high catalytic activity and is useful for catalyzing polymerizations that produce polyolefin polymers with broad molecular weight distribution (MWD). The catalytic activity of the inventive catalyst is enhanceable if the inventive catalyst is prepared by contacting the inventive procatalyst with an activator that is a hydrocarbylaluminoxane (instead of with a trialkylaluminum or aluminum halide activator, which are required to activate prior Ziegler-Natta procatalysts). A polyolefin made by polymerizing at least one olefin monomer with the inventive catalyst beneficially has a lower residual content of active halide compared to a polyolefin made with a standard halide-containing Ziegler-Natta catalyst. Also provided are methods of preparing the (pro)catalysts, methods of polymerizing olefins, and polyolefins made thereby.

[0012a] In one aspect, the present disclosure refers to an enhanced catalyst that comprises a product of a reaction of (A) a hydrocarbylaluminoxane and a suspension of (B) a magnesium halide-supported titanium procatalyst in (C) a saturated or aromatic hydrocarbon liquid, wherein the (B) magnesium halide-supported titanium procatalyst has been prepared by contacting (D) a solid particulate comprising magnesium halide with (E) titanium tetrachloride and (J) conditioning compound in the (C) saturated or aromatic hydrocarbon liquid so as to give the (B) magnesium halide-supported titanium procatalyst; wherein the (B) magnesium halide-supported titanium procatalyst is free of Al; and wherein the (J) conditioning compound is tetrakis(2,2,6,6-tetramethyl-3,5-heptanedionato)zirconium, zirconium tetraisopropoxide, tetrakis(2,2,6,6-tetramethyl-3,5-heptanedionato)hafnium, hafnium tetraisopropoxides, vanadium trichloride oxide, or vanadium triisopropoxy oxide.

[0012b] In another aspect, the present disclosure refers to a method of preparing an enhanced catalyst, the method comprising contacting (A) a hydrocarbylaluminoxane with a suspension of (B) a magnesium halide-supported titanium procatalyst in (C) a saturated or aromatic hydrocarbon liquid, thereby giving the enhanced catalyst, wherein the (B) magnesium halide-supported titanium procatalyst has been prepared by contacting a suspension of (D) solid particulate comprising magnesium halide in the (C) saturated or aromatic hydrocarbon liquid with (E) titanium tetrachloride and (J) conditioning compound so as to give the suspension of the (B) magnesium halide-supported titanium procatalyst in the (C) saturated or aromatic hydrocarbon liquid, wherein the (B) magnesium halide-supported titanium procatalyst is free of Al, and wherein the (J) conditioning compound is tetrakis(2,2,6,6-tetramethyl-3,5-heptanedionato)zirconium, zirconium tetraisopropoxide, tetrakis(2,2,6,6-tetramethyl-3,5-heptanedionato)hafnium, hafnium tetraisopropoxides, vanadium trichloride oxide, or vanadium triisopropoxy oxide; and further

comprising a preliminary step of preparing the (D) solid particulate comprising magnesium halide 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.

[0012c] In another aspect, the present disclosure refers to a method of polymerizing an olefin using an enhanced catalyst, the method comprising contacting a polymerizable olefin with the enhanced catalyst as disclosed herein or the enhanced catalyst prepared by the method as disclosed herein under effective conditions to give a polyolefin product.

[0012d] In another aspect, the present disclosure refers to a (B) magnesium halide-supported titanium procatalyst prepared by contacting (D) a solid particulate comprising magnesium halide with (E) titanium tetrachloride and (J) conditioning compound in (C) a saturated or aromatic hydrocarbon liquid, wherein the (D) solid particulate comprising magnesium halide has been prepared by contacting a solution of (F) a dialkylmagnesium compound dissolved in (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; wherein the (B) magnesium halide-supported titanium procatalyst is free of Al; and wherein the (J) conditioning compound is tetrakis(2,2,6,6-tetramethyl-3,5-heptanedionato)zirconium, zirconium tetraisopropoxide, tetrakis(2,2,6,6-tetramethyl-3,5-heptanedionato)hafnium, hafnium tetraisopropoxides, vanadium trichloride oxide, or vanadium triisopropoxy oxide.

[0012e] In another aspect, the present disclosure refers to a method of polymerizing an olefin using a magnesium halide-supported titanium catalyst, the method comprising contacting a polymerizable olefin with the enhanced catalyst as disclosed herein under effective conditions to give a polyolefin product.

[0012f] In yet another aspect, the present disclosure refers to a polyolefin product made by the polymerization method as disclosed herein.

DETAILED DESCRIPTION

[0013] The Brief Summary and Abstract are incorporated here by reference. Examples of embodiments include the following numbered aspects.

[0014] Aspect 1. An enhanced catalyst that consists essentially of a product of a reaction of (A) a hydrocarbylaluminoxane and a suspension of (B) a magnesium halide-supported titanium procatalyst in (C) a saturated or aromatic hydrocarbon liquid, wherein the (B) magnesium halide-supported titanium procatalyst has been prepared by contacting (D) a solid particulate consisting essentially of magnesium halide with (E) titanium tetrachloride in the (C) a saturated or aromatic hydrocarbon liquid so as to give the (B) magnesium halide-supported titanium procatalyst.

[0015] Aspect 2. The enhanced catalyst of aspect 1 wherein: (i) the (B) magnesium halide-supported titanium procatalyst is free of Al; (ii) the (B) magnesium halide-supported titanium procatalyst is characterized by a molar ratio of Al/Mg from > 0 to < 0.05; (iii) the magnesium halide of the (B) magnesium halide-supported titanium procatalyst is magnesium chloride; (iv) the magnesium halide of the (B) magnesium halide-supported titanium procatalyst is magnesium bromide; (v) both (i) and (iii); (vi) both (i) and (iv); (vii) both (ii) and (iii); (viii) both (ii) and (iv).

[0016] Aspect 3. The enhanced catalyst of aspect 1 or 2 wherein: (i) the (D) solid particulate consisting essentially of magnesium halide has a Brunauer, Emmett, Teller (BET) surface area of ≥ 200 square meters per gram (m^2/g) as measured by BET Surface Area Method, described later; or (ii) the (D) solid particulate consisting essentially of 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

CLAIMS

1. An enhanced catalyst that comprises a product of a reaction of (A) a hydrocarbylaluminoxane and a suspension of (B) a magnesium halide-supported titanium procatalyst in (C) a saturated or aromatic hydrocarbon liquid, wherein the (B) magnesium halide-supported titanium procatalyst has been prepared by contacting (D) a solid particulate comprising magnesium halide with (E) titanium tetrachloride and (J) conditioning compound in the (C) saturated or aromatic hydrocarbon liquid so as to give the (B) magnesium halide-supported titanium procatalyst; wherein the (B) magnesium halide-supported titanium procatalyst is free of Al; and

wherein the (J) conditioning compound is tetrakis(2,2,6,6-tetramethyl-3,5-heptanedionato)zirconium, zirconium tetraisopropoxide, tetrakis(2,2,6,6-tetramethyl-3,5-heptanedionato)hafnium, hafnium tetraisopropoxides, vanadium trichloride oxide, or vanadium triisopropoxy oxide.

2 The enhanced catalyst of claim 1 wherein: (i) the (B) magnesium halide-supported titanium procatalyst is characterized by a molar ratio of Al/Mg from > 0 to < 0.05; or (ii) the magnesium halide of the (B) magnesium halide-supported titanium procatalyst is magnesium chloride; or (iii) the magnesium halide of the (B) magnesium halide-supported titanium procatalyst is magnesium bromide; (or (iv) both (i) and (ii); or (v) both (i) and (iii).

3. The enhanced catalyst of claim 1 or 2 wherein: (i) 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 BET Surface Area Method; or (ii) 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; or (iii) both (i) and (ii).

4. The enhanced catalyst of any one of claims 1 to 3 wherein the (A) hydrocarbylaluminoxane is an alkylaluminoxane, a polymethylaluminoxane, an arylaluminoxane, an aralkylaluminoxane, or a combination of any two or more thereof.

5. A method of preparing an enhanced catalyst, the method comprising contacting (A) a hydrocarbylaluminoxane with a suspension of (B) a magnesium halide-supported titanium procatalyst in (C) a saturated or aromatic hydrocarbon liquid, thereby giving the enhanced

catalyst, wherein the (B) magnesium halide-supported titanium procatalyst has been prepared by contacting a suspension of (D) solid particulate comprising magnesium halide in the (C) saturated or aromatic hydrocarbon liquid with (E) titanium tetrachloride and (J) conditioning compound so as to give the suspension of the (B) magnesium halide-supported titanium procatalyst in the (C) saturated or aromatic hydrocarbon liquid, wherein the (B) magnesium halide-supported titanium procatalyst is free of Al, and wherein the (J) conditioning compound is tetrakis(2,2,6,6-tetramethyl-3,5-heptanedionato)zirconium, zirconium tetraisopropoxide, tetrakis(2,2,6,6-tetramethyl-3,5-heptanedionato)hafnium, hafnium tetraisopropoxides, vanadium trichloride oxide, or vanadium triisopropoxy oxide; and

further comprising a preliminary step of preparing the (D) solid particulate comprising magnesium halide 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.

6. A method of polymerizing an olefin using an enhanced catalyst, the method comprising contacting a polymerizable olefin with the enhanced catalyst of any one of claims 1 to 4 or the enhanced catalyst prepared by the method of claim 5 under effective conditions to give a polyolefin product.

7. A (B) magnesium halide-supported titanium procatalyst prepared by contacting (D) a solid particulate comprising magnesium halide with (E) titanium tetrachloride and (J) conditioning compound in (C) a saturated or aromatic hydrocarbon liquid, wherein the (D) solid particulate comprising magnesium halide has been prepared by contacting a solution of (F) a dialkylmagnesium compound dissolved in (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; wherein the (B) magnesium halide-supported titanium procatalyst is free of Al; and

wherein the (J) conditioning compound is tetrakis(2,2,6,6-tetramethyl-3,5-heptanedionato)zirconium, zirconium tetraisopropoxide, tetrakis(2,2,6,6-tetramethyl-3,5-heptanedionato)hafnium, hafnium tetraisopropoxides, vanadium trichloride oxide, or vanadium triisopropoxy oxide.

8. A method of polymerizing an olefin using a magnesium halide-supported titanium catalyst, the method comprising contacting a polymerizable olefin with the enhanced catalyst of any one of claims 1 to 4 under effective conditions to give a polyolefin product.

9. A polyolefin product made by the polymerization method of claim 6 or 8.