The inventive procatalyst may be prepared in a one-pot syntheses. The inventive procatalyst may be used to prepare a new magnesium halide-supported titanium catalyst, which has 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). The technical solution enables a method of polymerizing an olefin using a combination of a Ziegler-Natta catalyst and an unsupported molecular catalyst in a same reactor at the same time to give a polyolefin product with improvement in polyolefin density, polyolefin molecular weight, comonomer distribution, or short chain branching distribution. Also provided is the polyolefin product. 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 combination of (pro)catalysts.

[0012a] In one aspect, the present disclosure refers to a method of polymerizing an olefin using a Ziegler-Natta catalyst and an unsupported molecular catalyst in a same reactor at the same time, the method comprising simultaneously contacting at least one polymerizable olefin in the reactor with the Ziegler-Natta catalyst and the unsupported molecular catalyst in a saturated or aromatic hydrocarbon liquid under effective conditions to give a polyolefin product comprising a mixture of a first polyolefin made by a first polymerization reaction catalyzed by the Ziegler-Natta catalyst and a second polyolefin made by a second polymerization reaction catalyzed by the unsupported molecular catalyst; wherein the Ziegler-Natta catalyst is either an enhanced Ziegler-Natta catalyst that comprises a product of a first activation reaction of (A) a hydrocarbylaluminoxane that is a modified methylaluminoxane (MMAO) and (B) a magnesium halide-supported titanium procatalyst in (C) a saturated or aromatic hydrocarbon liquid; or the Ziegler-Natta catalyst is a magnesium halide-supported titanium catalyst, wherein the magnesium halide-supported titanium catalyst is a product of a second activation reaction of (B) a magnesium halide-supported titanium procatalyst with a trialkylaluminum compound; 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 unsupported molecular catalyst comprises a product of a third activation reaction of an unsupported molecular ligand-metal complex procatalyst

with (A) a hydrocarbylaluminoxane that is a modified methylaluminoxane (MMAO); 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; wherein said contacting comprises: (i) adding a first feed of the Ziegler-Natta catalyst and a second feed of the unsupported molecular catalyst into the reactor, which contains the at least one polymerizable olefin, wherein the first and second feeds are different; (ii) adding a first feed of the Ziegler-Natta catalyst into the reactor and preparing the unsupported molecular catalyst *in situ* in the reactor, wherein the unsupported molecular catalyst is prepared *in situ* in the reactor by adding a third feed containing the unsupported molecular ligand-metal complex procatalyst and a fourth feed containing the (A) hydrocarbylaluminoxane that is a modified methylaluminoxane (MMAO) into the reactor, which contains the at least one polymerizable olefin, wherein the first and third feeds are the same or different and wherein the first and fourth feeds are the same or different, with the proviso that the third and fourth feeds are different; (iii) adding a second feed of the unsupported molecular catalyst into the reactor and preparing the Ziegler-Natta catalyst *in situ* in the reactor, wherein the Ziegler-Natta catalyst is prepared *in situ* in the reactor by adding a fifth feed containing the suspension of the (B) magnesium halide-supported titanium procatalyst in the (C) saturated or aromatic hydrocarbon liquid and free of (lacking) the trialkylaluminum and a sixth feed containing the (A) hydrocarbylaluminoxane that is a modified methylaluminoxane (MMAO) and containing the trialkylaluminum, into the reactor, which contains the at least one polymerizable olefin, wherein the second and fifth feeds are the same or different and wherein the second and sixth feeds are the same or different, with the proviso that the fifth and sixth feeds are different; or (iv) adding a seventh feed of the suspension of the (B) magnesium halide-supported titanium procatalyst in the (C) saturated or aromatic hydrocarbon liquid and the unsupported molecular ligand-metal complex procatalyst and an eighth feed of the (A) hydrocarbylaluminoxane that is a modified methylaluminoxane (MMAO) or a mixture of the (A) hydrocarbylaluminoxane that is a modified methylaluminoxane (MMAO) and the trialkylaluminum into the reactor, which contains the at least one polymerizable olefin, wherein the seventh and eighth feeds are different; and wherein said first or second activation reaction further comprises contacting at least one of the (B) magnesium halide-supported titanium procatalyst with (G) an organoborate or (H) an organoboron; and/or the third activation reaction further comprises

contacting the unsupported molecular ligand-metal complex procatalyst with (G) an organoborate or (H) an organoboron.

[0012b] In another aspect, the present disclosure refers to a polymerization method of polymerizing an olefin using an enhanced Ziegler-Natta catalyst and an unsupported or supported molecular catalyst in solution-phase process in a same reactor at the same time, wherein the enhanced Ziegler-Natta catalyst comprises a product of a first activation reaction of (A) a hydrocarbylaluminoxane that is a modified methylaluminoxane (MMAO) and (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 in the (C) saturated or aromatic hydrocarbon liquid so as to give the (B) magnesium halide-supported titanium procatalyst; and wherein the unsupported or supported molecular catalyst comprises a product of a third activation reaction of an unsupported or supported molecular ligand-metal complex procatalyst with (A) a hydrocarbylaluminoxane that is a modified methylaluminoxane (MMAO) and/or (G) an organoborate or (H) an organoboron; the method comprising simultaneously contacting at least one polymerizable olefin in the solution phase in the reactor with the enhanced Ziegler-Natta catalyst and the unsupported or supported molecular catalyst in a saturated or aromatic hydrocarbon liquid under effective conditions to give a polyolefin product comprising a mixture of a third polyolefin made by a third polymerization reaction catalyzed by the Ziegler-Natta catalyst and a fourth polyolefin made by a fourth polymerization reaction catalyzed by the unsupported or supported molecular catalyst; 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; wherein said contacting comprises: (i) adding a first feed of the Ziegler-Natta catalyst and a second feed of the unsupported molecular catalyst into the reactor, which contains the at least one polymerizable olefin, wherein the first and second feeds are different; (ii) adding a first feed of the Ziegler-Natta catalyst into the reactor and preparing the unsupported molecular catalyst *in situ* in the reactor, wherein the unsupported molecular catalyst is prepared *in situ* in the reactor by adding a third feed containing the unsupported molecular ligand-metal complex procatalyst and a fourth feed containing the (A)

hydrocarbylaluminoxane that is a modified methylaluminoxane (MMAO) into the reactor, which contains the at least one polymerizable olefin, wherein the first and third feeds are the same or different and wherein the first and fourth feeds are the same or different, with the proviso that the third and fourth feeds are different; (iii) adding a second feed of the unsupported molecular catalyst into the reactor and preparing the Ziegler-Natta catalyst *in situ* in the reactor, wherein the Ziegler-Natta catalyst is prepared *in situ* in the reactor by adding a fifth feed containing the suspension of the (B) magnesium halide-supported titanium procatalyst in the (C) saturated or aromatic hydrocarbon liquid and free of (lacking) the trialkylaluminum and a sixth feed containing the (A) hydrocarbylaluminoxane that is a modified methylaluminoxane (MMAO) and containing the trialkylaluminum, into the reactor, which contains the at least one polymerizable olefin, wherein the second and fifth feeds are the same or different and wherein the second and sixth feeds are the same or different, with the proviso that the fifth and sixth feeds are different; or (iv) adding a seventh feed of the suspension of the (B) magnesium halide-supported titanium procatalyst in the (C) saturated or aromatic hydrocarbon liquid and the unsupported molecular ligand-metal complex procatalyst and an eighth feed of the (A) hydrocarbylaluminoxane that is a modified methylaluminoxane (MMAO) or a mixture of the (A) hydrocarbylaluminoxane that is a modified methylaluminoxane (MMAO) and the trialkylaluminum into the reactor, which contains the at least one polymerizable olefin, wherein the seventh and eighth feeds are different; and wherein said first or second activation reaction further comprises contacting at least one of the (B) magnesium halide-supported titanium procatalyst with (G) an organoborate or (H) an organoboron; and/or the third activation reaction further comprises contacting the unsupported molecular ligand-metal complex procatalyst with (G) an organoborate or (H) an organoboron.

DETAILED DESCRIPTION

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

[0014] Aspect 1. A method of polymerizing an olefin using a Ziegler-Natta catalyst and an unsupported molecular catalyst in a same reactor at the same time, the method comprising simultaneously contacting at least one polymerizable olefin in the reactor with the Ziegler-Natta catalyst and the unsupported molecular catalyst in a saturated or aromatic hydrocarbon liquid under effective conditions to give a polyolefin product comprising a mixture of a first polyolefin made by a first polymerization reaction catalyzed by the Ziegler-Natta catalyst and a second polyolefin made by a second polymerization reaction catalyzed by the unsupported molecular catalyst.

[0015] Aspect 2. The method of aspect 1 wherein the Ziegler-Natta catalyst is either an enhanced Ziegler-Natta catalyst that consists essentially of a product of a first activation reaction of (A) a hydrocarbylaluminoxane and (B) a magnesium halide-supported titanium procatalyst in (C) a saturated or aromatic hydrocarbon liquid; or the Ziegler-Natta catalyst is a magnesium halide-supported titanium catalyst, wherein the magnesium halide-supported titanium catalyst is a product of a second activation reaction of (B) a magnesium halide-supported titanium procatalyst with a trialkylaluminum compound; 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

CLAIMS

1. A method of polymerizing an olefin using a Ziegler-Natta catalyst and an unsupported molecular catalyst in a same reactor at the same time, the method comprising simultaneously contacting at least one polymerizable olefin in the reactor with the Ziegler-Natta catalyst and the unsupported molecular catalyst in a saturated or aromatic hydrocarbon liquid under effective conditions to give a polyolefin product comprising a mixture of a first polyolefin made by a first polymerization reaction catalyzed by the Ziegler-Natta catalyst and a second polyolefin made by a second polymerization reaction catalyzed by the unsupported molecular catalyst;

wherein the Ziegler-Natta catalyst is either an enhanced Ziegler-Natta catalyst that comprises a product of a first activation reaction of (A) a hydrocarbylaluminoxane that is a modified methylaluminoxane (MMAO) and (B) a magnesium halide-supported titanium procatalyst in (C) a saturated or aromatic hydrocarbon liquid; or the Ziegler-Natta catalyst is a magnesium halide-supported titanium catalyst, wherein the magnesium halide-supported titanium catalyst is a product of a second activation reaction of (B) a magnesium halide-supported titanium procatalyst with a trialkylaluminum compound; 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 unsupported molecular catalyst comprises a product of a third activation reaction of an unsupported molecular ligand-metal complex procatalyst with (A) a hydrocarbylaluminoxane that is a modified methylaluminoxane (MMAO);

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;

wherein said contacting comprises: (i) adding a first feed of the Ziegler-Natta catalyst and a second feed of the unsupported molecular catalyst into the reactor, which contains the at least one polymerizable olefin, wherein the first and second feeds are different; (ii) adding a first feed of the Ziegler-Natta catalyst into the reactor and preparing the unsupported molecular catalyst *in situ* in the reactor, wherein the unsupported molecular catalyst is prepared *in situ* in the reactor by adding a third feed containing the unsupported molecular ligand-metal complex procatalyst and a fourth feed containing the (A) hydrocarbylaluminoxane that is a modified methylaluminoxane (MMAO) into the

reactor, which contains the at least one polymerizable olefin, wherein the first and third feeds are the same or different and wherein the first and fourth feeds are the same or different, with the proviso that the third and fourth feeds are different; (iii) adding a second feed of the unsupported molecular catalyst into the reactor and preparing the Ziegler-Natta catalyst *in situ* in the reactor, wherein the Ziegler-Natta catalyst is prepared *in situ* in the reactor by adding a fifth feed containing the suspension of the (B) magnesium halide-supported titanium procatalyst in the (C) saturated or aromatic hydrocarbon liquid and free of (lacking) the trialkylaluminum and a sixth feed containing the (A) hydrocarbylaluminoxane that is a modified methylaluminoxane (MMAO) and containing the trialkylaluminum, into the reactor, which contains the at least one polymerizable olefin, wherein the second and fifth feeds are the same or different and wherein the second and sixth feeds are the same or different, with the proviso that the fifth and sixth feeds are different; or (iv) adding a seventh feed of the suspension of the (B) magnesium halide-supported titanium procatalyst in the (C) saturated or aromatic hydrocarbon liquid and the unsupported molecular ligand-metal complex procatalyst and an eighth feed of the (A) hydrocarbylaluminoxane that is a modified methylaluminoxane (MMAO) or a mixture of the (A) hydrocarbylaluminoxane that is a modified methylaluminoxane (MMAO) and the trialkylaluminum into the reactor, which contains the at least one polymerizable olefin, wherein the seventh and eighth feeds are different; and

wherein said first or second activation reaction further comprises contacting at least one of the (B) magnesium halide-supported titanium procatalyst with (G) an organoborate or (H) an organoboron; and/or the third activation reaction further comprises contacting the unsupported molecular ligand-metal complex procatalyst with (G) an organoborate or (H) an organoboron.

2. The method of claim 1 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.

3. The method of claim 1 or 2 wherein: (i) the (B) magnesium halide-supported titanium procatalyst is free of Al (molar ratio Al/Mg = 0); or (ii) the (B) magnesium halide-

supported titanium procatalyst has molar ratio Al/Mg from > 0 to < 0.05 ; or (iii) the magnesium halide of the (B) magnesium halide-supported titanium procatalyst is magnesium chloride; or (iv) the magnesium halide of the (B) 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).

4. The method of any one of claims 1 to 3 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 BET Surface Area Method.

5. The method of any one of claims 1 to 4 wherein the (C) saturated or aromatic hydrocarbon liquid is: (i) a saturated hydrocarbon liquid; or (ii) an aromatic hydrocarbon liquid; or (iii) a mixture of saturated hydrocarbon and aromatic hydrocarbon liquids.

6. The method of any one of claims 1 to 5 wherein the unsupported molecular ligand-metal complex procatalyst comprises an unsupported form of: (i) a cyclopentadienyl ligand-metal complex procatalyst; (ii) a cyclopentadienyl-free ligand-metal complex procatalyst; or (iii) both (i) and (ii).

7. A polymerization method of polymerizing an olefin using an enhanced Ziegler-Natta catalyst and an unsupported or supported molecular catalyst in solution-phase process in a same reactor at the same time, wherein the enhanced Ziegler-Natta catalyst comprises a product of a first activation reaction of (A) a hydrocarbylaluminoxane that is a modified methylaluminoxane (MMAO) and (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 in the (C) saturated or aromatic hydrocarbon liquid so as to give the (B) magnesium halide-supported titanium procatalyst; and wherein the unsupported or supported molecular catalyst comprises a product of a third activation reaction of an unsupported or supported molecular ligand-metal complex procatalyst with (A) a hydrocarbylaluminoxane that is a modified methylaluminoxane (MMAO) and/or (G) an organoborate or (H) an organoboron; the method comprising simultaneously contacting at least one polymerizable olefin in the solution phase in the reactor with the enhanced Ziegler-Natta catalyst and the unsupported or supported molecular catalyst in a saturated or aromatic hydrocarbon liquid under

effective conditions to give a polyolefin product comprising a mixture of a third polyolefin made by a third polymerization reaction catalyzed by the Ziegler-Natta catalyst and a fourth polyolefin made by a fourth polymerization reaction catalyzed by the unsupported or supported molecular catalyst; 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

wherein said contacting comprises: (i) adding a first feed of the Ziegler-Natta catalyst and a second feed of the unsupported molecular catalyst into the reactor, which contains the at least one polymerizable olefin, wherein the first and second feeds are different; (ii) adding a first feed of the Ziegler-Natta catalyst into the reactor and preparing the unsupported molecular catalyst *in situ* in the reactor, wherein the unsupported molecular catalyst is prepared *in situ* in the reactor by adding a third feed containing the unsupported molecular ligand-metal complex procatalyst and a fourth feed containing the (A) hydrocarbylaluminoxane that is a modified methylaluminoxane (MMAO) into the reactor, which contains the at least one polymerizable olefin, wherein the first and third feeds are the same or different and wherein the first and fourth feeds are the same or different, with the proviso that the third and fourth feeds are different; (iii) adding a second feed of the unsupported molecular catalyst into the reactor and preparing the Ziegler-Natta catalyst *in situ* in the reactor, wherein the Ziegler-Natta catalyst is prepared *in situ* in the reactor by adding a fifth feed containing the suspension of the (B) magnesium halide-supported titanium procatalyst in the (C) saturated or aromatic hydrocarbon liquid and free of (lacking) the trialkylaluminum and a sixth feed containing the (A) hydrocarbylaluminoxane that is a modified methylaluminoxane (MMAO) and containing the trialkylaluminum, into the reactor, which contains the at least one polymerizable olefin, wherein the second and fifth feeds are the same or different and wherein the second and sixth feeds are the same or different, with the proviso that the fifth and sixth feeds are different; or (iv) adding a seventh feed of the suspension of the (B) magnesium halide-supported titanium procatalyst in the (C) saturated or aromatic hydrocarbon liquid and the unsupported molecular ligand-metal complex procatalyst and an eighth feed of the (A) hydrocarbylaluminoxane that is a modified methylaluminoxane (MMAO) or a mixture of the (A) hydrocarbylaluminoxane that is a modified methylaluminoxane (MMAO) and the

trialkylaluminum into the reactor, which contains the at least one polymerizable olefin, wherein the seventh and eighth feeds are different; and

wherein said first or second activation reaction further comprises contacting at least one of the (B) magnesium halide-supported titanium procatalyst with (G) an organoborate or (H) an organoboron; and/or the third activation reaction further comprises contacting the unsupported molecular ligand-metal complex procatalyst with (G) an organoborate or (H) an organoboron.