FLUORINATED CATALYST SUPPORTS AND CATALYST SYSTEMS

BACKGROUND

[0001] A number of catalyst compositions containing single site catalysts have been used to prepare polyolefins, producing relatively homogeneous copolymers at good polymerization rates. In contrast to traditional Ziegler-Natta catalyst compositions, single site catalyst compositions, such as metallocene catalysts, are catalytic compounds in which each catalyst particle contains one or only a few types of polymerization sites.

[0002] To achieve acceptable and economically viable polymerization activities with single site catalyst systems, a large amount of activator such as methylaluminoxane ("MAO") is often required. Such activators are often expensive and the large amount of activator required to produce an active single site catalyst for polymerization has been a substantial impediment to the commercialization of single site catalysts for polyolefin production.

SUMMARY

[0003] An exemplary embodiment described herein provides a method for making a catalyst support. The method includes forming a mixture of a support material and a fluoride donor. The mixture is added to a fluidized bed reactor. The mixture is fluidized to form a fluidized bed with a height to diameter ratio of at least about 2.3. The mixture is calcined to decompose the fluoride donor, forming a fluorinated support.

[0003a] In one aspect, there is provided a method for making a fluorinated catalyst support, comprising:

forming a mixture of a support material and a fluoride donor, where the support material is an inorganic oxide;

adding the mixture to a fluidized bed reactor;

fluidizing the mixture in the fluidized bed reactor with a fluidizing gas at a flow rate that forms a fluidized bed with a height to diameter ratio of at least about 2.3; and

calcining the mixture to decompose the fluoride donor and fluorinate the support material thereby forming the fluorinated catalyst support.

[0004] Another exemplary embodiment described herein provides a catalyst system. The catalyst system includes a catalyst compound, a fluorinated support, and an aluminoxane compound. The fluorinated support is generated by heating a catalyst support and a fluoride donor compound at a temperature sufficient to decompose the fluoride donor compound in a fluidized bed reactor with a height to depth ratio of a fluidized bed of at least about 2.3. The aluminoxane is present in an amount of about 10 mmol or less per gram of the support.

[0004a] In another aspect, there is provided a method for forming a catalyst system, comprising:

combining a metallocene catalyst compound and an aluminoxane to produce a first mixture; and

forming a mixture of a support material and a fluoride donor, where the support material is an inorganic oxide;

adding the mixture to a fluidized bed reactor;

fluidizing the mixture in the fluidized bed reactor with a fluidizing gas at a flow rate that forms a fluidized bed with a height to diameter ratio of at least about 2.3; and

calcining the mixture to decompose the fluoride donor and fluorinate the support material thereby forming the fluorinated catalyst support;

adding the fluorinated catalyst support to the first mixture and drying to produce a catalyst system; or

combining a metallocene catalyst compound with a fluorinated catalyst support, and an aluminoxane, wherein the aluminoxane is present in an amount of about 10 mmol or less per gram of the fluorinated catalyst support;

wherein said fluorinated catalyst support is obtained by a method comprsing:

forming a mixture of a support material and a fluoride donor, where the support material is an inorganic oxide;

adding the mixture to a fluidized bed reactor;

fluidizing the mixture in the fluidized bed reactor with a fluidizing gas at a flow rate that forms a fluidized bed with a height to diameter ratio of at least about 2.3; and

calcining the mixture to decompose the fluoride donor and fluorinate the support material thereby forming the fluorinated catalyst support.

[0004b] In another aspect, there is provided a catalyst system, comprising:

a metallocene catalyst compound;

a support comprising a fluorinated catalyst support, wherein the fluorinated catalyst support is an alumina-containing support and is generated by heating a support material and a fluoride donor compound at a temperature sufficient to decompose the fluoride donor compound in a fluidized bed reactor with a fluidizing gas at a flow rate that forms a fluidized bed with a height to depth ratio of at least about 2.3, wherein the fluoride donor compound is ammonium fluoride, ammonium

bifluoride, ammonium tetrafluoroborate, ammonium hexafluorophosphate, ammonium heptafluorotantalate(V), ammonium hexafluorogermanate(IV), ammonium hexafluorotitanate(IV), ammonium hexafluorozirconate, aluminum fluoride, sodium hexafluoroaluminate, molybdenum(VI) fluoride, bromine pentafluoride, nitrogen trifluoride, difluoroamine, perfluorohexane, hexafluorobenzene, fluoromethane, trifluoroethanol, freons, derivatives thereof, or any combination thereof; and

an aluminoxane, wherein the aluminoxane is present in an amount of about 10 mmol or less per gram of the fluorinated catalyst support.

DESCRIPTION OF THE DRAWINGS

[0005] The advantages of the present techniques are better understood by referring to the following detailed description and the attached drawings, in which:

[0006] Figure 1 is a simplified process flow diagram of a catalyst activator system that may be used in embodiments;

[0007] Figure 2 is a simplified process flow diagram of another catalyst activator that may be used in embodiments;

[0008] Figure 3 is a plot showing the bed expansion of raw Siral 40 versus the flow of the fluidizing gas (SGV);

9. A method for forming a catalyst system, comprising:

combining a metallocene catalyst compound and an aluminoxane to produce a first mixture; and

forming a mixture of a support material and a fluoride donor, where the support material is an inorganic oxide;

adding the mixture to a fluidized bed reactor;

fluidizing the mixture in the fluidized bed reactor with a fluidizing gas at a flow rate that forms a fluidized bed with a height to diameter ratio of at least about 2.3; and

calcining the mixture to decompose the fluoride donor and fluorinate the support material thereby forming the fluorinated catalyst support;

adding the fluorinated catalyst support to the first mixture and drying to produce a catalyst system; or

combining a metallocene catalyst compound with a fluorinated catalyst support, and an aluminoxane, wherein the aluminoxane is present in an amount of about 10 mmol or less per gram of the fluorinated catalyst support;

wherein said fluorinated catalyst support is obtained by a method comprsing:

forming a mixture of a support material and a fluoride donor, where the support material is an inorganic oxide;

adding the mixture to a fluidized bed reactor;

fluidizing the mixture in the fluidized bed reactor with a fluidizing gas at a flow rate that forms a fluidized bed with a height to diameter ratio of at least about 2.3; and

calcining the mixture to decompose the fluoride donor and fluorinate the support material thereby forming the fluorinated catalyst support.

10. A catalyst system, comprising:

a metallocene catalyst compound;

a support comprising a fluorinated catalyst support, wherein the fluorinated catalyst support is an alumina-containing support and is generated by heating a support material and a fluoride donor compound at a temperature sufficient to decompose the fluoride donor compound in a fluidized bed reactor with a fluidizing gas at a flow rate that forms a fluidized bed with a height to depth ratio of at least about 2.3, wherein the fluoride donor compound is ammonium fluoride, ammonium bifluoride, ammonium tetrafluoroborate, ammonium hexafluorophosphate, ammonium heptafluorotantalate(V), ammonium hexafluorogermanate(IV), ammonium hexafluorotitanate(IV), ammonium hexafluorozirconate, aluminum fluoride, sodium hexafluoroaluminate, molybdenum(VI) fluoride, bromine pentafluoride, nitrogen trifluoride, difluoroamine, perfluorohexane, hexafluorobenzene, fluoromethane, trifluoroethanol, freons, derivatives thereof, or any combination thereof; and

an aluminoxane, wherein the aluminoxane is present in an amount of about 10 mmol or less per gram of the fluorinated catalyst support.

11. The catalyst system of claim 10, wherein a ratio of a pressure drop across a distributor plate to a pressure drop across the fluidized bed is maintained at greater than about 7 %.

12. The catalyst system of claim 10, wherein a flow rate of the fluidizing gas greater than about 0.35 ft. / sec is maintained at temperatures greater than about 370 °C.

13. The catalyst system of claim 10, wherein a flow rate of the fluidizing gas of about 0.1 ft. / sec is maintained at temperatures less than about 370 °C.

14. The catalyst system of claim 10, wherein a flow rate of the fluidizing gas is increased from about 0.1 ft. / sec. to about 0.4 ft./ sec starting at a temperature of between about 350 °C and about 370 °C.

15. The catalyst system of claim 10, wherein the fluorinated catalyst support has a fluoride concentration ranging from about 1 wt. % to about 10 wt. %, based on a weight of the