CLAIMS

1. A heterogeneous procatalyst comprising:

a titanium species;

a chlorinating agent having a structure $A(Cl)_x(R^1)_{3-x}$, where:

A is aluminum or boron;

R^1 is a (C_1–C_{30}) hydrocarbyl; and

x is 1, 2, or 3; and

a thermally-treated magnesium chloride component, wherein the thermally treated magnesium chloride component comprises a product of thermally treating a magnesium chloride slurry at a temperature of at least 150 °C for at least 30 minutes.

2. The heterogeneous procatalyst of claim 1, wherein ~~the thermally treated magnesium chloride component comprises a product of thermally treating a magnesium chloride slurry at a temperature of at least 100 °C for at least 30 minutes,~~ the magnesium chloride slurry ~~comprising~~ comprises at least magnesium chloride dispersed in a solvent.

3. The heterogeneous procatalyst of claim 2, wherein the magnesium chloride slurry comprises the titanium species and the chlorinating agent.

4. The heterogeneous procatalyst of claim 1, wherein the heterogeneous procatalyst comprises the product of:

thermally treating a slurry of magnesium chloride dispersed in a solvent at a temperature of at least 100 °C for at least 30 minutes; and

combining the titanium species and the chlorinating agent with the thermally treated magnesium chloride.

5. The heterogeneous procatalyst of claim 1, wherein the heterogeneous procatalyst comprises the product of:

combining the titanium species and the chlorinating agent with a slurry of magnesium chloride dispersed in a solvent to produce a procatalyst slurry; and

thermally treating the procatalyst slurry at a temperature of at least 100 °C for at least 30 minutes.

6. The heterogeneous procatalyst according to any one of the preceding claims, wherein a molar ratio of titanium to magnesium chloride in the heterogeneous procatalyst is from 0.0050 to 0.075 (mole/mole).

7. The heterogeneous procatalyst according to any one of the preceding claims, further comprising a vanadium species chosen from VX_4, VOX_3, or $VO(OR^2)_3$, where each X is independently a halogen atom or (C_1–C_{40}) heterohydrocarbyl anion; and R^2 is (C_1–C_{20}) hydrocarbyl or –C(O) R^{11}, where R^{11} is (C_1–C_{30}) hydrocarbyl.

8. The heterogeneous procatalyst according to claim 7, wherein the ratio of vanadium to titanium in the heterogeneous procatalyst is from 0.0 to 20 (mole/mole).

9. The heterogeneous procatalyst according to either of claims 7 or 8, wherein the molar ratio of vanadium to magnesium chloride in the heterogeneous procatalyst is from 0.0 to 0.10 (mole/mole).

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 to produce an ethylene-based polymer, wherein the catalyst system comprises the heterogeneous procatalyst according to any of the preceding claims and an optional co-catalyst chosen from an alkyl of aluminum, a haloalkyl of aluminum, an alkylaluminum halide, a Grignard reagent, an alkali metal aluminum hydride, an alkali metal borohydride, an alkali metal hydride, or an alkaline earth metal hydride.

11. An ethylene-based polymer prepared by the process according to claim 11.

12. A process for making a procatalyst, the process comprising:

thermally treating a magnesium chloride slurry at a treatment temperature of at least 100 °C and for at least 30 minutes, the magnesium chloride slurry comprising at least magnesium chloride ($MgCl_2$) dispersed in a solvent; and

combining a chlorinating agent and a titanium species with the magnesium chloride slurry, the chlorinating agent having a structure $A(Cl)_x(R^1)_{3-x}$, where:

A is aluminum or boron;

R^1 is (C_1-C_{30})hydrocarbyl; and

x is 1, 2, or 3.

13. The process according to claim 12, comprising thermally treating the magnesium chloride slurry before combining the chlorinating agent and the titanium species with the magnesium chloride slurry.

14. The process according to claim 12, comprising thermally treating the magnesium chloride slurry after combining the chlorinating agent and the titanium species with the magnesium chloride slurry.

15. The process according to any one of claims 12-14, further comprising combining a vanadium species with the magnesium chloride, titanium species, and the chlorinating agent.