SUMMARY

[0010] We provide modified, titanium-based, spray-dried Ziegler-Natta (pro)catalyst systems containing titanium-based Ziegler-Natta (pro)catalysts, a carrier material, and a tetrahydrofuran/ethanol modifier. The inventive catalyst system may be used to enhance the polymerization reaction rate of a chemical process for manufacturing a polyolefin composition. We also provide a method of making the inventive (pro)catalyst systems, a method of polymerizing olefin (co)monomer(s), polyolefins made by the method, and manufactured articles containing or made from the polyolefins. The polymerization may be conducted in a gas phase or a liquid-phase.

[0010a] In one aspect, there is provided a modified spray-dried Ziegler-Natta procatalyst system comprising a product of spray-drying a slurry of (A^+) a modified Ziegler-Natta procatalyst system and (B) a hydrophobic pre-treated fumed silica; wherein the (A^+) modified Ziegler-Natta procatalyst system comprises a complex of $TiCl_3$ and $MgCl_2$ and (C) a tetrahydrofuran/ethanol modifier, wherein the (C) tetrahydrofuran/ethanol modifier has a THF/EtOH weight/weight ratio of from 20:80 to 80:20.

[0010b] In another aspect, there is provided a method of making the modified spray-dried Ziegler-Natta procatalyst system as defined herein, the method comprising spray-drying the slurry of constituents (A^+) and (B) to give the modified spray-dried Ziegler-Natta procatalyst system; wherein in the slurry the (C) tetrahydrofuran/ethanol modifier has a THF/EtOH weight/weight ratio of from 20:80 to 80:20.

[0010c] In another aspect, there is provided a method of reducing a modified spray-dried Ziegler-Natta catalyst system, the method comprising contacting the modified spray-dried Ziegler-Natta procatalyst system as defined herein with a reducing agent effective for chemically reducing a complex of $TiCl_3$ and $MgCl_2$, thereby giving a chemically-reduced, modified spray-dried Ziegler-Natta procatalyst system.

[0010d] In another aspect, there is provided a method of activating a chemically-reduced, modified spray-dried Ziegler-Natta procatalyst system, the method comprising contacting the chemically-reduced, modified spray-dried Ziegler-Natta procatalyst system made by the method as defined herein with an activator, thereby making a modified spray-dried Ziegler-Natta catalyst system.

[0010e] In another aspect, there is provided a method of making a polyethylene composition, the method comprising contacting ethylene (monomer) and optionally zero, one, or more (C_3-C_{20})alpha-olefin (comonomer(s)) with the modified spray-dried Ziegler-Natta catalyst system of as defined herein to give a polyethylene composition comprising a polyethylene homopolymer or ethylene/(C_3-C_{20})alpha-olefin copolymer, respectively, and the modified spray-dried Ziegler-Natta catalyst system, or a by-product thereof.

DETAILED DESCRIPTION

[0011] The Introduction, Summary and Abstract are incorporated here by reference.

[0012] Certain inventive embodiments are described below as numbered aspects for easy cross-referencing. Additional embodiments are described elsewhere herein.

[0013] Aspect 1. A modified spray-dried Ziegler-Natta procatalyst system comprising a product of spray-drying a slurry of (A^+) a modified Ziegler-Natta procatalyst system and (B) a hydrophobic pre-treated fumed silica (substantially nonporous, alternatively completely nonporous); wherein the (A^+) modified Ziegler-Natta procatalyst system comprises a complex of $TiCl_3$ and $MgCl_2$ and an effective amount of (C) a tetrahydrofuran/ethanol modifier, wherein the (C) tetrahydrofuran/ethanol modifier has a THF/EtOH weight/weight ratio of from 20:80 to 80:20. The titanium of the modified spray-dried Ziegler-Natta procatalyst system may be formally Ti^{+3}. In some aspects the modified spray-dried Ziegler-Natta procatalyst system is made by spray-drying same from an excess of tetrahydrofuran and ethanol until a dried particulate solid of constant weight is obtained. In some aspects the (A^+) a modified Ziegler-Natta procatalyst system is made by contacting $TiCl_4$ and Mg metal in a first amount of dried tetrahydrofuran to give a first titanium complex containing the tetrahydrofuran, but free of ethanol. Then a second amount of dried ethanol is added to the first titanium complex to give the (A^+) modified Ziegler-Natta procatalyst system, wherein the first amount of dried tetrahydrofuran and the second amount of dried ethanol are chosen so as to give the THF/EtOH weight/weight ratio of from 20:80 to 80:20. In some aspects a slurry of constituents (A^+) and (B) is made by a first process comprising heating at a first temperature and for a first period of time $TiCl_4$ and Mg metal in the first amount of anhydrous tetrahydrofuran to give a first solution of the complex of $TiCl_3$ and $MgCl_2$ in the first amount of anhydrous tetrahydrofuran, then adding the second amount of dried ethanol to the first solution to give a second solution of the (A^+) modified Ziegler-Natta procatalyst system in

CLAIMS

1. A modified spray-dried Ziegler-Natta procatalyst system comprising a product of spray-drying a slurry of (A^+) a modified Ziegler-Natta procatalyst system and (B) a hydrophobic pre-treated fumed silica; wherein the (A^+) modified Ziegler-Natta procatalyst system comprises a complex of $TiCl_3$ and $MgCl_2$ and (C) a tetrahydrofuran/ethanol modifier, wherein the (C) tetrahydrofuran/ethanol modifier has a THF/EtOH weight/weight ratio of from 20:80 to 80:20.

2. The modified spray-dried Ziegler-Natta procatalyst system of claim 1 wherein the (C) tetrahydrofuran/ethanol modifier has a THF/EtOH weight/weight ratio of from 25:75 to 75:25.

3. The modified spray-dried Ziegler-Natta procatalyst system of claim 1 or 2 further described by any one of limitations (i) to (v): (i) the titanium complex is made from $TiCl_4$ and Mg metal; (ii) the titanium complex is made from $TiCl_3$.AA and $MgCl_2$; (iii) the (B) hydrophobic pre-treated fumed silica is a product of pre-treating an untreated fumed silica with a silicon-based hydrophobing agent; (iv) the hydrophobic pre-treated fumed silica is a product of pre-treating an untreated fumed silica with a silicon-based hydrophobing agent selected from trimethylsilyl chloride, dimethyldichlorosilane, a polydimethylsiloxane fluid, hexamethyldisilazane, an octyltrialkoxysilane (e.g., octyltrimethoxysilane), and a combination of any two or more thereof; and (v) both (ii) and (iv).

4. A method of making the modified spray-dried Ziegler-Natta procatalyst system of any one of claims 1 to 3, the method comprising spray-drying the slurry of constituents (A^+) and (B) to give the modified spray-dried Ziegler-Natta procatalyst system; wherein in the slurry the (C) tetrahydrofuran/ethanol modifier has a THF/EtOH weight/weight ratio of from 20:80 to 80:20.

5. A method of reducing a modified spray-dried Ziegler-Natta catalyst system, the method comprising contacting the modified spray-dried Ziegler-Natta procatalyst system of any one of claims 1 to 3 with a reducing agent effective for chemically reducing a complex of $TiCl_3$ and $MgCl_2$, thereby giving a chemically-reduced, modified spray-dried Ziegler-Natta procatalyst system.

6. A method of activating a chemically-reduced, modified spray-dried Ziegler-Natta procatalyst system, the method comprising contacting the chemically-reduced, modified spray-dried Ziegler-Natta procatalyst system made by the method of claim 5 with an activator, thereby making a modified spray-dried Ziegler-Natta catalyst system.

7. A method of making a polyethylene composition, the method comprising contacting ethylene (monomer) and optionally zero, one, or more (C_3-C_{20})alpha-olefin

(comonomer(s)) with the modified spray-dried Ziegler-Natta catalyst system of claim 1 to give a polyethylene composition comprising a polyethylene homopolymer or ethylene/(C_3-C_{20})alpha-olefin copolymer, respectively, and the modified spray-dried Ziegler-Natta catalyst system, or a by-product thereof.

8. The method of claim 7 comprising a gas phase polymerization in the presence of molecular hydrogen gas (H_2) and, optionally, an induced condensing agent (ICA) in one, two or more gas phase polymerization reactors under (co)polymerizing conditions, thereby making the polyethylene composition; wherein the (co)polymerizing conditions comprise a reaction temperature from 80 degrees (°) to 110° Celsius (C.); a molar ratio of the molecular hydrogen gas to the ethylene (H_2/C_2 molar ratio) from 0.001 to 0.050; and a molar ratio of the comonomer to the ethylene (Comonomer/C_2 molar ratio) from 0.005 to 0.10.