HAFNIUM METALLOCENES HAVING NONIDENTICAL LIGANDS

Field of Disclosure

[0001] Embodiments of the present disclosure are directed towards hafnium metallocenes having nonidentical ligands, spray-dried compositions including hafnium metallocenes having nonidentical ligands, and methods utilizing spray-dried compositions including hafnium metallocenes having nonidentical ligands are discussed herein.

Background

[0002] Metallocenes can be used in various applications, including as polymerization catalysts. Polymers may be utilized for a number of products including films, among others. Polymers can be formed by reacting one or more types of monomer in a polymerization reaction. There is continued focus in the industry on developing new and improved materials and/or processes that may be utilized to form polymers.

Summary

[0003] The present disclosure provides the following.

[0004] A spray-dried hafnium metallocene composition comprising:

a hafnium metallocene having nonidentical ligands represented by the formula $ABMX_2$, where: A is a substituted cyclopentadienyl ring and B is a substituted cyclopentadienyl ring, wherein substitution of the cyclopentadienyl ring of A is different than the substitution of the cyclopentadienyl ring of B; M is hafnium; and X is a leaving group; an activator; and a support.

[0004a] In one aspect, there is provided a spray-dried hafnium metallocene composition comprising: a hafnium metallocene having nonidentical ligands represented by formula (I) $ABMX_2$, where: A is a substituted cyclopentadienyl ring that is substituted with only one alkyl having from 1 to 3 carbons and B is a substituted cyclopentadienyl ring that is substituted with only one alkyl having from 1 to 2 carbons, wherein substitution of the cyclopentadienyl ring of A is different than the substitution of the cyclopentadienyl ring of B; M is hafnium; and X is a leaving group selected from halogen ions, hydrides, C_1 to C_{12} alkyls, C_2 to C_{12} alkenyls, C_6 to C_{12} aryls, C_7 to C_{20} alkylaryls, C_1 to C_{12} alkoxys, C_6 to C_{16} aryloxys, C_7 to C_8 alkylaryloxys, C_1 to C_{12} fluoroalkyls, C_6 to C_{12} fluoroaryls, C_1 to C_{12} heterotaom-containing hydrocarbons and substituted derivatives thereof, amines, phosphines, ethers,carboxylates, dienes, hydrocarbon radicals having

from 1 to 20 carbon atoms, fluorinated hydrocarbon radicals, fluorinated alkylcarboxylates, and combinations thereof; an activator selected from a Lewis acid, a non-coordinating ionic activator, an ionizing activator, a Lewis base, aluminum alkyls and conventional-type-co-catalysts; and a support selected from a porous support material, inorganic oxides, and inorganic chlorides.

[0005] In another aspect, there is provided a method of making a polymer, the method comprising: contacting the spray-dried hafnium metallocene composition as defined herein and an olefin under polymerization conditions to make the polymer.

Brief Description of the Drawings

[0006] Figure 1 shows molecular weight comonomer distribution index (MWCDI) in accordance a number of embodiments of the present disclosure.

Detailed Description

[0007] Hafnium metallocenes having nonidentical ligands are discussed herein. Advantageously, these hafnium metallocenes having nonidentical ligands can be utilized to make spray-dried compositions. These spray-dried compositions can be utilized to make polymers having an improved, i.e. greater, molecular weight comonomer

What is claimed is:

1. A spray-dried hafnium metallocene composition comprising:

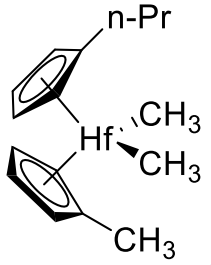
a hafnium metallocene having nonidentical ligands represented by formula (I) $ABMX_2$, where: A is a substituted cyclopentadienyl ring that is substituted with only one alkyl having from 1 to 3 carbons and B is a substituted cyclopentadienyl ring that is substituted with only one alkyl having from 1 to 2 carbons, wherein substitution of the cyclopentadienyl ring of A is different than the substitution of the cyclopentadienyl ring of B; M is hafnium; and X is a leaving group selected from halogen ions, hydrides, C_1 to C_{12} alkyls, C_2 to C_{12} alkenyls, C_6 to C_{12} aryls, C_7 to C_{20} alkylaryls, C_1 to C_{12} alkoxys, C_6 to C_{16} aryloxys, C_7 to C_8 alkylaryloxys, C_1 to C_{12} fluoroalkyls, C_6 to C_{12} fluoroaryls, C_1 to C_{12} heterotaom-containing hydrocarbons and substituted derivatives thereof, amines, phosphines, ethers,carboxylates, dienes, hydrocarbon radicals having from 1 to 20 carbon atoms, fluorinated hydrocarbon radicals, fluorinated alkylcarboxylates, and combinations thereof;

an activator selected from a Lewis acid, a non-coordinating ionic activator, an ionizing activator, a Lewis base, aluminum alkyls and conventional-type-co-catalysts; and

a support selected from a porous support material, inorganic oxides, and inorganic chlorides.

2. The spray-dried hafnium metallocene composition of claim 1, wherein A is substituted with an alkyl substituent selected from methyl, ethyl, n-propyl, and i-propyl.

3. The spray-dried hafnium metallocene composition of claim 1 or 2, wherein the hafnium metallocene having nonidentical ligands is represented by structure (I):



4. The spray-dried hafnium metallocene composition of any one of claims 1-3, wherein a molar ratio of metal in the activator to hafnium in the hafnium metallocene having nonidentical ligands is be 1500: 1 to 0.5: 1.

5. A method of making a polymer, the method comprising:

contacting the spray-dried hafnium metallocene composition of any one of claims 1-4 and an olefin under polymerization conditions to make the polymer.

6. The method of claim 5, wherein contacting the spray-dried hafnium metallocene composition and the olefin is in a single gas-phase reactor.

7. The method of claim 5 or 6, further comprising providing a greater molecular weight comonomer distribution index (MWCDI) as compared to another polymer made from a hafnium symmetric metallocene composition, wherein the polymer made from the spray-dried hafnium metallocene composition has a density difference of $\pm$ 0.01 g/cm^3 as compared to the another polymer made from the hafnium symmetric metallocene composition.