ZIEGLER-NATTA (PRO)CATALYST SYSTEMS MADE WITH AZAHETEROCYCLIC COMPOUND

FIELD

[0001] Ziegler-Natta (pro)catalyst systems made with an external electron donor compound, methods of synthesis of same, methods of olefin polymerization using same, and polyolefin polymers made thereby.

INTRODUCTION

[0002] Patent application publications and patents in or about the field include EP 0 136 163; EP 0 193 280; EP 0 208 524; EP 0 506 704; JP 61-055103 A; JP 61-268704 A; JP 63-308033 A; KR 1994-026081 A; KR 1999-010007 A; US 4,107,413; US 4,136,243; US 4,252,670; US 4,263,168; US 4,301,029; US 4,324,691; US 4,381,252; US 4,410,672; US 4,330,649; US 4,381,252; US 4,468,477; US 4,471,066; US 4,477,639; US 4,496,660; US 4,518,706; US 4,716,206; US 4,816,433; US 4,826,794; US 4,829,037; US 4,847,227; US 4,496,660; US 4,826,794; US 4,970,186; US 5,064,799; US 5,106,807; US 5,106,926; US 5,118,768; US 5,130,284; US 5,134,209; US 5,139,985; US 5,164,352; US 5,229,477; US 5,270,276; US 5,459,116; US 5,543,458; US 5,550,194; US 5,633,419; US 6,100,351; US 6,228,792 B1; US 6,329,315 B1; US 6,436,864 B1; US 6,958,378 B2; US 7,153,803 B2; US 7,560,521 B2; US 7,618,913 B2; US 7,871,952 B1; US 8,993,693 B2; US 9,487,608 B2; US 9,988,475 B2; US 2007/0259777 A1; US 2011/0082268 A1; US 2011/0082270 A1; US 2013/0137827 A1; US 2019/0002610 A1; WO 99/20694; WO 00/46025 A1; and WO 2019/241044 A1.

SUMMARY

[0003] We discovered an external electron donor-modified Ziegler-Natta procatalyst system, an external electron donor compound-modified Ziegler-Natta catalyst system made therefrom, methods of making same, methods of polymerizing olefin monomers using the catalyst system, and polyolefin polymers made thereby.

[0003a] In one aspect, the present disclosure provides a procatalyst system suitable for making an olefin polymerization catalyst and consisting essentially of a blend of (A) a pre-made solid procatalyst and (B) an azaheterocycle;

wherein the (A) pre-made solid procatalyst consists essentially of a titanium compound, magnesium chloride solids, and optionally a silica;

wherein the magnesium chloride solids consist essentially of $MgCl_2$ and, optionally, at least one of a cyclic (C_2-C_6)ether, a (C_1-C_6)alcohol, or a hydroxyl-substituted cyclic (C_3-C_7)ether;

wherein the procatalyst system is free of any other electron donor organic compound, wherein the expression “consisting essentially of” means that the procatalyst system, blend and constituent (A) is free of a nitrogen atom-containing organic compound that is not the (B)

azaheterocycle and free of an oxygen-containing organic compound that is not the optional at least one of a cyclic (C_2-C_6)ether, a (C_1-C_6)alcohol, or a hydroxyl-substituted cyclic (C_3-C_7)ether and free of an activator which would otherwise react with the (A) pre-made solid catalyst and make the catalyst system; and wherein the expression “free of any other electron donor organic compound” means that it is free of an organic compound containing at least one heteroatom selected from N, O, S, P that is not the (B) azaheterocycle or the at least one of a cyclic (C_2-C_6)ether, a (C_1-C_6)alcohol, or a hydroxyl-substituted cyclic (C_3-C_7)ether.

[0003b] In another aspect, the present disclosure provides a method of synthesizing a procatalyst system, the method comprising drying a mixture consisting essentially of a solution and, optionally, a silica, and being free of (B) an azaheterocycle and any other electron donor organic compound, wherein the solution consists essentially of a titanium compound, magnesium chloride, and, optionally, at least one of a cyclic (C_2-C_6)ether and a (C_1-C_6)alcohol mixed in a hydrocarbon solvent; thereby removing the hydrocarbon solvent from the mixture and crystallizing the magnesium chloride so as to give (A) a pre-made solid procatalyst; and contacting the (A) pre-made solid procatalyst with the (B) azaheterocycle; thereby making the blend of the procatalyst system as defined herein.

[0003c] In another aspect, the present disclosure provides a method of making a catalyst system suitable for polymerizing an olefin, the method comprising contacting the procatalyst system as defined herein, or the procatalyst system made by the method as defined herein, with an activating effective amount of (C) an activator, thereby making the catalyst system; wherein the catalyst system is free of the any other electron donor organic compound and is suitable for polymerizing an olefin.

[0003d] In another aspect, the present disclosure provides a method of making a catalyst system suitable for polymerizing an olefin, the method comprising contacting (A) a pre-made solid procatalyst, (B) an azaheterocycle, and an activating effective amount of (C) an activator, thereby making the catalyst system; wherein the (A) pre-made solid procatalyst consists essentially of a titanium compound, magnesium chloride solids, and optionally a silica; wherein the magnesium chloride solids consist essentially of $MgCl_2$ and, optionally, at least one of a cyclic (C_2-C_6)ether, a (C_1-C_6)alcohol, or a hydroxyl-substituted cyclic (C_3-C_7)ether; wherein the catalyst system is free of the any other electron donor organic compound and is suitable for polymerizing an olefin; wherein the expression “consisting essentially of” means that the constituent (A) is free of a nitrogen atom-containing organic compound that is not the (B) azaheterocycle and free of an oxygen-containing organic compound that is not the optional at least one of a cyclic (C_2-C_6)ether, a (C_1-C_6)alcohol, or a hydroxyl-substituted cyclic (C_3-C_7)ether and free of an activator which would otherwise react with the (A) pre-made solid

catalyst and make the catalyst system; and wherein the expression “free of any other electron donor organic compound” means that it is free of an organic compound containing at least one heteroatom selected from N, O, S, P that is not the (B) azaheterocycle or the at least one of a cyclic (C_2-C_6)ether, a (C_1-C_6)alcohol, or a hydroxyl-substituted cyclic (C_3-C_7)ether.

[0003e] In another aspect, the present disclosure provides a catalyst system made by the method as defined herein.

[0003f] In another aspect, the present disclosure provides a method of synthesizing a polyolefin polymer, the method comprising contacting at least one olefin monomer with the catalyst system as defined herein under effective polymerization conditions in a polymerization reactor, thereby making the polyolefin polymer.

BRIEF DESCRIPTION OF THE DRAWINGS

[0004] Pursuant to 37 C.F.R. §§ 1.58 and 1.84(d), Tables 1C, 2C, 3C, 4C, 5C, 6C, 7C, 8C, 9C, 10, and 11 are shown in landscape orientation in Figures 1 to 11, respectively.

[0005] Figure (FIG.) 1 is Table 1C containing improved comonomer content distribution (iCCD) results showing effects of EEDC-1 on PCAT-1.

[0006] FIG. 2 is Table 2C containing iCCD results showing effects of EEDC-1 on PCAT-1 that has been pre-treated with the EEDC-1.

[0007] FIG. 3 is Table 3C containing iCCD results showing effects of addition mode of components of catalyst system.

[0008] FIG. 4 is Table 4C containing iCCD results showing effects of molecular structure of EEDC on procatalyst system and catalyst system.

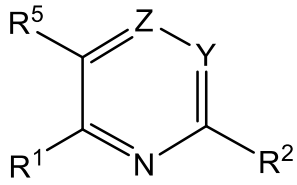
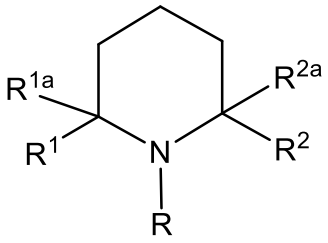
CLAIMS

1. A procatalyst system suitable for making an olefin polymerization catalyst and consisting essentially of a blend of (A) a pre-made solid procatalyst and (B) an azaheterocycle;

wherein the (A) pre-made solid procatalyst consists essentially of a titanium compound, magnesium chloride solids, and optionally a silica;

wherein the magnesium chloride solids consist essentially of $MgCl_2$ and, optionally, at least one of a cyclic (C_2-C_6)ether, a (C_1-C_6)alcohol, or a hydroxyl-substituted cyclic (C_3-C_7)ether; and

wherein the procatalyst system is free of any other electron donor organic compound.

2. The procatalyst system of claim 1 wherein the (B) azaheterocycle is -an aromatic azaheterocycle of formula (I):  (I) or a saturated azaheterocycle of formula (II):  (II); wherein Y is N or C-R^3; wherein Z is N or C-R^4; wherein R is H or an unsubstituted (C_1-C_{10})alkyl; wherein each of R^1, R^2, R^3, R^4, R^5, R^{1a}, and R^{2a} independently is H, a halogen atom, -OH, an unsubstituted (C_1-C_{10})alkyl group, a halo-substituted (C_1-C_{10})alkyl group, or a hydroxyl-substituted (C_1-C_{10})alkyl group, or formula (I) is defined by any one of limitations (i) to (iv): (i) R^1 and R^5 are taken together to be a divalent group that is 1,3-butadien-1,4-diyl, (ii) when Y is C-R^3, R^2 and R^3 are taken together to be a divalent group that is 1,3-butadien-1,4-diyl, (iii) wherein in formula (I) when Z is C-R^4, R^4 and R^5 are taken together to be a divalent group that is 1,3-butadien-1,4-diyl, or (iv) both limitation (i) and (ii). In some embodiments at least one of R^1, R^2, R^3, R^4, R^5, R^{1a}, and R^{2a}, alternatively at least R^1 is a halogen atom, -OH, an unsubstituted (C_1-C_{10})alkyl group, a halo-substituted (C_1-C_{10})alkyl group, or a hydroxyl-substituted (C_1-C_{10})alkyl group; alternatively at least one of R^1, R^2, R^3, R^4, R^5, R^{1a}, and R^{2a}, alternatively at least R^1 is a halogen atom or -OH; alternatively at least one of R^1, R^2, R^3, R^4, R^5, R^{1a}, and R^{2a}, alternatively at least R^1 is an unsubstituted (C_1-C_{10})alkyl group, a halo-substituted (C_1-C_{10})alkyl group, or a hydroxyl-substituted (C_1-C_{10})alkyl group; alternatively at least one of R^1, R^2, R^3, R^4, R^5,

R^{1a}, and R^{2a}, alternatively at least R^1 is an unsubstituted (C_1-C_{10})alkyl group.

3. The procatalyst system of any one of claims 1 to 2 wherein the magnesium chloride solids are free of the at least one of a cyclic (C_2-C_6)ether, a (C_1-C_6)alcohol, or a hydroxyl-substituted cyclic (C_3-C_7)ether.

4. The procatalyst system of any one of claims 1 to 2 wherein the magnesium chloride, solids consist essentially of $MgCl_2$ and the at least one of a cyclic (C_2-C_6)ether, a (C_1-C_6)alcohol, or a hydroxyl-substituted cyclic (C_3-C_7)ether

5. The procatalyst system of any one of claims 1 to 4 wherein the titanium compound is at least one compound of formula (III): TiX_4 (III), wherein each X independently is Cl, Br, I, or a (C_1-C_6)alkoxy.

6. The procatalyst system of any one of claims 1 to 5 further consisting essentially of a ligand-metal complex of formula (IV): MX_4 (IV), wherein M is Hf or Zr and each X independently is Cl, Br, I, or a (C_1-C_6)alkoxy.

7. A method of synthesizing a procatalyst system, the method comprising drying a mixture consisting essentially of a solution and, optionally, a silica, and being free of (B) an azaheterocycle and any other electron donor organic compound, wherein the solution consists essentially of a titanium compound, magnesium chloride, and, optionally, at least one of a cyclic (C_2-C_6)ether and a (C_1-C_6)alcohol mixed in a hydrocarbon solvent; thereby removing the hydrocarbon solvent from the mixture and crystallizing the magnesium chloride so as to give (A) a pre-made solid procatalyst; and contacting the (A) pre-made solid procatalyst with the (B) azaheterocycle; thereby making the blend of the procatalyst system of any one of claims 1 to 6.

8. A method of making a catalyst system suitable for polymerizing an olefin, the method comprising contacting the procatalyst system of any one of claims 1 to 6, or the procatalyst system made by the method of claim 7, with an activating effective amount of (C) an activator, thereby making the catalyst system; wherein the catalyst system is free of the any other electron donor organic compound and is suitable for polymerizing an olefin.

9. A method of making a catalyst system suitable for polymerizing an olefin, the method comprising contacting (A) a pre-made solid procatalyst, (B) an azaheterocycle, and an activating effective amount of (C) an activator, thereby making the catalyst system; wherein the (A) pre-made solid procatalyst consists essentially of a titanium compound, magnesium chloride solids, and optionally a silica; wherein the magnesium chloride solids consist essentially of $MgCl_2$ and, optionally, at least one of a cyclic (C_2-C_6)ether, a (C_1-C_6)alcohol, or a hydroxyl-substituted cyclic (C_3-C_7)ether; and wherein the catalyst system is free of the any other electron donor organic compound and is suitable for polymerizing an olefin.

10. A catalyst system made by the method of claim 8 or claim 9.

11. A method of synthesizing a polyolefin polymer, the method comprising contacting at least one olefin monomer with the catalyst system of claim 10 under effective polymerization conditions in a polymerization reactor, thereby making the polyolefin polymer.