CLAIMS

1. A process to produce a catalyst composition, the process comprising:

(i) contacting an activator-support and an organoaluminum compound for a first period of time to form a precontacted mixture; and

(ii) contacting the precontacted mixture with a metallocene compound for a second period of time to form the catalyst composition.

2. The process of claim 1, wherein:

the activator-support comprises a fluorided solid oxide, a sulfated solid oxide, a phosphated solid oxide, or a combination thereof; and

the metallocene compound comprises a bridged zirconium or hafnium based metallocene compound with a cyclopentadienyl group and a fluorenyl group.

3. The process of claim 1, wherein:

the first period of time is at least about 5 minutes; and

an activity of the catalyst composition is from about 15% to about 1000% greater than that of a catalyst system obtained by first combining the activator-support and the metallocene compound, and then combining the organoaluminum compound, under the same polymerization conditions.

4. The process of claim 1, wherein:

the organoaluminum compound comprises trimethylaluminum, triethylaluminum, tri-n-propylaluminum, tri-n-butylaluminum, triisobutylaluminum, tri-n-hexylaluminum, tri-n-octylaluminum, diisobutylaluminum hydride, diethylaluminum ethoxide, diethylaluminum chloride, or any combination thereof; and

the activator-support comprises fluorided silica-alumina, fluorided silica-coated alumina, sulfated alumina, or a combination thereof.

5. The process of claim 1, wherein:

the weight ratio of the metallocene compound to the activator-support is in a range from about 1:10 to about 1:10,000; and

the weight ratio of the activator-support to the organoaluminum compound is in a range from about 1:5 to about 1000:1.

6. An olefin polymerization process, the olefin polymerization process comprising contacting a catalyst composition with an olefin monomer and an optional olefin

comonomer in a polymerization reactor system under polymerization conditions to produce an olefin polymer, wherein the catalyst composition is produced by the process of claim 1.

7. The olefin polymerization process of claim 6, wherein:

the activator-support comprises fluorided silica-alumina, fluorided silica-coated alumina, sulfated alumina, phosphated alumina, or a combination thereof;

the polymerization reactor system comprises a slurry reactor, a gas-phase reactor, a solution reactor, or a combination thereof; and

the olefin monomer comprises ethylene and the olefin comonomer comprises a C_3-C_{10} alpha-olefin.

8. A process to produce a dual metallocene catalyst composition, the process comprising:

(a) contacting a first metallocene compound and an organoaluminum compound with a slurry of an activator-support for a first period of time to form a first mixture; and

(b) contacting the first mixture with a second metallocene compound for a second period of time to form the dual metallocene catalyst composition.

9. The process of claim 8, wherein:

the first metallocene compound is less reactive with the activator-support than the second metallocene compound; and

a weight ratio of the first metallocene compound to the second metallocene compound is in a range from about 1:10 to about 10:1.

10. The process of claim 8, wherein:

the activator-support comprises sulfated alumina;

the first metallocene compound comprises a bridged metallocene compound; and

the second metallocene compound comprises an unbridged metallocene compound.

11. The process of claim 8, wherein:

the activator-support comprises a fluorided solid oxide, a sulfated solid oxide, a phosphated solid oxide, or a combination thereof;

the organoaluminum compound comprises trimethylaluminum, triethylaluminum, tri-n-propylaluminum, tri-n-butylaluminum, triisobutylaluminum, or any combination thereof;

the first metallocene compound comprises a bridged zirconium or hafnium based metallocene compound with a cyclopentadienyl group and a fluorenyl group; and

the second metallocene compound comprises an unbridged zirconium or hafnium based metallocene compound containing two cyclopentadienyl groups, two indenyl groups, or a cyclopentadienyl and an indenyl group.

12. The process of claim 8, wherein an activity of the catalyst composition is greater than that of a dual catalyst system obtained by combining the activator-support, a mixture of the first metallocene compound and the second metallocene compound, and the organoaluminum compound, under the same polymerization conditions.

13. An olefin polymerization process, the olefin polymerization process comprising contacting a dual metallocene catalyst composition with an olefin monomer and an optional olefin comonomer in a polymerization reactor system under polymerization conditions to produce an olefin polymer, wherein the dual metallocene catalyst composition is produced by the process of claim 8.

14. The olefin polymerization process of claim 13, wherein:

the polymerization reactor system comprises a slurry reactor, a gas-phase reactor, a solution reactor, or a combination thereof;

the olefin monomer comprises ethylene and the olefin comonomer comprises a C_3-C_{10} alpha-olefin; and

the first metallocene compound produces a higher molecular weight component of the olefin polymer than the second metallocene compound.

15. The olefin polymerization process of claim 14, wherein a Mw of the olefin polymer produced by the polymerization process is greater than a Mw of an olefin polymer produced under the same polymerization conditions using a dual catalyst system obtained by combining the activator-support, a mixture of the first metallocene compound and the second metallocene compound, and the organoaluminum compound.

16. The olefin polymerization process of claim 14, wherein:

the olefin polymer comprises a higher molecular weight component and a lower molecular weight component; and

a ratio of the higher molecular weight component to the lower molecular weight component of the olefin polymer produced by the polymerization process is greater than a ratio of the higher molecular weight component to the lower molecular weight component of an olefin polymer produced under the same polymerization conditions using a dual catalyst system obtained by combining the activator-support, a mixture of the first metallocene compound and the second metallocene compound, and the organoaluminum compound.

17. The olefin polymerization process of claim 14, wherein the catalyst composition is contacted with ethylene and an olefin comonomer comprising 1-butene, 1-hexene, 1-octene, or a mixture thereof.

18. A process to produce a dual metallocene catalyst composition, the process comprising:

(A) contacting an activator-support and an organoaluminum compound for a first period of time to form a precontacted mixture;

(B) contacting the precontacted mixture with a first metallocene compound for a second period of time to form a first mixture; and

(C) contacting the first mixture with a second metallocene compound for a third period of time to form the dual metallocene catalyst composition.

19. The process of claim 18, wherein:

the activator-support comprises a fluorided solid oxide, a sulfated solid oxide, a phosphated alumina, or a combination thereof;

the organoaluminum compound comprises trimethylaluminum, triethylaluminum, tri-n-propylaluminum, tri-n-butylaluminum, triisobutylaluminum, or any combination thereof;

the first metallocene compound comprises a bridged zirconium or hafnium based metallocene compound with a cyclopentadienyl group and a fluorenyl group; and

the second metallocene compound comprises an unbridged zirconium or hafnium based metallocene compound containing two cyclopentadienyl groups, two indenyl groups, or a cyclopentadienyl and an indenyl group.

20. The process of claim 19, wherein:

the activator-support comprises sulfated alumina;

the first metallocene compound is less reactive with the activator-support than the second metallocene compound; and

a weight ratio of the first metallocene compound to the second metallocene compound is in a range from about 1:10 to about 10:1.

CLAIMS

We claim:

1. A process to produce a catalyst composition, the process comprising:

(i) contacting an activator-support and an organoaluminum compound for a first period of time to form a precontacted mixture; and

(ii) contacting the precontacted mixture with a metallocene compound for a second period of time to form the catalyst composition; wherein:

an activity of the catalyst composition is from about 15% to about 1000% greater than that of a catalyst system obtained by first combining the activator-support and the metallocene compound, and then combining the organoaluminum compound, under the same polymerization conditions.

2. The process of claim 1, wherein:

the activator-support comprises a fluorided solid oxide, a sulfated solid oxide, a phosphated solid oxide, or a combination thereof; and

the metallocene compound comprises a bridged zirconium or hafnium based metallocene compound with a cyclopentadienyl group and a fluorenyl group.

3. The process of claim 1, wherein:

the first period of time is at least about 5 minutes; and

the activity of the catalyst composition is from about 25% to about 750% greater than that of a catalyst system obtained by first combining the activator-support and the metallocene compound, and then combining the organoaluminum compound, under the same polymerization conditions.

4. The process of claim 1, wherein:

the organoaluminum compound comprises trimethylaluminum, triethylaluminum, tri-n-propylaluminum, tri-n-butylaluminum, triisobutylaluminum, tri-n-hexylaluminum, tri-n-octylaluminum, diisobutylaluminum hydride, diethylaluminum ethoxide, diethylaluminum chloride, or any combination thereof; and

the activator-support comprises fluorided silica-alumina, fluorided silica-coated alumina, sulfated alumina, or a combination thereof.

5. The process of claim 1, wherein:

the weight ratio of the metallocene compound to the activator-support is in a range from about 1:10 to about 1:10,000; and

the weight ratio of the activator-support to the organoaluminum compound is in a range from about 1:5 to about 1000:1.

6. An olefin polymerization process, the olefin polymerization process comprising:

(i) contacting an activator-support and an organoaluminum compound for a first period of time to form a precontacted mixture;

(ii) contacting the precontacted mixture with a metallocene compound for a second period of time to form the catalyst composition; and

(iii) contacting the catalyst composition with an olefin monomer and an optional olefin comonomer in a polymerization reactor system under polymerization conditions to produce an olefin polymer; wherein:

an activity of the catalyst composition is from about 15% to about 1000% greater than that of a catalyst system obtained by first combining the activator-support and the metallocene compound, and then combining the organoaluminum compound, under the same polymerization conditions.

7. The olefin polymerization process of claim 6, wherein:

the activator-support comprises fluorided silica-alumina, fluorided silica-coated alumina, sulfated alumina, phosphated alumina, or a combination thereof;

the polymerization reactor system comprises a slurry reactor, a gas-phase reactor, a solution reactor, or a combination thereof; and

the olefin monomer comprises ethylene and the olefin comonomer comprises a C_3-C_{10} alpha-olefin.

8. The process of claim 1, wherein the weight ratio of the metallocene compound to the activator-support is in a range from about 1:20 to about 1:1000.

9. The process of claim 8, wherein the metallocene compound comprises a bridged zirconium or hafnium based metallocene compound with a cyclopentadienyl group and a fluorenyl group.

10. The process of claim 9, wherein the organoaluminum compound comprises trimethylaluminum, triethylaluminum, tri-n-propylaluminum, tri-n-butylaluminum, triisobutylaluminum, tri-n-hexylaluminum, tri-n-octylaluminum, diisobutylaluminum hydride, diethylaluminum ethoxide, diethylaluminum chloride, or any combination thereof.

11. The process of claim 1, wherein the activator-support comprises a fluorided solid oxide.

12. The process of claim 1, wherein the activator-support comprises a sulfated solid oxide.

13. The process of claim 1, wherein the activator-support comprises fluorided silica-alumina, fluorided silica-coated alumina, sulfated alumina, or a combination thereof.

14. The process of claim 1, wherein the metallocene compound comprises an unbridged zirconium or hafnium based metallocene compound containing two cyclopentadienyl groups, two indenyl groups, or a cyclopentadienyl and an indenyl group.

15. The process of claim 1, wherein the first period of time is from about 30 seconds to about 6 hours.

16. The process of claim 1, wherein:

the activator-support comprises a fluorided solid oxide, a sulfated solid oxide, a phosphated alumina, or a combination thereof; and

the organoaluminum compound comprises trimethylaluminum, triethylaluminum, tri-n-propylaluminum, tri-n-butylaluminum, triisobutylaluminum, or any combination thereof.

17. The process of claim 16, wherein the activity of the catalyst composition is from about 25% to about 750% greater than that of a catalyst system obtained by first combining the activator-support and the metallocene compound, and then combining the organoaluminum compound, under the same polymerization conditions.

18. The olefin polymerization process of claim 6, wherein the polymerization reactor system comprises a loop slurry reactor.

19. The olefin polymerization process of claim 6, wherein:

the activator-support comprises a fluorided solid oxide, a sulfated solid oxide, a phosphated solid oxide, or a combination thereof; and

the olefin polymer is an ethylene homopolymer, an ethylene/1-butene copolymer, an ethylene/1-hexene copolymer, or an ethylene/1-octene copolymer.

20. The olefin polymerization process of claim 6, wherein:

the metallocene compound comprises a bridged zirconium or hafnium based metallocene compound with a cyclopentadienyl group and a fluorenyl group; and

the organoaluminum compound comprises trimethylaluminum, triethylaluminum, tri-n-propylaluminum, tri-n-butylaluminum, triisobutylaluminum, tri-n-hexylaluminum, tri-n-octylaluminum, diisobutylaluminum hydride, diethylaluminum ethoxide, diethylaluminum chloride, or any combination thereof.

21. The olefin polymerization process of claim 20, wherein the catalyst composition is contacted with ethylene and an olefin comonomer comprising 1-butene, 1-hexene, 1-octene, or a mixture thereof.

22. The olefin polymerization process of claim 21, wherein the activity of the catalyst composition is from about 25% to about 750% greater than that of a catalyst system obtained by first combining the activator-support and the metallocene compound, and then combining the organoaluminum compound, under the same polymerization conditions.