

CLAIMS

1. A method of making an attenuated hybrid catalyst, the method comprising combining a faster-light-off catalyst with an effective amount of a kinetics modifier compound ("KMC") of formula (A¹), (B¹), or (C¹): R⁵-C≡C-R⁶ (A¹), (R⁵)₂C=C=C(R⁶)₂ (B¹), or (R⁵)(R⁷)C=C(R⁶)(R⁷) (C¹) under effective reaction conditions to give an attenuated-light-off hybrid catalyst that exhibits an attenuated light-off kinetics profile (relative to that of the faster-light-off catalyst); wherein the faster-light-off catalyst has been made by activating a hybrid precatalyst of structural formula (I): (Cp)(L)_k(X)_x (I); wherein in formula (A¹), (B¹), or (C¹) each of R⁵ and R⁶ independently is H or R⁷; and each R⁷ independently is a (C₁-C₂₀)hydrocarbyl, -C(=O)-O-(unsubstituted C₁-C₂₀)hydrocarbyl, a (C₁-C₁₉)heterohydrocarbyl, or a tri((C₁-C₂₀)hydrocarbyl)silyl, or two R⁷ are taken together to form a (C₃-C₆)alkylene; with the proviso that each R⁷ lacks a carbon-carbon double bond; wherein each (C₁-C₂₀)hydrocarbyl independently is unsubstituted or substituted with from 1 to 4 substituent groups R^S; wherein each substituent group R^S is independently selected from halogen, unsubstituted (C₁-C₅)alkyl, -C≡CH, -OH, (C₁-C₅)alkoxy, -C(=O)-(unsubstituted (C₁-C₅)alkyl), -NH₂, -N(H)(unsubstituted (C₁-C₅)alkyl), -N(unsubstituted (C₁-C₅)alkyl)₂, -COOH, -C(=O)-NH₂, -C(=O)-N(H)(unsubstituted (C₁-C₅)alkyl), -C(=O)-N(unsubstituted (C₁-C₅)alkyl)₂, -S(unsubstituted (C₁-C₅)alkyl), -S(=O)₂-(unsubstituted (C₁-C₅)alkyl), -S(=O)₂-NH₂, -S(=O)₂-N(H)(unsubstituted (C₁-C₅)alkyl), -S(=O)₂-N(unsubstituted (C₁-C₅)alkyl)₂, -C(=S)-(unsubstituted (C₁-C₅)alkyl) and -COO(unsubstituted (C₁-C₅)alkyl); and wherein in formula (I): metal M is Ti, Hf, or Zr; subscript k is 0 or 1; subscript x is 1, 2, or 3; the Cp group is an unsubstituted cyclopentadienyl group; a hydrocarbyl-substituted cyclopentadienyl group; or an organoheterylene-substituted cyclopentadienyl group; group L is a monodentate organoheteryl group; each X is a monodentate group independently selected from a halogen atom, ((C₁-C₂₀)alkyl)₃-g-(phenyl)_gSi- wherein subscript g is 0, 1, 2, or 3; CH₃, a (C₂-C₂₀)alkyl-CH₂, a (C₆-C₁₂)aryl-((C₀-C₁₀)alkylene)-CH₂, a (C₁-C₆)alkyl-substituted (C₆-C₁₂)aryl, a (C₁-C₆)alkoxy-substituted (C₆-C₁₂)aryl, a (C₁-C₆)alkoxy-substituted benzyl, and a (C₁-C₆)alkyl-substituted benzyl.

2. The method of claim 1 wherein the faster-light-off catalyst is of formula (II): (Cp)(L)_k(X)_{x-1} A⁻ (II), wherein subscripts k and x; metal M; and ligand L, and leaving group X are as defined for formula (I); and wherein the attenuated hybrid catalyst is of formula (III):

$(\text{Cp})(\text{L})_k(\text{X})_{x-2}(\text{R}) \text{A}^-$ (III); wherein subscripts k and x ; metal M ; and ligand L are as defined for formula (I); each X is the monodentate group as defined for formula (I); wherein A^- is an anion (used to formally balance the positive charge of metal M); and wherein R is a ligand of formula (A), (B), or (C): $-\text{C}(\text{R}^5)=\text{C}(\text{X})\text{R}^6$ (A), $-\text{C}(\text{R}^5)_2-\text{C}(\text{X})=\text{C}(\text{R}^6)_2$ (B), or $-\text{C}(\text{R}^5)(\text{R}^7)-\text{C}(\text{X})(\text{R}^6)(\text{R}^7)$ (C), respectively; and wherein R^5 to R^7 are as defined previously for formula (A¹), (B¹), or (C¹) respectively.

3. The method of claim 1 or 2 wherein the hybrid precatalyst is of formula (Ia): $\text{CpM}(\text{X})_x$ (Ia), wherein metal M is Ti, Hf, or Zr; subscript x is 1, 2 or 3; Cp is the organoheterylene-substituted cyclopentadienyl group; and each X is as defined for formula (I).

4. The method of claim 1 or 2 wherein the hybrid precatalyst of formula (I) is of formula (Ib): $(\text{Cp})(\text{L})(\text{X})_x$ (Ib); wherein M , L , X , and subscript x are as defined for formula (I); and Cp is the unsubstituted cyclopentadienyl group or hydrocarbyl-substituted cyclopentadienyl group.

5. The method of any one of claims 1 to 4 wherein the kinetics modifier compound is of formula (A¹): $\text{R}^5-\text{C}\equiv\text{C}-\text{R}^6$ (A¹) that is selected from phenylacetylene; a (substituted-phenyl)acetylene; diphenylacetylene; a substituted diphenylacetylene; a cycloalkylacetylene; an acetylene of formula $\text{HC}\equiv\text{CSi}(\text{phenyl})_h((\text{C}_1-\text{C}_{20})\text{alkyl})_{3-h}$, wherein subscript h is an integer from 0 to 3; and an acetylene of formula $\text{HC}\equiv\text{C}-(\text{CH}_2)_m\text{CH}_3$, wherein subscript m is an integer from 1 to 15.

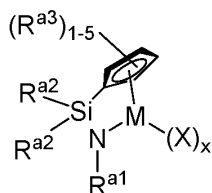
6. The method of any one of claim 1 to 4 wherein the kinetics modifier compound is of formula (B¹) $(\text{R}^5)_2\text{C}=\text{C}=\text{C}(\text{R}^6)_2$ (B¹) and is selected from a cycloalkylallene; an alkylallene; a dialkylallene; a trialkylallene; a trialkylsilyllallene; a vinylidenecycloalkane; and an alkyl ester of an allenecarboxylic acid.

7. The method of any one of claims 1 to 4 wherein the kinetics modifier compound is of formula (C¹) $(\text{R}^5)(\text{R}^7)\text{C}=\text{C}(\text{R}^6)(\text{R}^7)$ (C¹) and the kinetics modifier compound of formula (C¹) is an internal alkene.

8. The method of any one of claims 1 to 7 wherein the method further comprises making a mixture of the attenuated hybrid catalyst, a support material, and an inert hydrocarbon solvent and removing the inert hydrocarbon solvent from the mixture so as to give the

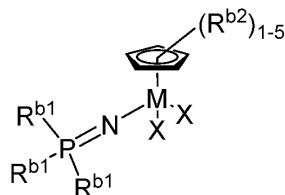
attenuated hybrid catalyst disposed on the support material.

9. The method of any one of claims 1 to 3 wherein the hybrid precatalyst of formula (I)



is of formula (Ia)-1 (Ia)-1; wherein each group R^{a1} and R^{a2} independently is a (C_1-C_{20}) alkyl; and each group R^{a3} independently is H or a (C_1-C_{20}) alkyl; each subscript 1-5 independently is 0, 1, 2, 3, 4, or 5; and M, X, and subscript x are as defined for formula (I).

10. The method of any one of claims 1, 2, and 4 wherein the hybrid precatalyst is of



formula (Ib)-1: (Ib)-1, wherein each group R^{b1} independently is a (C_1-C_{20}) alkyl; and each group R^{b2} independently is H or a (C_1-C_{20}) alkyl; each subscript 1-5 independently is 0, 1, 2, 3, 4, or 5; and M and X are as defined for formula (I).

11. An attenuated hybrid catalyst made by the method of any one of claims 1 to 10.

12. A method of feeding a hybrid catalyst to a slurry-phase or gas-phase polymerization reactor containing an olefin monomer and a moving bed of polyolefin polymer, the method comprising making the attenuated hybrid catalyst outside of the reactor and according to the method of any one of claims 1 to 10, and feeding the attenuated hybrid catalyst in neat form or as a solution or slurry thereof in an inert hydrocarbon liquid through a feed line free of olefin monomer into the slurry-phase or gas-phase polymerization reactor.

13. A multimodal catalyst system comprising the attenuated hybrid catalyst of claim 11 and at least one second catalyst selected from the group consisting of an unattenuated a hybrid catalyst described herein, a different attenuated hybrid catalyst, a post-metallocene catalyst, and a metallocene catalyst.

14. A method of making a polyolefin polymer, the method comprising contacting at least

one 1-alkene monomer with the attenuated hybrid catalyst made by the method of any one of claims 1 to 10, or the multimodal catalyst system of claim 13, under slurry-phase or gas-phase polymerization conditions in a slurry-phase or gas-phase polymerization reactor containing a moving bed of polyolefin resin, thereby making the polyolefin polymer.