The phrases “activator” and “cocatalyst” have the same meaning and are interchangeable terms in the present application.

Summary ~~of Invention~~

Thus, ~~viewed from one aspect~~ the ~~invention~~disclosure relates to a catalyst system for producing ethylene copolymers in a high temperature solution process at a temperature greater than 100°C, the catalyst system comprising

(i) a metallocene complex of a group 4 transition metal comprising at least one ligand selected from optionally substituted cyclopentadienyl (Cp), indenyl (Ind) and fluorenyl (Flu) ligands and

(ii) a solid alkyl aluminium oxide cocatalyst.

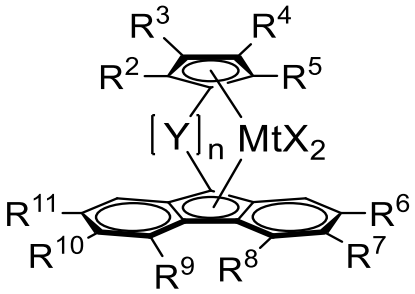
~~Viewed from a second aspect the invention~~The disclosure relates to a catalyst system for producing ethylene copolymers in a high temperature solution process at a temperature greater than 100°C, the catalyst system comprising

(i) a metallocene complex of a group 4 transition metal comprising at least one ligand selected from optionally substituted cyclopentadienyl (Cp), indenyl (Ind) and fluorenyl (Flu) ligands and

(ii) a solid alkyl alumoxane cocatalyst provided as a suspension in an aliphatic C_5 to C_{24} hydrocarbon solvent or mixture of said aliphatic hydrocarbon solvents.

In one aspect, the present disclosure relates to a catalyst system for producing ethylene copolymers in a high temperature solution process at a temperature greater than 100°C, the catalyst system comprising

(i) a metallocene complex of formula (II)



(II)

wherein

Mt is Zr, Hf or a mixture of Hf and Zr, wherein the mixture of Hf and Zr is a mixture of complexes of formula (II) with Zr or Hf metal,

X is a sigma ligand,

Y is is a bridge of formula $–(WR^y)_n$ - ,

n is 1, 2 or 3, preferably 1 or 2, more preferably 1,

W is C or Si;

each R^y is as defined in formula (I),

R^2 to R^{11} are independently hydrogen or a saturated or unsaturated, linear, branched or cyclic C_1-C_{10} hydrocarbyl group, C_6-C_{10} aryl, C_6-C_{20} alkylaryl group or C_6-C_{20} arylalkyl group, which optionally contain up to 2 heteroatoms or silicon atoms; and

(ii) a solid alkyl alumoxane cocatalyst;

provided as a suspension in an aliphatic C_5 to C_{24} hydrocarbon solvent or mixture of said aliphatic hydrocarbon solvents.

~~Viewed from another aspect the invention~~The disclosure provides a process for the preparation of an ethylene copolymer comprising polymerizing ethylene and a C_{4-12} alpha-olefin comonomer in a high temperature solution process at a temperature greater than 100°C in the presence of a catalyst system comprising:

(i) a metallocene complex of a group 4 transition metal comprising at least one ligand selected from optionally substituted cyclopentadienyl (Cp), Indenyl (Ind) and fluorenyl (Flu) ligands and

(ii) a solid alkyl alumoxane cocatalyst.

~~Viewed still from another aspect the invention~~The disclosure provides a process for the preparation of an ethylene copolymer comprising polymerizing ethylene and a C_{4-12} alpha-olefin comonomer in a high temperature solution process at a temperature greater than 100°C in the presence of a catalyst system comprising:

(i) a metallocene complex of a group 4 transition metal comprising at least one ligand selected from optionally substituted cyclopentadienyl (Cp), Indenyl (Ind) and fluorenyl (Flu) ligands and

(ii) a solid alkyl alumoxane cocatalyst provided as a suspension in an aliphatic C_5 to C_{24} hydrocarbon solvent or mixture of said aliphatic hydrocarbon solvents.

In another aspect, the present disclosure provides a process for the preparation of an ethylene - C_4-C_{12} copolymer comprising polymerizing ethylene and a C_{4-10} alpha-olefin comonomer in a high temperature solution process at a temperature greater than 100°C in the presence of a catalyst system comprising:

(i) a metallocene complex of a group 4 transition metal comprising at least one ligand selected from optionally substituted cyclopentadienyl (Cp), indenyl (Ind) and fluorenyl (Flu) ligands and

(ii) a solid alkyl alumoxane cocatalyst;

provided as a suspension in an aliphatic C_5 to C_{24} hydrocarbon solvent or mixture of said aliphatic hydrocarbon solvents.

In another aspect, the present disclosure provides a process for producing a catalyst system comprising the steps

a) providing the solid AlkAO, preferably solid MAO, as a suspension in one or more liquid C_5 to C_{24} aliphatic hydrocarbon solvents as described herein;

b) contacting the suspension of step a) with the metallocene complex as described herein in solid form;

c) stirring the suspension for at least 2 h;

d) obtaining the product in a form of a slurry of alkyl alumoxane-supported, preferably of MAO-supported solid catalyst.

~~Viewed from a further aspect the invention~~The disclosure provides an ethylene C_{4-12} alpha-olefin copolymer made by a process as hereinbefore defined.

~~Viewed from another aspect the invention~~The disclosure provides use of a catalyst system comprising:

(i) a metallocene complex of a group 4 transition metal comprising at least one ligand selected from optionally substituted cyclopentadienyl (Cp), indenyl (Ind) and fluorenyl (Flu) ligands and

(ii) a solid alkyl alumoxane cocatalyst

in a high temperature solution process at a temperature greater than 100°C for preparing ethylene C_{4-12} alpha-olefin copolymers.

~~Viewed from a further aspect the invention~~The disclosure provides use of a catalyst system comprising:

(i) a metallocene complex of a group 4 transition metal comprising at least one ligand selected from optionally substituted cyclopentadienyl (Cp), indenyl (Ind) and fluorenyl (Flu) ligands and

(ii) a solid alkyl alumoxane cocatalyst cocatalyst provided as a suspension in an aliphatic C_5 to C_{24} hydrocarbon solvent or mixture of said aliphatic hydrocarbon solvents

in a high temperature solution process at a temperature greater than 100°C for preparing ethylene C_{4-12} alpha-olefin copolymers.

In another aspect, the present disclosure provides use of a catalyst system as described herein or prepared by the process as described herein in a high temperature solution process at a temperature greater than 100°C for copolymerizing ethylene and a C_{4-12} alpha-olefin comonomer.

Alkyl aluminium oxide and alkyl alumoxane have the same meaning and are interchangeable terms in the present application.

Detailed Description of the Invention

Metallocene Complex

The single site metallocene complex used for manufacture of the ethylene C_{4-12} alpha-olefin copolymer is a metallocene complex of group 4 transition metal comprising at least one ligand selected from optionally substituted cyclopentadienyl (Cp), Indenyl (Ind) and fluorenyl (Flu) ligands and optionally containing a covalent bridge connecting the two ligands.

Such metallocene complexes, without a bridge are of formula (A)

Claims:

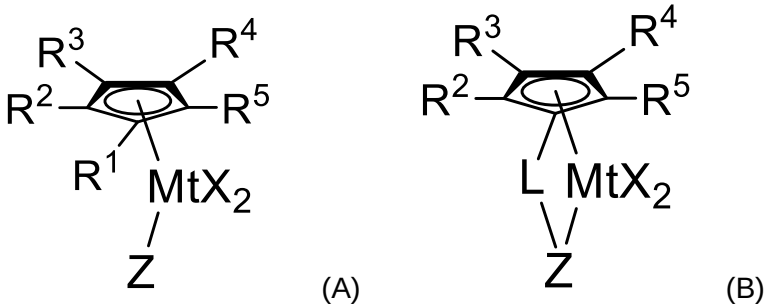
1. A process for the preparation of an ethylene - C_4-C_{12} copolymer comprising polymerizing ethylene and a C_{4-10} alpha-olefin comonomer in a high temperature solution process at a temperature greater than 100°C in the presence of a catalyst system ~~for producing ethylene copolymers in a high temperature solution process at a temperature greater than 100°C, the catalyst system~~ comprising:

(i) a metallocene complex of a group 4 transition metal comprising at least one ligand selected from optionally substituted cyclopentadienyl (Cp), indenyl (Ind) and fluorenyl (Flu) ligands and

(ii) a solid alkyl alumoxane cocatalyst~~,~~;

provided as a suspension in an aliphatic C_5 to C_{24} hydrocarbon solvent or mixture of said aliphatic hydrocarbon solvents.

2. A ~~Catalyst system~~process according to claim 1, wherein the metallocene complex in i) is of formula (A) or (B)



where

Z is a ligand coordinating to Mt,

Mt is Ti, Zr, Hf or a mixture of Zr and Hf, wherein the mixture of Zr and Hf is a mixture of complexes of formula (A) with Zr or Hf metal, or a mixture of complexes of formula (B) with Zr or Hf metal,

X is a sigma ligand,

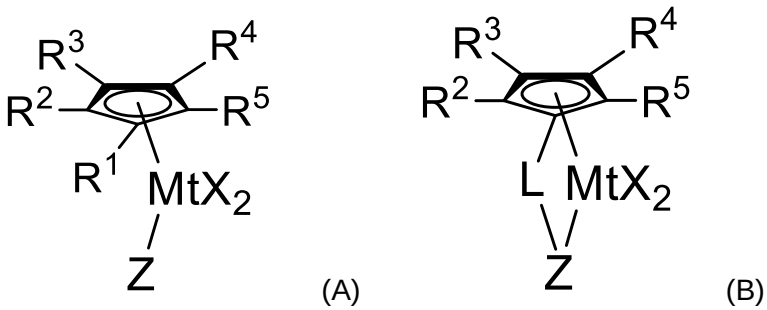
L is a covalent bridge connecting the ligands,

R^1 to R^5 are independently a hydrogen atom, a saturated or unsaturated, linear, branched or cyclic C_1-C_{10} hydrocarbyl group, a C_6-C_{10} aryl group, a C_6-C_{20} alkylaryl group or a C_6-C_{20} arylalkyl group, which optionally contains one or two heteroatoms or silicon atoms,

or two adjacent groups R^1 to R^5 can form a ring comprising from 4 to 8 ring atoms, where the atoms being part of the formed ring can be substituted by one or more R^{12} groups

selected from saturated or unsaturated, linear or branched C_1-C_{10} hydrocarbyl, a C_5-C_{10}aromatic group, C_6-C_{20} alkylaryl or C_6-C_{20} arylalkyl groups, which optionally contain one or two heteroatoms or silicon atoms.

3. A ~~catalyst system~~process of claim 1 wherein the metallocene complex in i) is of formula (A) or (B)



where

Z is a ligand coordinating to Mt,

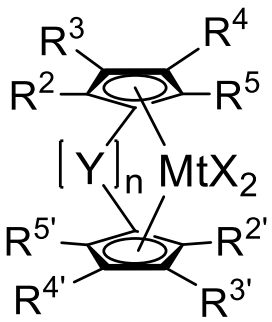
Mt is Ti, Zr, Hf or mixture of Zr and Hf, wherein the mixture of Zr and Hf is a mixture of complexes of formula (A) with Zr or Hf metal, or a mixture of complexes of formula (B) with Zr or Hf metal,

X is a sigma ligand,

L is a covalent bridge connecting the ligands,

R^1 to R^5 are independently a hydrogen atom, a saturated or unsaturated, linear, branched or cyclic C_1-C_{10} hydrocarbyl group, a C_6-C_{10} aryl group, a C_6-C_{20} alkylaryl group or a C_6-C_{20} arylalkyl group, in which up to two C atoms of the arylic ring(s) can be replaced by up to two heteroatoms, and which optionally carry substituents attached to their ring atoms, and such substituents optionally contain one or two heteroatoms or silicon atoms, or two adjacent groups of R^1 to R^5 can form a ring comprising from 4 to 8 ring atoms, where the atoms being part of the formed ring can be substituted by one or more R^{12} groups selected from saturated or unsaturated, linear or branched C_1-C_{10} hydrocarbyl, a C_5-C_{10} aromatic group , C_6-C_{20} alkylaryl or C_6-C_{20} arylalkyl groups, which optionally contain one or two heteroatoms or silicon atoms.

4. A ~~Catalyst system~~process according to claim 1, wherein the metallocene complex in i) is of formula (I)



(I)

wherein

Mt is Zr, Hf or a mixture of Hf and Zr, wherein the mixture of Hf and Zr is a mixture of complexes of formula (I) with Zr or Hf metal,

X is a sigma ligand,

Y is a bridge of formula $–(WR^y)_n$ -,

n is 1, 2 or 3, preferably 1 or 2, more preferably 1,

W is C or Si;

each R^y is independently a hydrogen atom, a saturated or unsaturated, linear, branched or cyclic C_1-C_{10} hydrocarbyl group, a C_6-C_{10} aryl, a C_6-C_{20} alkylaryl group or a C_6-C_{20} arylalkyl group, any of which optionally contains one or two heteroatoms or silicon atoms, or

a heteroatom-containing saturated or unsaturated ring of 3 to 7 ring-atoms optionally substituted with a linear, branched or cyclic saturated or unsaturated C_1 to C_{20} hydrocarbyl group,

R^2 to R^5 and $R^{2'}$ to $R^{5'}$ are independently hydrogen or a saturated or unsaturated, linear, branched or cyclic C_1-C_{10} hydrocarbyl group, a C_6-C_{10} aryl, C_6-C_{20} alkylaryl or C_6-C_{20} arylalkyl group, which optionally contain one or two heteroatoms or silicon atoms, or

any two adjacent groups of R^1 to R^5 and/or of $R^{1'}$ to $R^{5'}$ can form a ring comprising from 4 to 8 ring atoms, and the atoms being part of the formed ring may be further substituted by one or more R^{12} groups selected from a saturated or unsaturated, linear or branched C_1-C_{10} hyrocarbyl, a C_5-C_{10} aromatic group, C_6-C_{20} alkylaryl or C_6-C_{20} arylalkyl groups, which may contain one or two heteroatoms or silicon atoms, or

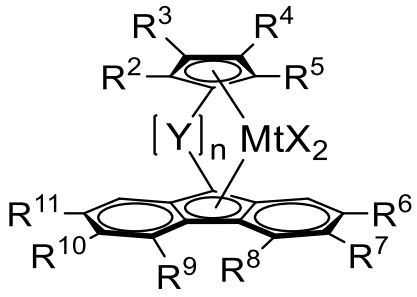
R^1 to R^5 and $R^{2'}$ to $R^{5'}$ are independently a hydrogen atom, a saturated or unsaturated, linear, branched or cyclic C_1-C_{10} hydrocarbyl group, a C_6-C_{10} aryl group, a C_6-C_{20} alkylaryl group or a C_6-C_{20} arylalkyl group, in which up to two C atoms of the arylic ring(s) can be replaced by up to two heteroatoms, and which optionally carry substituents attached to their ring atoms, and such substituents optionally contain one or two heteroatoms or silicon atoms, or two adjacent groups of R^1 to R^5 and/or $R^{2'}$ to $R^{5'}$ can form a ring comprising from 4 to 8 ring atoms, where the atoms being part of the formed ring can be

substituted by one or more R^{12} groups selected from saturated or unsaturated, linear or branched C_1-C_{10} hydrocarbyl, a C_5-C_{10} aromatic group , C_6-C_{20} alkylaryl or C_6-C_{20} arylalkyl groups, which optionally contain one or two heteroatoms or silicon atoms,

each X may be the same or different and is a sigma ligand, preferably a hydrogen atom, a halogen atom, a R^{14}, OR^{14}, OSO_2CF_3, $OCOR^{14}$, SR^{14}, NR^{14}_2 or PR^{14}_2 group, where R^{14} is a linear or branched, cyclic or acyclic, C_1-C_{20}-alkyl, C_2-C_{20}-alkenyl, C_2-C_{20}-alkynyl, C_6-C_{20}-aryl, C_7-C_{20}-alkylaryl or C_7-C_{20}-arylalkyl group optionally containing one or more heteroatoms belonging to groups 15 or 16, or is SiR^{14}_3, $SiHR^{14}_2$ or SiH_2R^{14}, where R^{14} is preferably $C_{1\text{-}6}$-alkyl, phenyl or benzyl group,

preferably each X is independently a halogen atom or a R^{14} or OR^{14} group, whereby R^{14} is a $C_{1\text{-}6}$-alkyl, phenyl or benzyl group, most preferably X is methyl, chloro or benzyl group.

5. A ~~Catalyst system~~process according to claim 1, wherein the metallocene complex in i) is of formula (II)



(II)

wherein

Mt is Zr, Hf or a mixture of Hf and Zr, wherein the mixture of Hf and Zr is a mixture of complexes of formula (II) with Zr or Hf metal,

Y is a bridge of formula $–(WR^y)_n$-,

n is 1, 2 or 3, preferably 1 or 2, more preferably 1

W is C or Si;

each R^y is as defined in formula (I),

each X is as defined in formula (I),

R^2 to R^{11} are independently hydrogen or a saturated or unsaturated, linear, branched or cyclic C_1-C_{10} hydrocarbyl group, a C_6-C_{10}aryl, C_6-C_{20} alkylaryl group or C_6-C_{20} arylalkyl group, which optionally contain up to 2 heteroatoms or silicon atoms, or

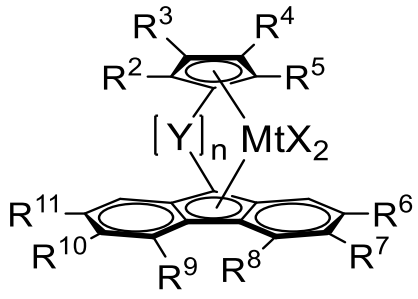
any two adjacent groups of R^2 to R^{11} can form a ring, comprising from 4 to 8 atoms. The atoms being part of the formed ring may be further substituted by one or more R^{12} groups selected from or a saturated or unsaturated, linear or branched C_1-C_{10} hydrocarbyl, a C_5-

C_{10} aromatic group, C_6-C_{20} alkylaryl or C_6-C_{20} arylalkyl groups, which may contain up to 2 heteroatoms or silicon atoms, or

R^1 to R^{11} are independently a hydrogen atom, a saturated or unsaturated, linear, branched or cyclic C_1-C_{10} hydrocarbyl group, a C_6-C_{10} aryl group, a C_6-C_{20} alkylaryl group or a C_6-C_{20} arylalkyl group, in which up to two C atoms of the arylic ring(s) can be replaced by up to two heteroatoms, and which optionally carry substituents attached to their ring atoms, and such substituents optionally contain one or two heteroatoms or silicon atoms, or two adjacent groups of R^1 to R^{11} can form a ring comprising from 4 to 8 ring atoms, where the atoms being part of the formed ring can be substituted by one or more R^{12} groups selected from saturated or unsaturated, linear or branched C_1-C_{10} hydrocarbyl, a C_5-C_{10} aromatic group , C_6-C_{20} alkylaryl or C_6-C_{20} arylalkyl groups, which optionally contain one or two heteroatoms or silicon atoms.

6. A catalyst system for producing ethylene copolymers in a high temperature solution process at a temperature greater than 100°C, the catalyst system comprising

(i) a metallocene complex of formula (II)



(II)

wherein

Mt is Zr, Hf or a mixture of Hf and Zr, wherein the mixture of Hf and Zr is a mixture of complexes of formula (II) with Zr or Hf metal,

X is a sigma ligand,

Y is is a bridge of formula $–(WR^y)_n-$,

n is 1, 2 or 3, preferably 1 or 2, more preferably 1,

W is C or Si;

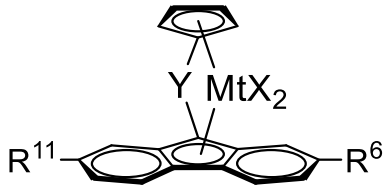
each R^y is as defined in formula (I),

R^2 to R^{11} are independently hydrogen or a saturated or unsaturated, linear, branched or cyclic C_1-C_{10} hydrocarbyl group, C_6-C_{10} aryl, C_6-C_{20} alkylaryl group or C_6-C_{20} arylalkyl group, which optionally contain up to 2 heteroatoms or silicon atoms; and

(ii) a solid alkyl alumoxane cocatalyst;

provided as a suspension in an aliphatic C_5 to C_{24} hydrocarbon solvent or mixture of said aliphatic hydrocarbon solvents.

~~6~~7. A Catalyst system according to claim ~~1~~6, wherein the metallocene complex in i) is of formula (V)



(V)

wherein Mt, X, Y and R^6 and R^{11} are as defined in claim ~~5~~6, most preferably, R^6 and R^{11} are tertiary alkyl groups, X is methyl or chlorine, and Mt is Hf.

~~7~~8. A catalyst system according to any of claims ~~1~~ 6 to ~~6~~7, wherein the solid alkyl alumoxane cocatalyst ii) is a solid alkyl alumoxane (AlkAO), wherein the alkyl group is a C_1 to C_6 alkyl, preferably a C_1 to C_3 alkyl.

~~8~~9. A catalyst system according to any of ~~the preceding~~ claims 6 to 8, wherein the cocatalyst is a solid methylalumoxane (MAO).

~~9~~10. A catalyst system according to claim ~~7~~ 9 wherein the Al content in the solid MAO is in the range of 25 to 60 wt-%, preferably in the range of 30 to 50 wt-%.

~~10~~11. A catalyst system according to any of ~~the preceding~~ claims 6 to 10, wherein the ~~solid alkyl alumoxane cocatalyst~~catalyst system is provided as a suspension in one or more aliphatic C_6 to C_{12} hydrocarbon solvents.

~~11~~12. A catalyst system according to ~~claim 1 or 10~~any of claims 6 to 11, wherein the average particle size of the solid alkyl alumoxane cocatalyst in the suspension is of 2 to 20 µm, preferably in the range of 4 to 12 µm.

~~12~~13. A catalyst system according to claim ~~11~~12, wherein the content of the solid AlkAO, preferably solid MAO, in the suspension, is in the range of 3 to 30 wt-%, preferably in the range of 6 to 20 wt-%, more preferably 8 to 15 wt-%.

~~13~~14. A process for producing a catalyst system comprising the steps

a) providing the solid AlkAO, preferably solid MAO, as a suspension in one or more liquid C_5 to C_{24} aliphatic hydrocarbon solvents as defined in any of claims ~~7 to 12~~8 to 13;

b) contacting the suspension of step a) with the metallocene complex as defined in any of claims 1 to ~~6~~ 7 in solid form;

c) stirring the suspension for at least 2 h;

d) obtaining the product in a form of a slurry of alkyl alumoxane-supported, preferably of MAO-supported solid catalyst.

~~14~~15. The process according to claim ~~13~~14, wherein the product from step b) or c) is diluted with light hydrocarbon solvent, preferably a solvent of C_6 to C_{12} alkanes or mixtures thereof.

~~15~~16. Use of a catalyst system as defined in any of claims ~~1 to 12~~6 to 13 or prepared by the process as defined in claims ~~13~~ 14 or ~~14~~ 15 in a high temperature solution process at a temperature greater than 100°C for copolymerizing ethylene and a C_{4-12} alpha-olefin comonomer.

~~16. Process for the preparation of an ethylene - C_4-C_{12} copolymer comprising polymerizing ethylene and a C_{4-10} alpha-olefin comonomer in a high temperature solution process at a temperature greater than 100°C in the presence of a catalyst system as defined in any of the claims 1 to 12 comprising:~~

~~(i) a metallocene complex of as defined in any of preceding claims 1 to 6 and~~

~~(ii) a solid alkyl alumoxane cocatalyst as defined in any of the claims 1 or 7 to 12,~~

~~or in the presence of a catalyst system prepared by the process as defined in claim 13 or 14.~~

17. ~~Process~~ A process according to ~~claim 16~~any of claims 1 to 5, wherein the polymerization is performed

a) at a polymerization temperature of at least 110°C,

b) a pressure in the range of 10 to 100 bar and

c) in a liquid hydrocarbon solvent selected from the group of C_{5-12}-hydrocarbons, which may be unsubstituted or substituted by C_{1-4} alkyl group.

~~18. Ethylene copolymer obtained by a polymerization process according to claim 16 or 17.~~