give the (B) magnesium halide-supported titanium procatalyst; and wherein the (D) solid particulate comprising magnesium halide has been prepared by contacting a solution of (F) a dialkylmagnesium compound dissolved in the (C) saturated or aromatic hydrocarbon liquid with 1.95 to 2.05 mole equivalents of hydrogen halide to give a suspension of the (D) solid particulate comprising magnesium halide in the (C) saturated or aromatic hydrocarbon liquid; and wherein the modified catalyst system further comprises (G) an organoborate.

[0013b] In another aspect, the present disclosure refers to a solution phase polymerization process of polymerizing an olefin using a modified catalyst system that is a product of a reaction of a modified Ziegler-Natta procatalyst with an activator, the process comprising contacting at least one polymerizable olefin in the reactor with the modified catalyst system under effective conditions to give a polyolefin product; wherein the modified Ziegler-Natta procatalyst is prepared prior to the contacting step by mixing an initial Ziegler-Natta procatalyst and a molecular ligand-metal complex (pro)catalyst together under modifying conditions comprising a modifying temperature less than 100° C. and a modifying time of at least 1 minute, and optionally an activator, to give the modified Ziegler-Natta procatalyst;

wherein the initial Ziegler-Natta procatalyst is (B) a magnesium halide-supported titanium procatalyst; wherein the (B) magnesium halide-supported titanium procatalyst has been prepared by contacting (D) a solid particulate comprising magnesium halide with (E) titanium tetrachloride in the (C) saturated or aromatic hydrocarbon liquid so as to give the (B) magnesium halide-supported titanium procatalyst; and wherein the (D) solid particulate comprising magnesium halide has been prepared by contacting a solution of (F) a dialkylmagnesium compound dissolved in the (C) saturated or aromatic hydrocarbon liquid with 1.95 to 2.05 mole equivalents of hydrogen halide to give a suspension of the (D) solid particulate comprising magnesium halide in the (C) saturated or aromatic hydrocarbon liquid; and wherein the modified catalyst system further comprises (G) an organoborate.

CLAIMS

1. A method of polymerizing an olefin using a modified catalyst system that comprises a product of a reaction of a modified Ziegler-Natta procatalyst with an activator in (C) a saturated or aromatic hydrocarbon liquid, the method comprising contacting at least one polymerizable olefin in a reactor with the modified catalyst system under effective conditions to give a polyolefin product; wherein the modified Ziegler-Natta procatalyst is prepared prior to the contacting step by mixing an initial Ziegler-Natta procatalyst and a molecular (pro)catalyst together in (C) a saturated or aromatic hydrocarbon liquid under modifying conditions comprising a modifying temperature less than 100° C. and a modifying time of at least 1 minute, and optionally an activator, to give the modified Ziegler-Natta procatalyst;

wherein the initial Ziegler-Natta procatalyst is (B) a magnesium halide-supported titanium procatalyst; wherein the (B) magnesium halide-supported titanium procatalyst has been prepared by contacting (D) a solid particulate comprising magnesium halide with (E) titanium tetrachloride in the (C) saturated or aromatic hydrocarbon liquid so as to give the (B) magnesium halide-supported titanium procatalyst;

wherein the (D) solid particulate comprising magnesium halide has been prepared by contacting a solution of (F) a dialkylmagnesium compound dissolved in the (C) saturated or aromatic hydrocarbon liquid with 1.95 to 2.05 mole equivalents of hydrogen halide to give a suspension of the (D) solid particulate comprising magnesium halide in the (C) saturated or aromatic hydrocarbon liquid; and

wherein the modified catalyst system further comprises (G) an organoborate.

2. The method of claim 1 wherein the molecular (pro)catalyst comprises a molecular ligand-metal complex (pro)catalyst;.

3. The method of claim 1 or 2 wherein the modifying conditions comprise: (i) a modifying temperature from 0° C. to 50° C.; (ii) a modifying time from 3 hours to 3 months; (iii) an inert gas atmosphere (e.g., molecular nitrogen, helium, argon, or a mixture of any two or more thereof); (iv) both (i) and (ii); (v) both (i) and (iii); (vi) both (ii) and (iii); or (vii) each of (i), (ii), and (iii).

4. The method of any one of claims 1 to 3 wherein: (i) the at least one polymerizable olefin is ethylene and the polyolefin product comprises a polyethylene; (ii) the at least one polymerizable olefin is at least one (C_3-C_{40})alpha-olefin and the polyolefin product comprises a poly((C_3-C_{40})alpha-olefin); or (iii) the at least one polymerizable olefin comprises a combination of ethylene and at least one (C_3-C_{40})alpha-olefin and the polyolefin product comprises a poly(ethylene-*co*-(C_3-C_{40})alpha-olefin) copolymer.

5. The method of any one of claims 1 to 4 wherein: (i) the initial magnesium halide-supported titanium procatalyst is free of Al (molar ratio of Al/Mg = 0); or (ii) the initial magnesium halide-supported titanium procatalyst has a molar ratio of Al/Mg from > 0 to < 0.05; or (iii) the magnesium halide of the initial magnesium halide-supported titanium procatalyst is magnesium chloride; or (iv) the magnesium halide of the initial magnesium halide-supported titanium procatalyst is magnesium bromide; or (v) both (i) and (iii); or (vi) both (i) and (iv); or (vii) both (ii) and (iii); or (viii) both (ii) and (iv).

6. The method of any one of claims 1 to 5 wherein the (D) solid particulate comprising magnesium halide has a Brunauer, Emmett, Teller (BET) surface area of ≥ 200 square meters per gram (m^2/g) as measured by Brunauer, Emmett, Teller (BET) Surface Area Method; wherein the (D) solid particulate has 0 mol% to <5 mol% of an active halide impurity.

7. The method of any one of claims 1 to 6 wherein the activator used with the modified Ziegler-Natta procatalyst comprises (A) a hydrocarbylaluminoxane.

8. The method of any one of claims 1 to 7 wherein the molecular ligand-metal (pro)catalyst comprises: (i) a cyclopentadienyl ligand-metal complex (pro)catalyst; (ii) a cyclopentadienyl-free ligand-metal complex (pro)catalyst; or (iii) both (i) and (ii).

9. The method of any one of claims 1 to 8 wherein the contacting comprises: (i) adding the modified catalyst system into the reactor, which contains the at least one polymerizable olefin; (ii) adding the at least one polymerizable olefin into the reactor, which contains the modified catalyst system; or (iii) adding a first feed of the modified catalyst

system into the reactor and a second feed of the at least one polymerizable olefin into the reactor.

10. A solution phase polymerization process of polymerizing an olefin using a modified catalyst system that is a product of a reaction of a modified Ziegler-Natta procatalyst with an activator, the process comprising contacting at least one polymerizable olefin in the reactor with the modified catalyst system under effective conditions to give a polyolefin product; wherein the modified Ziegler-Natta procatalyst is prepared prior to the contacting step by mixing an initial Ziegler-Natta procatalyst and a molecular ligand-metal complex (pro)catalyst together under modifying conditions comprising a modifying temperature less than 100° C. and a modifying time of at least 1 minute, and optionally an activator, to give the modified Ziegler-Natta procatalyst;

wherein the initial Ziegler-Natta procatalyst is (B) a magnesium halide-supported titanium procatalyst; wherein the (B) magnesium halide-supported titanium procatalyst has been prepared by contacting (D) a solid particulate comprising magnesium halide with (E) titanium tetrachloride in the (C) saturated or aromatic hydrocarbon liquid so as to give the (B) magnesium halide-supported titanium procatalyst;

wherein the (D) solid particulate comprising magnesium halide has been prepared by contacting a solution of (F) a dialkylmagnesium compound dissolved in the (C) saturated or aromatic hydrocarbon liquid with 1.95 to 2.05 mole equivalents of hydrogen halide to give a suspension of the (D) solid particulate comprising magnesium halide in the (C) saturated or aromatic hydrocarbon liquid; and

wherein the modified catalyst system further comprises (G) an organoborate.