Claims

1. Method for preparing a catalyst composition for the oligomerization of ethylene comprising the steps:

   a) preparing in a first solvent, a first solution by mixing of a co-catalyst and a modifier, wherein the co-catalyst is selected from trialkyl aluminum, alkyl aluminum sesquichloride, dialkyl aluminum chloride, alkyl aluminum dichloride, wherein alkyl is preferably methyl, ethyl, isopropyl or isobutyl, methylaluminoxane (MAO) or mixtures thereof, and wherein the modifier is selected from ammonium or phosphonium salts of the type $[H_4E]X$, $[H_3ER]X$, $[H_2ER_2]X$, $[HER_3]X$ or $[ER_4]X$ or HX or RX with E = N or P, X = Cl, Br or I and R = alkyl, cycloalkyl, acyl, aryl, alkenyl, alkynyl or the corresponding bridging di-, tri- or multiunits, or ammonium or phosphonium salts based on cyclic amines;

   b) adding a chromium compound and a ligand to the first solution obtained in step a) to obtain a second solution; and

   c) optionally mixing the second solution obtained in step b) for 10 seconds to 5 hours, preferably 0.5 hours to 2.5 hours.

2. Method according to claim 1, wherein the chromium compound is selected from organic or inorganic salts, coordination complexes and organometallic complexes of Cr(II) or Cr(III), preferably $CrCl_3(THF)_3$, Cr(III)acetylacetonate, Cr(III)octanoate, chromium hexacarbonyl, Cr(III)-2-ethylhexanoate, benzene(tricarbonyl)-chromium or Cr(III)chloride.

3. Method according to claim 1 or 2, wherein the ligand has the general structure R_1R_2P-$N(R_3)$-$P(R_4)$-$N(R_5)$-H, wherein R_1, R_2, R_3, R_4 and R_5 are independently selected from halogen, amino, trimethylsilyl, C_1-C_{10}-alkyl, substituted C_1-C_{10}-alkyl, aryl and substituted aryl.

4. Method according to any of the preceding claims, wherein the chromium compound and the ligand are added to the first solution obtained in step a) simultaneously, preferably dissolved in a second solvent.

5. Method according to any of the preceding claims, wherein the first and/or second solvent is an aromatic or aliphatic solvent or mixtures thereof, preferably toluene, benzene, ethylbenzene, cumenene, xylenes, mesitylene, hexane, octane, cyclohexane, olefins, such as hexene, heptane, octene, or ethers, such as diethylether or tetrahydrofurane, more preferably an aromatic solvent, most preferably toluene.

6. Method according to any of the preceding claims, wherein the co-catalyst is trialkyl aluminum (AlR'_3 with R' = alkyl or aryl), and the modifier is an ammonium or phosphonium salt of the type $[ER_4]X$, resulting after mixing in a reaction product having the formula $[ER_4][Al_2R'_6X]^*(solvent)_n$ with $0 \leq n \leq 100$, preferably $1 \leq n \leq 20$, according to reaction scheme:

$$[ER_4]X + 2AlR'_3 + n\ solvent \rightarrow [ER_4][Al_2R'_6X]^*(solvent)_n$$

7. Method according to any of the preceding claims, wherein the molar ligand/Cr ratio is from 0.5 to 50, preferably from 0.8 to 2.0.

8. Method according to any of the preceding claims, wherein the molar Al/Cr ratio is from 1.0 to 1,000, preferably from 10 to 100.

9. Method according to any of the preceding claims, wherein the molar modifier/Cr ratio is from 0.1 to 100, preferably from 1 to 20.

10. Catalyst composition pre-formation unit for preparing a catalyst composition for the oligomerization of ethylene, the catalyst composition, comprising a chromium compound, a ligand, a modifier and a co-catalyst, wherein the pre-formation unit comprises a first vessel (1) containing a solution of co-catalyst and modifier, a second ves-

sel (2) containing chromium compound and ligand, the first and second vessel (1, 2) being connected via lines, optionally each having dosing pumps (4, 5), to a mixing unit (3), the mixing unit (3) being connected via a line, optionally having a dosing pump (6), to an oligomerization reactor (7).

11. Catalyst composition pre-formation unit according to claim 11, wherein the mixing unit is a vessel comprising stirring means.

Claims

1. Method for preparing a catalyst composition for the oligomerization of ethylene comprising the steps:

   a) preparing in a first solvent, a first solution by mixing of a co-catalyst and a modifier, wherein the co-catalyst is selected from trialkyl aluminum, alkyl aluminum sesquichloride, dialkyl aluminum chloride, alkyl aluminum dichloride and wherein the modifier is selected from ammonium or phosphonium salts of the type $[H_4E]X$, $[H_3ER]X$, $[H_2ER_2]X$, $[HER_3]X$ or $[ER_4]X$ or HX or RX with E = N or P, X = Cl, Br or I and R = alkyl, cycloalkyl, acyl, aryl, alkenyl, alkynyl or the corresponding bridging di-, tri- or multiunits, or ammonium salts based on cyclic amines; and

   b) adding a chromium compound and a ligand to the first solution obtained in step a) to obtain a second solution.

2. Method according to claim 1, further comprising mixing the second solution obtained in step b) for 10 seconds to 5 hours.

3. Method according to claim 1 or 2, wherein the chromium compound is selected from organic or inorganic salts, coordination complexes and organometallic complexes of Cr(II) or Cr(III).

4. Method according to any of the preceding claims, wherein the ligand has the general structure $R_1R_2P\text{-}N(R_3)\text{-}P(R_4)\text{-}N(R_5)\text{-}H$, wherein R_1, R_2, R_3, R_4 and R_5 are independently selected from halogen, amino, trimethylsilyl, C_1-C_{10}-alkyl, substituted C_1-C_{10}-alkyl, aryl and substituted aryl.

5. Method according to any of the preceding claims, wherein the chromium compound and the ligand are added to the first solution obtained in step a) simultaneously.

6. Method according to any of the preceding claims, wherein the first and/or second solvent is an aromatic or aliphatic solvent or mixtures thereof.

7. Method according to any of the preceding claims, wherein the co-catalyst is trialkyl aluminum (AlR'_3 with R' = alkyl or aryl), and the modifier is an ammonium or phosphonium salt of the type $[ER_4]X$, resulting after mixing in a reaction product having the formula $[ER_4][Al_2R'_6X]^*(solvent)_n$ with $0 \leq n \leq 100$, according to reaction scheme:

   $[ER_4]X + 2AlR'_3 + n\ solvent \rightarrow [ER_4][Al_2R'_6X]^*(solvent)_n.$

8. Method according to any of the preceding claims, wherein the molar ligand/Cr ratio is from 0.5 to 50.

9. Method according to any of the preceding claims, wherein the molar Al/Cr ratio is from 1.0 to 1,000.

10. Method according to any of the preceding claims, wherein the molar modifier/Cr ratio is from 0.1 to 100.

11. Catalyst composition pre-formation unit for preparing a catalyst composition for the oligomerization of ethylene, the catalyst composition comprising a chromium compound, a ligand, a modifier and a co-catalyst, wherein the pre-formation unit comprises a first vessel containing a solution of the co-catalyst and the modifier, a second vessel containing the chromium compound and the ligand, the first and second vessel being connected via lines to a mixing unit, the mixing unit being connected via a line to an oligomerization reactor.

12. Catalyst composition pre-formation unit according to claim 11, wherein the mixing unit is a vessel comprising stirring means.

13. Catalyst composition pre-formation unit according to claim 11 or 12, wherein the lines, via which the first and second vessel is connected to a mixing unit, each have dosing pumps.

14. Catalyst composition pre-formation unit according to any one of claims 11-13, wherein the line, via which the mixing unit is connected to the oligomerization reactor, has a dosing pump.

15. Method for preparing a catalyst composition for the oligomerization of ethylene comprising the steps:

a) preparing in a first solvent, a first solution by mixing of a co-catalyst and a modifier, wherein the co-catalyst is selected from trialkyl aluminum, alkyl aluminum sesquichloride, dialkyl aluminum chloride, alkyl aluminum dichloride, wherein the alkyl is preferably methyl, ethyl, isopropyl or isobutyl, methylaluminoxane (MAO) or mixtures thereof, and wherein the modifier is selected from ammonium or phosphonium salts of the type $[H_4E]X$, $[H_3ER]X$, $[H_2ER_2]X$, $[HER_3]X$ or $[ER_4]X$ or HX or RX with E = N or P, X = Cl, Br or I and R = alkyl, cycloalkyl, acyl, aryl, alkenyl, alkynyl or the corresponding bridging di-, tri- or multiunits, or ammonium or phosphonium salts based on cyclic amines;

b) adding a chromium compound and a ligand to the first solution obtained in step a) to obtain a second solution; and

c) optionally mixing the second solution obtained in step b) for 10 seconds to 5 hours, preferably 0.5 hours to 2.5 hours.