ZIEGLER-NATTA (PRO)CATALYST SYSTEMS MADE WITH (MULTI-ALKOXY)SILANE 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 US4242479; US4522930; US4927797; US5869418; US7196152B2; US7371806B2; US10113018B2; CA2510679C; CN103304869B; CN108586640A; EP0731114A1; EP1017493A1; US20180030179A1; WO2002038624A1; WO2005058982; WO2009027270A1; WO2009148487A1; and WO2014102813A1. See also Iidar Salakhov et al., Polypropylene synthesis in liquid monomer with titanium-magnesium catalyst: effect of different (multi-alkoxy)silanes as external donors, Journal of Polymer Research, June 2019, 26(6). DOI: 10.1007/s10965-019-1794-5.

SUMMARY

[0003] The present disclosure relates to 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 relates to a procatalyst system suitable for making an olefin polymerization catalyst and comprising a blend of (A) a pre-made solid procatalyst and (B) a (multi-alkoxy)silane; 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 $MgCl_2$ formed in the presence of tetrahydrofuran; and wherein the procatalyst system is free of any other electron donor organic compound.

[0003b] In another aspect, the present disclosure relates to 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) a (multi-alkoxy)silane and any other electron donor organic compound, wherein the solution consists essentially of a titanium compound, magnesium chloride formed in the presence of tetrahydrofuran 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) (multi-alkoxy)silane; thereby making the blend of the procatalyst system as disclosed herein.

[0003c] In another aspect, the present disclosure relates to a method of making a catalyst system suitable for polymerizing an olefin, the method comprising contacting the procatalyst system as disclosed herein, or the procatalyst system made by the method as disclosed 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 relates to a method of making a catalyst system suitable for polymerizing an olefin, the method comprising simultaneously or sequentially contacting an activating effective amount of (C) an activator, (B) a (multi-alkoxy)silane, and (A) a pre-made solid procatalyst, 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 $MgCl_2$ formed in the presence of tetrahydrofuran; and wherein the catalyst system is free of the any other electron donor organic compound and is suitable for polymerizing an olefin.

[0003e] In another aspect, the present disclosure relates to a catalyst system comprising the procatalyst system as disclosed herein, and (C) an activator.

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

DETAILED DESCRIPTION

[0004] 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.

[0005] A procatalyst system consisting essentially of a blend of a pre-made solid procatalyst and a (multi-alkoxy)silane. The procatalyst system is a Ziegler-Natta-type procatalyst system that is suitable for making a Ziegler-Natta-type olefin polymerization catalyst, which is made by contacting the procatalyst system with an activator. Based upon how the (multi-alkoxy)silane is used and how it is formulated with the pre-made solid procatalyst in the procatalyst system, the (multi-alkoxy)silane functions as the external electron donor compound (EEDC) in the procatalyst system. The pre-made solid procatalyst consists essentially of a titanium compound, magnesium chloride solids, and optionally a silica. The magnesium chloride solids consist essentially of $MgCl_2$ and 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. The procatalyst system is free of any other electron donor organic compound. The procatalyst system, when

CLAIMS

1. A procatalyst system suitable for making an olefin polymerization catalyst and comprising a blend of (A) a pre-made solid procatalyst and (B) a (multi-alkoxy)silane; 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 $MgCl_2$ formed in the presence of tetrahydrofuran; and wherein the procatalyst system is free of any other electron donor organic compound.

2. The procatalyst system of claim 1 wherein the (B) (multi-alkoxy)silane is of formula (I): $R^1{}_mH_nSi(OR^2)_{4-m-n}$ (I); wherein subscript m is 0 and subscript n is 0, 1, or 2 or wherein subscript m is 1 and subscript n is 0 or 1 or wherein subscript m is 2 and subscript n is 0; wherein R^1 is an unsubstituted $(C_1\text{-}C_{20})$alkyl group, an unsubstituted $(C_3\text{-}C_{12})$cycloalkyl group, a $(C_1\text{-}C_{10})$alkyl-substituted $(C_3\text{-}C_{12})$cycloalkyl group, a $(C_3\text{-}C_{10})$cycloalkyl-substituted $(C_1\text{-}C_{10})$alkyl group, an unsubstituted $(C_6\text{-}C_{12})$aryl group, a $(C_1\text{-}C_{10})$alkyl-substituted $(C_6\text{-}C_{10})$aryl group, or an unsubstituted $(C_7\text{-}C_{20})$aralkyl group; and wherein R^2 is an unsubstituted $(C_1\text{-}C_{20})$alkyl group, an unsubstituted $(C_3\text{-}C_{12})$cycloalkyl group, a $(C_1\text{-}C_{10})$alkyl-substituted $(C_3\text{-}C_{12})$cycloalkyl group, a $(C_3\text{-}C_{10})$cycloalkyl-substituted $(C_1\text{-}C_{10})$alkyl group, or an unsubstituted $(C_7\text{-}C_{20})$aralkyl group.

3. The procatalyst system of any one of claims 1 to 2 wherein the (B) (multi-alkoxy)silane is of formula (Ia): $R^1{}_mSi(OR^2)_{4-m-n}$ (Ia); wherein subscript m is 0, 1, or 2; wherein R^1 is an unsubstituted $(C_1\text{-}C_{20})$alkyl group, an unsubstituted $(C_3\text{-}C_{12})$cycloalkyl group, a $(C_1\text{-}C_{10})$alkyl-substituted $(C_3\text{-}C_{12})$cycloalkyl group, a $(C_3\text{-}C_{10})$cycloalkyl-substituted $(C_1\text{-}C_{10})$alkyl group, an unsubstituted $(C_6\text{-}C_{12})$aryl group, a $(C_1\text{-}C_{10})$alkyl-substituted $(C_6\text{-}C_{10})$aryl group, or an unsubstituted $(C_7\text{-}C_{20})$aralkyl group; and wherein R^2 is an unsubstituted $(C_1\text{-}C_{20})$alkyl group, an unsubstituted $(C_3\text{-}C_{12})$cycloalkyl group, a $(C_1\text{-}C_{10})$alkyl-substituted $(C_3\text{-}C_{12})$cycloalkyl group, a $(C_3\text{-}C_{10})$cycloalkyl-substituted $(C_1\text{-}C_{10})$alkyl group, or an unsubstituted $(C_7\text{-}C_{20})$aralkyl group.

4. The procatalyst system of any one of claims 1 to 3 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 $(C_1\text{-}C_{12})$alkoxy, alternatively a $(C_1\text{-}C_6)$alkoxy.

5. The procatalyst system of any one of claims 1 to 4 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 $(C_1\text{-}C_6)$alkoxy.

6. The procatalyst system of claim 1 wherein the procatalyst system is free of an activator,

which would otherwise react with the (A) pre-made solid procatalyst and make the catalyst system.

7. The procatalyst system of claim 1 wherein the procatalyst system, and the catalyst system made therefrom, is free of a nitrogen atom-containing compound that is an azaheterocycle.

8. The procatalyst system of claim 1 wherein the blend is free of an activator, which would otherwise react with the (A) pre-made solid procatalyst and make the catalyst system.

9. The procatalyst system of claim 1 wherein the blend is free of a nitrogen atom-containing compound that is an azaheterocycle.

10. 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) a (multi-alkoxy)silane and any other electron donor organic compound, wherein the solution consists essentially of a titanium compound, magnesium chloride formed in the presence of tetrahydrofuran 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) (multi-alkoxy)silane; thereby making the blend of the procatalyst system of any one of claims 1 to 9.

11. 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 9, or the procatalyst system made by the method of claim 10, 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.

12. A method of making a catalyst system suitable for polymerizing an olefin, the method comprising simultaneously or sequentially contacting an activating effective amount of (C) an activator, (B) a (multi-alkoxy)silane, and (A) a pre-made solid procatalyst, 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 $MgCl_2$ formed in the presence of tetrahydrofuran; and wherein the catalyst system is free of the any other electron donor organic compound and is suitable for polymerizing an olefin.

13. A catalyst system comprising the procatalyst system of any one of claims 1 to 9, and (C) an activator.

14. A method of synthesizing a polyolefin polymer, the method comprising contacting at least one olefin monomer with the catalyst system of claim 13 under effective polymerization conditions in a polymerization reactor, thereby making the polyolefin polymer.