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 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) 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 (D) solid particulate has 0 mol% to <5 mol% of an active halide impurity.

[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 consisting essentially of magnesium halide in the (C) saturated or aromatic hydrocarbon liquid with (E) titanium tetrachloride so as to give the suspension of the (B) magnesium halide-supported titanium procatalyst in the (C) saturated or aromatic hydrocarbon liquid; further comprising a preliminary step of preparing the (D) solid particulate consisting essentially of 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 consisting essentially of magnesium halide in the (C) saturated or aromatic hydrocarbon liquid; and wherein the (D) solid particulate has 0 mol% to <5 mol% of an active halide impurity.

[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 magnesium halide-supported titanium procatalyst prepared by contacting (D) a solid particulate consisting essentially of magnesium halide with (E) titanium tetrachloride in (C) a saturated or aromatic hydrocarbon liquid, wherein the (D) solid particulate consisting essentially of 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 consisting essentially of magnesium halide in the (C) saturated or aromatic hydrocarbon liquid; wherein the magnesium halide-supported titanium procatalyst is free of aluminum halides; wherein the (B) magnesium halide-supported titanium procatalyst is free of Al; and wherein the (D) solid particulate has 0 mol% to <5 mol% of an active halide impurity.

[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;

[0016] (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).

[0017] 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 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) 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 (D) solid particulate has 0 mol% to <5 mol% of an active halide impurity.

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 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; 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 hydrogen halide to give a suspension of the (D) solid particulate consisting essentially of 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 consisting essentially of

magnesium halide in the (C) saturated or aromatic hydrocarbon liquid with (E) titanium tetrachloride so as to give the suspension of the (B) magnesium halide-supported titanium procatalyst in the (C) saturated or aromatic hydrocarbon liquid;

further comprising a preliminary step of preparing the (D) solid particulate consisting essentially of 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 consisting essentially of magnesium halide in the (C) saturated or aromatic hydrocarbon liquid; and

wherein the (D) solid particulate has 0 mol% to <5 mol% of an active halide impurity.

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 magnesium halide-supported titanium procatalyst prepared by contacting (D) a solid particulate consisting essentially of magnesium halide with (E) titanium tetrachloride in (C) a saturated or aromatic hydrocarbon liquid, wherein the (D) solid particulate consisting essentially of 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 consisting essentially of magnesium halide in the (C) saturated or aromatic hydrocarbon liquid; wherein the magnesium halide-supported titanium procatalyst is free of aluminum halides; wherein the (B) magnesium halide-supported titanium procatalyst is free of Al; and

wherein the (D) solid particulate has 0 mol% to <5 mol% of an active halide impurity.

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.