CLAIMS

1. A heterogeneous procatalyst comprising:

a titanium species,

a hydrocarbon-soluble transition metal compound having a structure $M(OR^1)_z$, where:

M is a non-reducing transition metal other than titanium, the non-reducing transition metal being in an oxidation state of +2 or +3;

each R^1 is independently $(C_1–C_{30})$hydrocarbyl or $–C(O)R^{11}$, where R^{11} is $(C_1–C_{30})$hydrocarbyl; and

z is 2 or 3;

wherein each R^1 and R^{11} may be optionally substituted with one or more than one halogen atoms, or one or more than one $–Si(R^S)_3$, where each R^S is $(C_1–C_{30})$hydrocarbyl;

a chlorinating agent having a structure $A(Cl)_x(R^2)_{3–x}$, where:

A is aluminum or boron;

R^2 is $(C_1–C_{30})$hydrocarbyl; and

x is 1, 2, or 3; and

a magnesium chloride component.

2. The procatalyst according to claim 1, wherein M is chosen from zinc, copper, cobalt, manganese, iron, or chromium.

3. The procatalyst according to claim 1, wherein $M(OR^1)_z$ is aliphatic or cycloaliphatic hydrocarbon-soluble.

4 The procatalyst according to claim 1, wherein the procatalyst further comprises a vanadium component.

5. The procatalyst according to claim 4, wherein the vanadium component is chosen from VX_4, VOX_3, or $VO(OR^3)_3$, where each X is independently a halogen atom or; and R^3 is $(C_1–C_{20})$hydrocarbyl or $–C(O)R^{31}$, where R^{31} is is $(C_1–C_{30})$hydrocarbyl, wherein each R^3 and R^{31} may optionally be substituted with one or more halogen atoms or one or more $–Si(R^S)_3$ where each R^S is independently $(C_1–C_{30})$hydrocarbyl.

6 The procatalyst according to claim 1, wherein the ratio of transition metal to titanium is from 0.1 to 10 (mole/mole).

7. The procatalyst according to claim 5 or claim 6, wherein the ratio of vanadium to titanium is from 0.1 to 10 (mole/mole).

8. The procatalyst according to claim 1, wherein the ratio of magnesium chloride to titanium is from 1 to 100 (mole/mole).

9. The procatalyst according to claim 1, wherein the magnesium chloride component has a surface area of greater than or equal to 100 m^2/g as measured according to the BET method.

10. A process for polymerizing ethylene-based polymers, the process comprising:

contacting ethylene and optionally one or more α-olefins in the presence of a catalyst system, wherein the catalyst system comprises a heterogeneous procatalyst, the heterogeneous procatalyst comprising:

a titanium species,

a hydrocarbon-soluble transition metal compound having a structure $M(OR^1)_z$, where:

M is a transition metal in an oxidation state of +2 or +3; and

each R^1 is independently $(C_1–C_{30})$hydrocarbyl or $–C(O)R^{11}$, wherein R^{11} is $(C_1–C_{30})$hydrocarbyl; and

z is 2 or 3;

wherein each R^1 and R^{11} may be optionally substituted with one or more than one halogen atoms, or one or more than one $–Si(R^S)_3$, where each R^S is $(C_1–C_{30})$hydrocarbyl;;

a chlorinating agent having a structure $A(Cl)_x(R^2)_{3–x}$, where:

A is aluminum or boron;

R^2 is $(C_1–C_{30})$hydrocarbyl; and

x is 1, 2, or 3; and

a magnesium chloride component.

11. The process according to claim 10, wherein M is chosen from zinc, copper, cobalt, manganese, iron, or chromium.

12. The process according to claim 10 wherein the heterogeneous procatalyst further comprises a vanadium component.

13. The process according to claim 12, wherein the vanadium component is chosen from VX_4, VOX_3, or $VO(OR^3)_3$, where each X is independently a halogen atom or (; and R^3 is $(C_1–C_{20})$hydrocarbyl or $–C(O)R^{31}$, where R^{31} is is $(C_1–C_{30})$hydrocarbyl, wherein each R^3 and R^{31} may optionally be substituted with one or more halogen atoms or one or more $–Si(R^S)_3$ where each R^S is independently $(C_1–C_{30})$hydrocarbyl.

14. The process according to– claim 10, wherein the ratio of transition metal to titanium is from 0.1 to 10 (mole/mole).

15. The process according to claim 12, wherein the ratio of vanadium to titanium is from 0.1 to 10 (mole/mole).

16. The process according to– claim 10, wherein the ratio of magnesium chloride to titanium is from 5 to 100 (mole/mole).

17. The process according to claim 10, wherein the catalyst system further comprises an activator.

18. The process according to claim 10, wherein the polymerization process is a solution polymerization process.

19. A process of making the procatalyst, the process comprising:
preparing a $MgCl_2$ slurry in a hydrocarbon solvent; and
mixing a chlorinating agent, a hydrocarbon-soluble transition metal compound, and a titanium species into the $MgCl_2$ slurry,
wherein
the transition metal compound has a structure $M(OR^1)_z$, where:
M is a non-reducing transition metal in an oxidation state of +2 or +3;
each R^1 is independently $(C_1–C_{30})$hydrocarbyl or $–C(O)R^{11}$, wherein R^{11} is $(C_1–C_{30})$hydrocarbyl; and
z is 2 or 3;

wherein each R^1 and R^{11} may be optionally substituted with one or more than one halogen atoms, or one or more than one –$Si(R^S)_3$, where each R^S is $(C_1–C_{30})$hydrocarbyl; and

the chlorinating agent has a structure $A(Cl)_x(R^2)_{3-x}$, where:

A is aluminum or boron;

R^2 is $(C_1–C_{30})$hydrocarbyl; and

x is 1, 2, or 3.

20. The process of making the procatalyst according to claim 19, wherein the hydrocarbon solvent comprises non-halogenated $(C_3–C_{30})$alkyl or non-halogenated $(C_3–C_{30})$cycloalkyl.

M is a non-reducing transition metal in an oxidation state of +2 or +3;

each R^1 is independently $(C_1–C_{30})$hydrocarbyl or $–C(O)R^{11}$, wherein R^{11} is $(C_1–C_{30})$hydrocarbyl; and

z is 2 or 3;

wherein each R^1 and R^{11} may be optionally substituted with one or more than one halogen atoms, or one or more than one –$Si(R^S)_3$, where each R^S is $(C_1–C_{30})$hydrocarbyl; and

the chlorinating agent has a structure $A(Cl)_x(R^2)_{3-x}$, where:

A is aluminum or boron;

R^2 is $(C_1–C_{30})$hydrocarbyl; and

x is 1, 2, or 3.

21. The process of making the procatalyst according to claim 19, wherein the hydrocarbon solvent comprises non-halogenated $(C_3–C_{30})$alkyl or non-halogenated $(C_3–C_{30})$cycloalkyl.