁–C₄₀)heterohydrocarbyl, or a halogen atom; and
n is 1 or 2.
12. The polymerization process of claim 11, wherein the catalyst system further comprises a trialkylaluminum cocatalyst Al(R²)₃, where each R² is independently (C₁–C₂₀)alkyl.
13. The polymerization process of claim 11 or claim 12, wherein the heterogeneous catalyst is a bulk catalyst.
14. The polymerization process of any one of claims 11 to 13, 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.

15. The polymerization process of any one of claims 11 to 14, wherein the heterogeneous catalyst comprises heterogeneous procatalyst particles with a non-controlled particle morphology.
16. The polymerization process of any one of claims 11 to 15, wherein the (C₂–C₁₂) α -olefins in solution are reacted in a reactor at a reaction temperature from 150 °C to 350 °C.