

CLAIMS

1. A spray-dried zirconocene catalyst system comprising 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): $((R^1)_x\text{-cyclopentadienyl})((R^2)_y\text{-cyclopentadienyl})\text{zirconium}$ 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-(C₃-C₁₀)alkyl (linear), or an iso-(C₃-C₁₀)alkyl; or a zirconocene procatalyst of formula (II): $((R^3)_z\text{-(4,5,6,7-tetrahydroindenyl)})((R^2)_y\text{-cyclopentadienyl})\text{zirconium}$ 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-(C₃-C₁₀)alkyl (linear), or an iso-(C₃-C₁₀)alkyl; or a zirconocene procatalyst of formula (III): $((R^3)_z\text{-(4,5,6,7-tetrahydroindenyl)})((R^4)_t\text{-(4,5,6,7-tetrahydroindenyl)})\text{zirconium}$ 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-(C₃-C₁₀)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 $\text{Si}(R^5)_2$, wherein each R^5 is independently a (C₁-C₃)alkyl.
2. The spray-dried zirconocene catalyst system of claim 1 comprising 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 comprising the zirconocene procatalyst of formula (I): a $((R^1)_x\text{-cyclopentadienyl})((R^2)_y\text{-cyclopentadienyl})\text{zirconium}$ 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-(C₃-C₁₀)alkyl (linear), or an iso-(C₃-C₁₀)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 $((R^1)_x\text{-cyclopentadienyl})((R^2)_y\text{-cyclopentadienyl})\text{zirconium}$ 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 $((R^1)_x\text{-cyclopentadienyl})((R^2)_y\text{-cyclopentadienyl})\text{zirconium}$ 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. The spray-dried zirconocene catalyst system of claim 1 comprising 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 comprising the zirconocene procatalyst of formula (III): $((R^3)_z\text{-(4,5,6,7-tetrahydroindenyl)})((R^4)_t\text{-(4,5,6,7-tetrahydroindenyl)})\text{zirconium}$ 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 $\text{Si}(R^5)_2$, wherein each R^5 is independently a (C_1 - C_3)alkyl.

6. The spray-dried zirconocene catalyst system of claim 5 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 $\text{Si}(R^5)_2$, wherein each R^5 is methyl.

7. The spray-dried zirconocene catalyst system of any one of claims 1 to 6 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. The spray-dried zirconocene catalyst system of any one of claims 1 to 7 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. The spray-dried zirconocene catalyst system of any one of claims 1 to 8 wherein the activator is an alkylaluminum, an alkylaluminumoxane, or a combination thereof.
10. The spray-dried zirconocene catalyst system of any one of claims 1 to 9 further comprising any one of limitations (i) to (vii): (i) an olefin monomer (e.g., ethylene) or alpha-olefin; (ii) a polyolefin; (iii) a metal carboxylate salt, wherein the metal carboxylate salt is represented by the formula: $MQ_m(O_2CR)_n$, wherein M is a metal atom of Group 2 or Group 13 of the Periodic table of Elements; Q is a halogen, hydroxy, alkyl, alkoxy, aryloxy, siloxy, silane, or sulfonate group; R is a (C₅-C₃₀)hydrocarbyl; subscript m is an integer from 0 to 3; subscript n is an integer from 1 to 4; and the sum of subscripts m and n is equal to the valence of M; and (iv) both (i) and (ii); (v) both (i) and (iii); (vi) both (ii) and (iii); and (vii) each of (i) to (iii).
11. 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 10, and a hydrophobic fumed silica, and, optionally, a metal carboxylate salt of the formula: $MQ_m(O_2CR)_n$, wherein M, Q, R, subscript m and subscript n are as defined in claim 10, 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.
12. A method of making a polyethylene composition, the method comprising contacting ethylene and optionally zero, one, or more (C₃-C₂₀)alpha-olefin with the spray-dried zirconocene catalyst system of any one of claims 1 to 10 in a polymerization reactor to generate a polymerization reaction giving a polyethylene composition comprising a polyethylene homopolymer or ethylene/(C₃-C₂₀)alpha-olefin copolymer, respectively, and the spray-dried zirconocene catalyst system, or a by-product thereof.
13. A polyethylene composition made by the method of claim 12.

14. A manufactured article comprising a shaped form of the polyethylene composition of claim 13.
15. A film comprising the polyethylene composition of claim 13.