SiO_2 (Fuji Davison Co., Ltd.), and then treated the resulting calcined #952 SiO_2 with $Cl_2Si(CH_3)_2$ to give a treated calcined silica as carrier material. Soga et al. made their supported metallocene by embodiments of the filtering method.

[0006] Commercial metallocene catalysts include XCAT™ Metallocene Catalysts HP-100 and EZ-100 from Univation Technologies, LLC. Resins produced with XCAT™ Metallocene Catalysts feature outstanding toughness, clarity and improved processability. XCAT™ Metallocene Catalysts deliver the ability to control polymer molecular structure, allowing independent manipulation of MWD, CD and long chain branching. This results in resins with excellent clarity, controllable peak melting points, lower heat seal initiation temperatures and a broad sealing range. Resins made with XCAT™ Metallocene Catalysts have narrow compositional distributions, resulting in superior toughness, high hot tack and faster line speeds.

SUMMARY

[0007] We recognized, and conceived a technical solution to, one or more of the introduced problems of: (a) how to increase catalyst activity of a supported metallocene catalyst; (b) how to narrow molecular weight distribution (MWD) of an ethylene-based polymer (e.g., an ethylene/alpha-olefin copolymer); (c) how to narrow comonomer composition distribution (CCD) of an ethylene/alpha-olefin copolymer; (d) how to increase (melt) strength of an ethylene-based polymer (e.g., an ethylene/alpha-olefin copolymer); and (e) how to improve shrinkage properties of a film of an ethylene-based polymer (e.g., an ethylene/alpha-olefin copolymer). The technical solution provides an alternative to filtered or precipitated supported metallocene catalysts.

[0008] An ~~embodiment~~ example includes a spray-dried zirconocene catalyst system comprising a zirconocene catalyst and a hydrophobic fumed silica, which supports the zirconocene catalyst. Also included is a spray-drying method of making same.

[0008a] In one aspect, the present disclosure refers to a spray-dried zirconocene catalyst system consisting essentially of a zirconocene catalyst and a hydrophobic fumed silica, which supports the zirconocene catalyst, wherein the zirconocene catalyst of the spray-dried zirconocene catalyst system is made from a reaction of an activator and a zirconocene procatalyst of formula (I), (II), or (III): a zirconocene procatalyst of formula (I): $((R^1)_x$-cyclopentadienyl)$((R^2)_y$-cyclopentadienyl)zirconium dichloride/dibromide/dialkyl (I), wherein subscript x is an integer from 1 to 5; subscript y is an integer from 0 to 5; and each R^1 and R^2 independently is methyl, ethyl, a normal-(C_3-C_{10})alkyl (linear), or an iso-(C_3-C_{10})alkyl, wherein the $((R^1)_x$-cyclopentadienyl)$((R^2)_y$-cyclopentadienyl)zirconium

dichloride/dibromide/dialkyl is selected from bis(1-methyl-3-butylcyclopentadienyl)zirconium dichloride, bis(1-methyl-3-butylcyclopentadienyl)zirconium dibromide, and bis(1-methyl-3-butylcyclopentadienyl)zirconium dimethyl;

or a zirconocene procatalyst of formula (II): $((R^3)_z$-(4,5,6,7-tetrahydroindenyl))$((R^2)_y$-cyclopentadienyl)zirconium dichloride/dibromide/dialkyl (II), wherein subscript z is an integer from 0 to 3; subscript y is an integer from 0 to 5; each R^3 is H or R^2; and each R^2 independently is methyl, ethyl, a normal-$(C_3$-$C_{10})$alkyl (linear), or an iso-$(C_3$-$C_{10})$alkyl;

or a zirconocene procatalyst of formula (III): $((R^3)_z$-(4,5,6,7-tetrahydroindenyl))$((R^4)_t$-(4,5,6,7-tetrahydroindenyl))zirconium dichloride/dibromide/dialkyl (III), wherein subscript z is an integer from 0 to 3; subscript t is an integer from 0 to 3; and each R^3 and R^4 independently is H, methyl, ethyl, or a normal-$(C_3$-$C_{10})$alkyl (linear); or each of subscripts z and t independently is an integer from 1 to 3 and a first R^3 is in the 1-position of the 4,5,6,7-tetrahydroindenyl to which it is bonded and a first R^4 is in the 1-position of the 4,5,6,7-tetrahydroindenyl to which it is bonded and the first R^3 is covalently bonded to the first R^4 to form a divalent bridging group of formula $Si(R^5)_2$, wherein each R^5 is independently a $(C_1$-$C_3)$alkyl.

[0008b] In another aspect, the present disclosure refers to a method of making a spray-dried zirconocene catalyst system, the method comprising contacting in a hydrocarbon solvent an activator with a zirconocene procatalyst as defined herein, and a hydrophobic fumed silica, to give a suspension of the hydrophobic fumed silica in a solution of the zirconocene catalyst, which is made *in situ*, in the hydrocarbon solvent, and then spray-drying the suspension to give the spray-dried zirconocene catalyst system.

[0009] Also included is a process for polymerizing an olefin monomer such as ethylene and, optionally, an olefin comonomer such as an alpha-olefin, with the spray-dried zirconocene catalyst system to make a polyolefin such as an ethylene-based polymer such as a polyethylene homopolymer or an ethylene/alpha-olefin copolymer. The zirconocene catalyst of the spray-dried zirconocene catalyst system may have increased catalyst productivity relative to catalyst productivity of a comparative filtered or concentrated zirconocene catalyst system that has been prepared by a filtering or concentrating method, respectively, instead of the present spray-drying method. Also included is the polyolefin made by the inventive polymerization process. ~~Embodiments~~ Examples of the ethylene-based polymer may have a narrowed molecular weight distribution (MWD) and, for ethylene/alpha-olefin copolymers, a narrowed comonomer composition distribution (CCD) relative to MWD or CCD, respectively, of a

comparative polyolefin made by a comparative polymerization process using the comparative filtered or concentrated zirconocene catalyst system instead of the spray-dried zirconocene catalyst system. Without wishing to be bound by theory, it is believed that ~~embodiments~~ examples of the ethylene-based polymer having a narrower MWD and/or narrower CCD may, all other things being equal, decrease optical haze and optical gloss and may increase tear strength of films made therefrom and composed thereof. Without wishing to be bound by theory, it is believed that the polyolefin such as the ethylene-based polymer may have increased melt strength and/or increased strength (solid phase), and a film thereof may have improved shrinkage properties relative to those of the comparative polyolefin or film, respectively. Additional ~~embodiments~~ examples are a method of forming films of the inventive polyolefin and the films made thereby. The inventive films are useful in many different applications. The film may be particularly useful in shrink-wrap applications.

[0009a] In another aspect, the present disclosure refers to a method of making a polyethylene composition, the method comprising contacting ethylene and optionally zero, one, or more (C_3-C_{20})alpha-olefin with the spray-dried zirconocene catalyst system as described herein in a polymerization reactor to generate a polymerization reaction giving a polyethylene composition comprising a polyethylene homopolymer or ethylene/(C_3-C_{20})alpha-olefin copolymer, respectively, and the spray-dried zirconocene catalyst system, or a by-product thereof.

DETAILED DESCRIPTION

[0010] Certain inventive embodiments are described below as numbered aspects for easy cross-referencing. Additional embodiments are described elsewhere herein.

[0011] Aspect 1. A spray-dried zirconocene catalyst system comprising a zirconocene catalyst and a hydrophobic fumed silica, which carries or supports the zirconocene catalyst, wherein the zirconocene catalyst of the spray-dried zirconocene catalyst system is made from a reaction of an activator and a zirconocene procatalyst of formula (I), (II), or (III): a zirconocene procatalyst of formula (I): ((R^1)$_x$-cyclopentadienyl)((R^2)$_y$-cyclopentadienyl)zirconium dichloride/dibromide/dialkyl (I), wherein subscript x is an integer from 1 to 5; subscript y is an integer from 0 to 5; and each R^1 and R^2 independently is methyl, ethyl, a normal-(C_3-C_{10})alkyl (linear), or an iso-(C_3-C_{10})alkyl; or a zirconocene procatalyst of formula (II): ((R^3)$_z$-(4,5,6,7-tetrahydroindenyl))((R^2)$_y$-cyclopentadienyl)zirconium dichloride/dibromide/dialkyl (II), wherein subscript z is an integer from 0 to 3; subscript y is an integer from 0 to 5; each R^3 is H or R^2; and each R^2 independently is methyl, ethyl, a normal-(C_3-C_{10})alkyl (linear), or an iso-(C_3-C_{10})alkyl; or a

zirconocene procatalyst of formula (III): $((R^3)_z$-(4,5,6,7-tetrahydroindenyl))$((R^4)_t$-(4,5,6,7-tetrahydroindenyl))zirconium dichloride/dibromide/dialkyl (III), wherein subscript z is an integer from 0 to 3; subscript t is an integer from 0 to 3; and each R^3 and R^4 independently is H, methyl, ethyl, or a normal-(C_3-C_{10})alkyl (linear); or each of subscripts z and t independently is an integer from 1 to 3 and a first R^3 is in the 1-position of the 4,5,6,7-tetrahydroindenyl to which it is bonded and a first R^4 is in the 1-position of the 4,5,6,7-tetrahydroindenyl to which it is bonded and the first R^3 is covalently bonded to the first R^4 to

CLAIMS

1. A spray-dried zirconocene catalyst system consisting essentially of a zirconocene catalyst and a hydrophobic fumed silica, which supports the zirconocene catalyst, wherein the zirconocene catalyst of the spray-dried zirconocene catalyst system is made from a reaction of an activator and a zirconocene procatalyst of formula (I), (II), or (III): a zirconocene procatalyst of formula (I): $((R^1)_x$-cyclopentadienyl)$((R^2)_y$-cyclopentadienyl)zirconium dichloride/dibromide/dialkyl (I), wherein subscript x is an integer from 1 to 5; subscript y is an integer from 0 to 5; and each R^1 and R^2 independently is methyl, ethyl, a normal-$(C_3$-$C_{10})$alkyl (linear), or an iso-$(C_3$-$C_{10})$alkyl, wherein the $((R^1)_x$-cyclopentadienyl)$((R^2)_y$-cyclopentadienyl)zirconium dichloride/dibromide/dialkyl is selected from bis(1-methyl-3-butylcyclopentadienyl)zirconium dichloride, bis(1-methyl-3-butylcyclopentadienyl)zirconium dibromide, and bis(1-methyl-3-butylcyclopentadienyl)zirconium dimethyl;

or a zirconocene procatalyst of formula (II): $((R^3)_z$-(4,5,6,7-tetrahydroindenyl))$((R^2)_y$-cyclopentadienyl)zirconium dichloride/dibromide/dialkyl (II), wherein subscript z is an integer from 0 to 3; subscript y is an integer from 0 to 5; each R^3 is H or R^2; and each R^2 independently is methyl, ethyl, a normal-$(C_3$-$C_{10})$alkyl (linear), or an iso-$(C_3$-$C_{10})$alkyl;

or a zirconocene procatalyst of formula (III): $((R^3)_z$-(4,5,6,7-tetrahydroindenyl))$((R^4)_t$-(4,5,6,7-tetrahydroindenyl))zirconium dichloride/dibromide/dialkyl (III), wherein subscript z is an integer from 0 to 3; subscript t is an integer from 0 to 3; and each R^3 and R^4 independently is H, methyl, ethyl, or a normal-$(C_3$-$C_{10})$alkyl (linear); or each of subscripts z and t independently is an integer from 1 to 3 and a first R^3 is in the 1-position of the 4,5,6,7-tetrahydroindenyl to which it is bonded and a first R^4 is in the 1-position of the 4,5,6,7-tetrahydroindenyl to which it is bonded and the first R^3 is covalently bonded to the first R^4 to form a divalent bridging group of formula $Si(R^5)_2$, wherein each R^5 is independently a $(C_1$-$C_3)$alkyl.

2. The spray-dried zirconocene catalyst system of claim 1, wherein the zirconocene catalyst of the spray-dried zirconocene catalyst system is made from a reaction of an activator and a zirconocene procatalyst comprising the zirconocene procatalyst of formula (I): a $((R^1)_x$-cyclopentadienyl)$((R^2)_y$-cyclopentadienyl)zirconium dichloride/dibromide/dialkyl (I), wherein subscript x is an integer from 1 to 5; subscript y is an integer from 0 to 5; and each R^1 and R^2 independently is methyl, ethyl, a normal-$(C_3$-$C_{10})$alkyl (linear), or an iso-$(C_3$-$C_{10})$alkyl.

3. The spray-dried zirconocene catalyst system of claim 1 or 2 wherein the zirconium procatalyst is characterized by any one of limitations (i) to (x): (i) subscript x is 1 and subscript y is 0, (ii) subscripts x and y are each 1, (iii) subscript x is 1 and subscript y is 2, (iv) subscript x is 2 and subscript y is 0, (v) subscript x is 2 and subscript y is 1, (vi) subscript x is 2 and subscript y is 2, (vii) subscript x is 1 or 2 and subscript y is 0, 1 or 2, (viii) subscript x is 3 and subscript y is 1, (ix) subscript x is 4 and subscript y is 1, and (x) subscript x is an integer from 1 to 4 and subscript y is 1 or 2.

~~4. The spray-dried zirconocene catalyst system of any one of claims 1 to 3 wherein the zirconium procatalyst is the ((R1)x-cyclopentadienyl)((R2)y-cyclopentadienyl)zirconium dichloride/dibromide/dialkyl selected from (tetramethylcyclopentadienyl)(n-propylcyclopentadienyl)zirconium dichloride; (tetramethylcyclopentadienyl)(n-propylcyclopentadienyl)zirconium dibromide; (tetramethylcyclopentadienyl)(n-propylcyclopentadienyl)zirconium dimethyl; bis(butylcyclopentadienyl)zirconium dichloride, bis(butylcyclopentadienyl)zirconium dibromide, and bis(butylcyclopentadienyl)zirconium dimethyl; or the zirconium procatalyst is the ((R1)x-cyclopentadienyl)((R2)y-cyclopentadienyl)zirconium dichloride/dibromide/dialkyl selected from bis(1-methyl-3-butylcyclopentadienyl)zirconium dichloride, bis(1-methyl-3-butylcyclopentadienyl)zirconium dibromide, and bis(1-methyl-3-butylcyclopentadienyl)zirconium dimethyl.~~

~~5~~4. The spray-dried zirconocene catalyst system of claim 1, wherein the zirconocene catalyst of the spray-dried zirconocene catalyst system is made from a reaction of an activator and a zirconocene procatalyst comprising the zirconocene procatalyst of formula (III): ((R3)z-(4,5,6,7-tetrahydroindenyl))((R4)t-(4,5,6,7-tetrahydroindenyl))zirconium dichloride/dibromide/dialkyl (III), wherein subscript z is an integer from 0 to 3; subscript t is an integer from 0 to 3; and each R^3 and R^4 independently is H, methyl, ethyl, or a normal-(C_3-C_{10})alkyl (linear); or each of subscripts z and t independently is an integer from 1 to 3 and a first R^3 is in the 1-position of the 4,5,6,7-tetrahydroindenyl to which it is bonded and a first R^4 is in the 1-position of the 4,5,6,7-tetrahydroindenyl to which it is bonded and the first R^3 is covalently bonded to the first R^4 to form a divalent bridging group of formula $Si(R^5)_2$, wherein each R^5 is independently a (C_1-C_3)alkyl.

~~6~~5. The spray-dried zirconocene catalyst system of claim ~~5~~4 wherein each of subscripts z and t is 1 and a first R^3 is in the 1-position of the 4,5,6,7-tetrahydroindenyl to which it is bonded and first R^4 is in the 1-position of the 4,5,6,7-tetrahydroindenyl to which it is bonded

and the first R^3 is covalently bonded to the first R^4 to form the divalent bridging group of formula $Si(R^5)_2$, wherein each R^5 is methyl.

~~7~~6. The spray-dried zirconocene catalyst system of any one of claims 1 to ~~6~~5 made by mixing the activator, the zirconocene procatalyst, and the hydrophobic fumed silica in a hydrocarbon solvent to make a suspension of the hydrophobic fumed silica in a solution of the zirconocene catalyst, which is made *in situ*, in the hydrocarbon solvent; and spray-drying the suspension to give the spray-dried zirconocene catalyst system.

~~8~~7. The spray-dried zirconocene catalyst system of any one of claims 1 to ~~7~~6 wherein the hydrophobic fumed silica is made by contacting an untreated fumed silica, having surfaces containing silicon-bonded hydroxyl groups, with a silicon-based hydrophobing agent, containing on average per molecule one or more functional groups reactive with a SiOH group, to give the hydrophobic fumed silica.

~~9~~8. The spray-dried zirconocene catalyst system of any one of claims 1 to ~~8~~7 wherein the activator is an alkylaluminoxane.

~~10~~9. A method of making a spray-dried zirconocene catalyst system, the method comprising contacting in a hydrocarbon solvent an activator with a zirconocene procatalyst as defined in any one of claims 1 to ~~9~~8, and a hydrophobic fumed silica, to give a suspension of the hydrophobic fumed silica in a solution of the zirconocene catalyst, which is made *in situ*, in the hydrocarbon solvent, and then spray-drying the suspension to give the spray-dried zirconocene catalyst system.

~~11~~10. A method of making a polyethylene composition, the method comprising contacting ethylene and optionally zero, one, or more (C_3-C_{20})alpha-olefin with the spray-dried zirconocene catalyst system of any one of claims 1 to ~~9~~8 in a polymerization reactor to generate a polymerization reaction giving a polyethylene composition comprising a polyethylene homopolymer or ethylene/(C_3-C_{20})alpha-olefin copolymer, respectively, and the spray-dried zirconocene catalyst system, or a by-product thereof.