(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
25 January 2007 (25.01.2007)

PCT

(10) International Publication Number
WO 2007/009977 A1

(51) International Patent Classification:
C08F 10/00 (2006.01) *C07D 307/52* (2006.01)
C07F 15/04 (2006.01) *C07D 213/38* (2006.01)
C07C 251/38 (2006.01)

(21) International Application Number:
PCT/EP2006/064335

(22) International Filing Date: 17 July 2006 (17.07.2006)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
05291547.7 19 July 2005 (19.07.2005) EP

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*
— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 2007/009977 A1

(54) Title: POLYMERISATION CATALYST SYSTEM BASED ON DIOXIME LIGANDS

(57) Abstract: The present invention discloses active oligomerisation and polymerisation catalyst systems based on dioxime ligands.

POLYMERISATION CATALYST SYSTEM BASED ON DIOXIME LIGANDS.

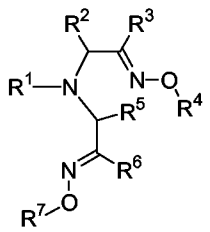
This invention relates to the field of dioxime ligands and their use in catalyst system for the oligomerisation and polymerisation of ethylene and alpha-olefins.

There exists a multitude of catalyst systems available for polymerising or oligomerising ethylene and alpha-olefins, but there is a growing need for finding new systems capable to tailor polymers with very specific properties. More and more post-metallocene catalyst components based on early or late transition metals from Groups 3 to 10 of the Periodic Table have recently been investigated such as for example those disclosed in Gibson and al. review (Gibson, V.C.; Spitzmesser, S.K., *Chem. Rev.* 2003, *103*, p. 283). But there is still a need to improve either the specificities or the performances of these systems.

It is an aim of the present invention to prepare a polymerisation catalyst system based on dioxime ligands.

It is also an aim of the present invention to use dioxime ligand-based catalyst system for the homo- or co-polymerisation of ethylene and alpha-olefins.

Accordingly, the present invention uses dioxime ligands of general formula I



(I)

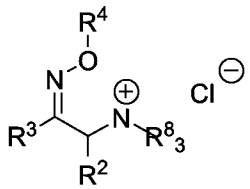
wherein R^1 R^2 R^3 R^4 R^5 R^6 and R^7 are selected from H or alkyl having from 1 to 20 carbon atoms or aryl having from 3 to 18 carbon atoms or functional groups such as heterocycles and two neighbouring R^i can be joined together to make a ring. Preferably R^2 and $R^5$are the same, R^3 and R^6 are the same and R^4 and R^7 are the same.

The dioxime ligands are prepared according to a method that comprises the steps of:

a) dissolving in a solvent a primary amine R^1-NH_2

wherein R^1 is as described here-above,

b) suspending in the same or another solvent an oxime precursor of formula



wherein R^8 is an alkyl group and R^2, R^3 and R^4 are as described above;

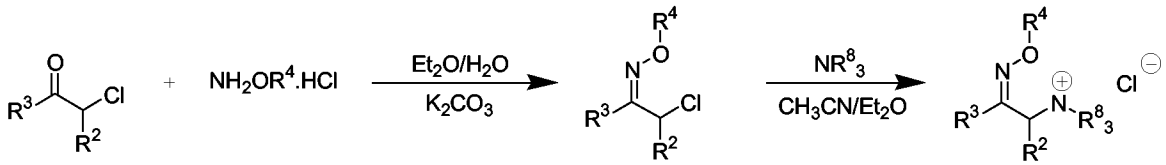
c) reacting the primary amine with at least 2 equivalents of the oxime precursor;

d) separating the dioxime ligand from residual oxime precursor and salt by-product;

e) retrieving the dioxime ligand.

An oxime precursor TACO is described for example in Goldcamp et al. (M.J. Goldcamp, S.D. Edison, L.N. Squires, D.T. Rosa, N.K. Vowels, N.L. Coker, J.A. Krause Bauer, and M.J. Baldwin, in Inorg. Chem., 42, 717-728, 2003) or in Pavlishehuk et al. (V. V. Pavlishehuk, S.V. Kolotilov, A.W. Addison, M.J. Prushan, R.J. Butcher and L.K. Thompson, in Inorg. Chem. 38, 1759-1766, 1999).

The oxime precursor can be prepared according to the scheme



Preferably, R^2 and R^4 are the same and are hydrogen, R^3 is methyl and R^8 is ethyl : this preferred precursor is called TACO.

Among the preferred embodiments according to the present invention, R^i can each be independently selected from isopropyl, n-butyl, benzyl, cyclohexyl, pyridine, thiophene, furane, phenyl, mesityl.

Preferably, both the primary amine and the oxime precursor are suspended in the same solvent. The solvent is polar, preferably, it is acetonitrile.

The catalyst component is then prepared by complexing the ligand with a metallic precursor in a ratio from 1/1 to 2/1. The metallic precursor and the ligand are placed in a solvent and they are allowed to react under stirring for a period of time of from 2 to 10 hours at a temperature of from 10 to 80 °C.

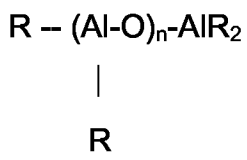
The metal is selected from groups 6 to 10 of the Periodic Table. Preferably, it is Fe, Co, Cr and Ni.

The solvent may be polar or apolar, preferably it is tetrahydrofuran (THF).

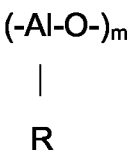
An active catalyst system is then prepared by adding an activating agent having an ionising action.

Any activating agent having an ionising action known in the art may be used for activating the monooxime catalyst component. For example, it can be selected from aluminium-containing or boron-containing compounds. The aluminium-containing compounds comprise aluminoxane and/or alkyl aluminium.

The aluminoxanes are preferred and may comprise oligomeric linear and/or cyclic alkyl aluminoxanes represented by the formula:



for oligomeric, linear aluminoxanes and



for oligomeric, cyclic aluminoxane,

wherein n is 1-40, preferably 10-20, m is 3-40, preferably 3-20 and R is a C_1-C_8 alkyl group and preferably methyl.

Suitable boron-containing activating agents that can be used comprise a triphenylcarbenium boronate such as tetrakis-pentafluorophenyl-borato-triphenylcarbenium as described in EP-A-0427696, or those of the general formula [L'-H] + [B Ar_1 Ar_2 X_3 X_4]- as described in EP-A-0277004 (page 6, line 30 to page 7, line 7).

The preferred activating agent is aluminoxane. The amount of aluminoxane necessary to activate the catalyst component is selected to have a Al/M ratio of from 100 to 3000, preferably it is about 1000.

The catalyst system can also be supported. The support if present can be a porous mineral oxide, advantageously selected from silica, alumina and mixtures thereof. Preferably it is silica.

The present invention also discloses a method for oligomerising and for homo- or co-polymerising ethylene and alpha-olefins that comprises the steps of:

a) injecting the active catalyst system into the reactor;
b) injecting the monomer and optional comonomer into the reactor;
c) maintaining under polymerising conditions;

d) retrieving the oligomers and polymers.

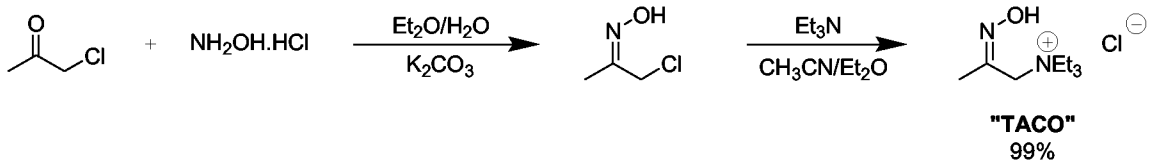
The polymerisation and oligomerisation methods are not particularly limited and can be carried out at a temperature of from 20 to 80 °C and under a pressure of from 5 to 50 bars.

The preferred monomers and comonomers are selected from ethylene, propylene and hexene.

Examples.

Synthesis of the ligand.

a) Synthesis of the oxime precursor, TACO.



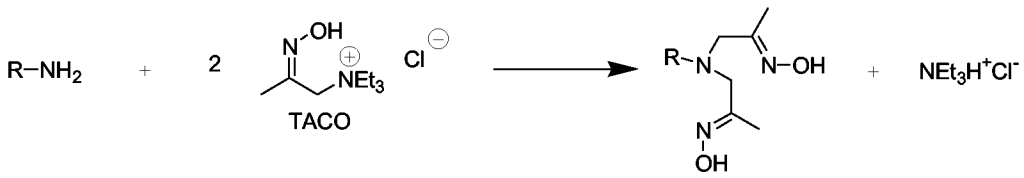
"TACO"
99%

In a 250 mL flask, 3.82 g (55 mmol, 1.1 equ) of hydroxylamine hydrochloride were dissolved in 20 mL of water. A solution of 4.15 mL (50 mmol, 1 equ) of chloroacetone in 50 mL of ether was added to the flask. 3.8 g (27.5 mmol, 0.5 equ) of potassium carbonate were slowly added little by little, under stirring, at a temperature of 0 °C. The biphasic mixture was brought back to room temperature (about 25 °C) and was stirred for a period of time of 2 hours.

The two phases were then separated and the aqueous phase was extracted with 15 mL of ether. The two ether phases were combined and 7.31 g (52 mmol, 1.04 equ) of triethylamine diluted in 15 mL of acetonitrile were added drop-wise, under stirring. It was kept under stirring for a period of time of 30 minutes and gave a white precipitate that was filtered out and washed with 30 mL of cold acetonitrile. After drying under vacuum, 10.31 g of solid (TACO) were obtained with a yield of 99 %. The structure of TACO was confirmed by ^{1}H NMR analysis.

b) Synthesis of dioxime ligands.

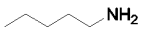
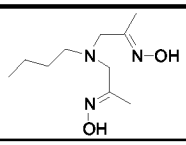
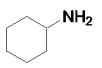
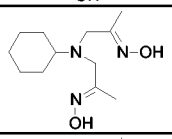
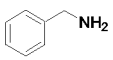
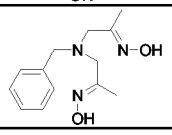
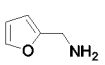
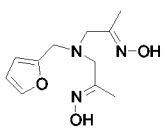
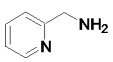
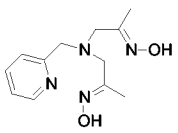
A primary amine is used to prepare ligands according to the following general scheme:



1.5 mmol (1 equ) of the primary amine was dissolved in 20 mL of acetonitrile and 689 mg of TACO (3.3 mmol, 2.2 equ) were added. The mixture was heated at a temperature of 80 °C for a period of time of 3h30. The solvent was vaporised and the residue was mixed with ethyl acetate. The mixture was then filtered to remove residual TACO and triethylamine salt and the filtrate was vaporised under vacuum.

The reaction conditions and resulting ligands are displayed in Table I.

TABLE I.

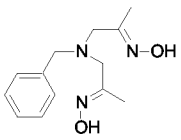
Amine	Ligand	TACO	Yield
		690 mg 3.3 mmol 2.2 éq.	>99 %
			97 %
			98 %
			98 %
			63%

c) **Polymerisation of ethylene.**

Preparation of active catalyst system.

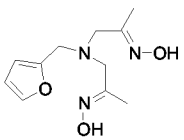
Three ligands were complexed with several metallic precursors.

Ligand L1(*N*-benzyl-*N,N*-bis(1-propan-2-onyl oxime)amine)



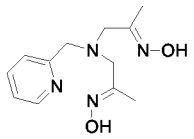
RMN ^{1}H (300 MHz, $CDCl_3$) δ : 7.33-7.27 (m, 5H), 3.54 (s, 2H), 3.05 (s, 4H), 1.92 (s, 6H).;
RMN ^{13}C (75 MHz, $CDCl_3$) δ : 157.0, 129.0, 128.4, 127.3, 58.5, 57.7, 12.3;
EIMS *m/z* $[M\text{-}OH]^+$ 232.1445, calcd for $C_{13}H_{18}N_3O$ 232.1450; **Anal.** Calcd C, 62.63; H, 7.68; N, 16.85. Found: C, 62.16; H, 7.46; N, 17.35.

Ligand L2 (*N*-(furan-2-yl)methyl-*N,N*-bis(1-propan-2-onyl oxime)amine)



RMN ^{1}H (300 MHz, $CDCl_3$) δ : 8.59 (sl, 2H), 7.71 (td, J_1 = 1.5 Hz, J_2 = 7.5 Hz, 1H), 7.47 (d, J = 7.9 Hz, 1H), 7.21(d, J = 6.8 Hz, 1H), 3.78 (s, 2H), 3.15 (s, 4H), 1.90 (s, 6H);
RMN ^{13}C (75 MHz, DMSO) δ : 154.3, 152.1, 142.9, 110.7, 109.4, 57.3, 49.2, 12.5;
EIMS *m/z* $[M]^+$ 239.1257, calcd for $C_{11}H_{17}N_3O_3$ 239.1270; **Anal.** Calcd C, 55.22; H, 7.16; N, 17.56. Found: C, 54.80; H, 7.04; N, 18.63.

Ligand L3 (*N*-(pyridin-2-yl)methyl-*N,N*-bis(1-propan-2-onyl oxime)amine)



RMN ^{1}H (300 MHz, $CDCl_3$) δ : 8.56 (d, J = 4.9 Hz, 1H), 7.71 (td, J_1 = 1.9 Hz, J_2 = 7.9 Hz, 1H), 7.48 (d, J = 7.9 Hz, 1H), 7.20 (m, 1H), 3.78 (s, 2H), 3.15 (s, 4H), 1.92 (s, 6H);
RMN ^{13}C (75 MHz, $CDCl_3$) δ : 157.0, 142.2, 110.1, 109.2, 57.4, 50.3, 12.2.

In a glovebox, a solution of 25 μmol of ligand in 6 mL of tetrahydrofuran (THF) was added to a Schlenk, followed by a solution of 25 μmol of metallic precursor in 6 mL of THF. The complexation reaction was carried out for a period of time of 4 h under stirring. THF was then removed under vacuum for a period of time of 3 h.

The catalyst component was then activated with 1000 equivalents of methylaluminoxane (MAO). 4 mL of a 30 % solution of MAO in toluene (730 equ) were added to the untreated complexation product and the mixture was kept under stirring for 5 to 10 minutes. In the reactor under inert atmosphere 50 mL of toluene were added followed by the addition of a scavenger solution prepared from 1.5 mL of a 30 % solution of MAO in toluene (270 equ) and 3.5 mL of toluene, followed by the addition of the activated complex diluted in 1 mL of toluene. The temperature was raised to 35 °C and the polymerisation of ethylene was carried out at a temperature of 35 °C and under an ethylene pressure of 15 bar, for a period of time of about 2 h.

Oligomers and polymers of ethylene were recovered after degassing. The polymers were washed with a 5 % MeOH/HCl, then with MeOH and finally with acetone. They were then dried under vacuum overnight.

The results are summarised in Table II

TABLE II.

Catalyst	Colour before	Colour after activation	Mass PE (g)	Polym. time	C2 consumption	Activity (kg PE/h.mol)	$T_f^{(d)}$

	activation			(min)	(kg/h.mol)[a]		(°C)
$Ni(DME)Br_2$ + **L1**	**green**	**orange**	1.1	152	454	17.4[b]	112 and 120
$Ni(DME)Br_2$ + **L2**	**green**	**orange**	0.11	143	610	1.8[b]	112
$Ni(DME)Br_2$ + **L3**	**green**	**orange**	0.17	130	391	3.1[b]	111
$CoCl_2$ + **L3**	**Pink (violet in THF)**	**salmon**	0.21	99	/	8.4[c]	138
$FeCl_3$ + **L1**	**orange**	**plum**	0.84	145	/	33.6[c]	140
$CrCl_3(THF)_3$	**violet**	**rose**	0.68	60	1320	11	85/111
$CrCl_3(THF)_3$ + **L1**	**vert**	**brown**	0.66	60	/	22	139
$CrCl_3(THF)_3$ + **L2**	**vert**	**brown**	0.32	60	/	11	
$CrCl_3(THF)_3$ + **L3**	**vert**	**brown**	0.41	60	/	15.1	
$CrCl_2$	**vert**	**vert**	0.06	60	/	1.4	132
$CrCl_2$ + **L1**	**vert**	**green/brown**	2.48	60	/	99.2	
$CrCl_2$ + **L2**	**vert**	**green/brown**	0.96	60	/	37.2	

(a) measured after 1 h

(b) continuous consumption

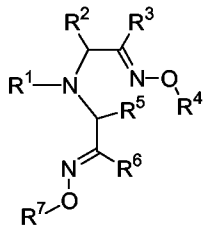
(c)calculated on the basis of the total amount of PE obtained after 2 hours but adjusted to 1 h as the system did not show any significant evolution.

(d) Melting point measured by Differential Scanning Calorimetry (DSC) method.

The complexes based on nickel produced both oligomers and polymers. The complexes based on Fe produced no significant amounts of oligomers and an improved activity with ligand L1. Cr (III) and Cr (II) produced no significant amounts of oligomers and an improved activity with all ligands, the most active being Cr (II).

CLAIMS.

1. A method for preparing a catalyst component by complexation reaction of a metallic precursor, wherein the metal is chromium (II) or chromium (III), and a dioxime ligand of general formula I



wherein R^1, R^2, R^3, R^4, R^5, R^6 and R^7 are selected from H or an alkyl having from 1 to 20 carbon atoms, or an aryl having from 3 to 18 carbon atoms or functional groups such as heterocycles and two neighbouring R^i can be joined together to make a ring.

2. The method of claim 1 wherein R^2 and R^5 are the same, R^3 and R^6 are the same and R^4 and R^7 are the same.

3. The method of claim 1 or claim 2 wherein R^1, R^2, R^3, R^4, R^5, R^6 and R^7 are selected from hydrogen, methyl, isopropyl, n-butyl, benzyl, cyclohexyl, pyridine, thiophene, furane, phenyl, mesityl.

4. A catalyst component obtainable by the method of any one of claims 1 to 3.

5. An active catalyst system comprising the catalyst component of claim 4 and an activating agent having an ionising action.

6. The active catalyst system of claim 5 wherein the activating agent is aluminoxane.

7. A method for homo- or co-polymerising ethylene or alpha olefins that comprises the steps of

a) injecting the active catalyst system of claim 5 or claim 6 into the reactor;
b) injecting the monomer and optional comonomer into the reactor;
c) maintaining under polymerising conditions;
d) retrieving the polymers.

8. The method of claim 7 wherein the alpha-olefin is propylene or 1-hexene.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2006/064335

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08F10/00 C07F15/04 C07C251/38 C07D307/52 C07D213/38

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08F C07C C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2004/047972 A (FINA TECHNOLOGY, INC) 10 June 2004 (2004-06-10) examples 7-9	1-8
Y	US 6 727 330 B1 (DEDECKER MARK N ET AL) 27 April 2004 (2004-04-27) claim 3	1-8
Y	GOLDCAMP, MICHAEL J. ET AL: "Structural and Spectroscopic Studies of Nickel(II) Complexes with a Library of Bis(oxime)amine-Containing Ligands" INORGANIC CHEMISTRY , 42(3), 717-728 CODEN: INOCAJ; ISSN: 0020-1669, 2003, XP008057165 cited in the application page 717 page 724	1-8

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
21 November 2006	28/11/2006

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2006/064335

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		JP 2006507345 T	02-03-2006
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