

(19) World Intellectual Property  
Organization  
International Bureau



(43) International Publication Date  
9 September 2005 (09.09.2005)

PCT

(10) International Publication Number  
**WO 2005/082815 A1**

(51) International Patent Classification<sup>7</sup>: C07C 2/32, C08F 10/02, 4/69, 4/00, 110/02

(21) International Application Number:  
PCT/EP2005/050565

(22) International Filing Date: 9 February 2005 (09.02.2005)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
04100506.7 11 February 2004 (11.02.2004) EP  
04018325.3 3 August 2004 (03.08.2004) EP

(71) Applicant (for all designated States except US): **TOTAL PETROCHEMICALS RESEARCH FELUY** [BE/BE]; Zone Industrielle C, B-7181 Seneffe (Feluy) (BE).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **BODART, Philippe** [BE/BE]; Rue aux Granges, 108, B-4480 Clermont-sous-Huy (Engis) (BE). **NENU, Cristina** [NL/NL]; Anjerhof, 70, NL-3434 HS Nieuwegein (NL). **WECKHUYSEN, Bert** [NL/NL]; Kriekengaarde, 54, NL-3992 KK Houten (NL).

(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, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, 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, 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

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.

(54) Title: HETEROGENEOUS CHROMIUM CATALYSTS

(57) Abstract: The present invention relates to a heterogeneous chromium catalyst system for the polymerisation of ethylene and/or alpha olefins prepared by the steps of: (a) providing a silica-containing support, (b) treating the silica-containing support with a chromium compound to form a chromium-based silica-containing support, (c) activating the chromium-based silica-containing support, (d) chemically reducing the activated chromium-based silica-containing support to produce a precursor catalyst, (e) reacting the reduced precursor catalyst with a tridentate ligand compound to obtain a catalyst and (f) optionally activating the catalyst issued from step (e) with a cocatalyst.

WO 2005/082815 A1

### **Heterogeneous chromium catalysts**

The present invention relates to heterogeneous catalysts for the polymerisation of alpha olefins, particularly for the polymerisation of ethylene to hexene. The present invention further relates to methods for producing the catalysts and to the use of such catalysts

A variety of homogeneous catalysts are known in the literature for the polymerisation of alpha olefins. These systems, as referred here below, are based on chromium complexes comprising a chromium core bound to a ligand that comprises electron donors. Nitrogen is the most common electron donor but phosphorus, oxygen or sulphur have also been used. However, a major drawback of these known homogeneous complexes lies in that at the end of the polymerisation, it is difficult to separate these complexes from the components.

Patent WO03/7175 relates to catalyst systems comprising chromium pyrrolide complexes and metal alkyl compound. Said catalyst systems were reported to be active in ethylene trimerization.

Patent WO03/084902 relates to homogeneous multi-dentate chromium complexes activated with alkylaluminum in order to oligomerize olefins. The chromium systems can have different ligands, such as 1,3,5 triazacyclohexane with different substituents, cyclopentadienyl ligands with different substituents and N-methylimidazole ligands reported by Ruther T. et al., Organometallics 2001, volume 20, pages 1247 -1250.

Patent WO03/076368 discloses a method for the oligomerization of alpha olefins comprising at least 3 carbon atoms wherein the olefin is brought into contact with a catalyst system obtained from a chromium source, a 1,3,5 -trialkyl-

1,3,5-triazacyclohexane and from at least one activator comprising a boron compound.

Patent WO03/076367 discloses a method for the oligomerization of olefins in presence of a homogeneous catalyst based on 1,3,5 triazacyclohexane -CrCl<sub>3</sub> complex with 1,3,5 triazacyclohexane substituted in 1,3,5 positions with cycloalkylalkyl groups. An alkyl aluminium compound or an alkylalumoxane is used as activator.

10 R.D. Köhn et al. disclose in Chemical Communications, 2000, pages 1927 - 1928 substituted 1,3,5-triazacyclohexane chromium (III) homogeneous complexes activated with methylalumoxane or N,N-dimethylanilinium tetrakis(pentafluorophenyl) borate and triisobutylaluminium. These complexes are active in the polymerisation of ethylene. The main product is polyethylene, although 1-hexene and some decenes as co-trimers of 1-hexene and ethene were also found in the reaction mixture.

The Chemical abstract of JP 10 130319 A relates to supported catalysts prepared by reacting in a first step a chromium halide with a cyclic polyamine compound to form a multidentate coordination complex. Said complex is reacted in a second step with a silylamide salt such as for example Li bis(trimethylsilyl)amide and further with aluminoxane. This catalyst is active in the polymerization of ethylene with a wide molecular weight distribution.

25 It is an object of the present invention to provide a method for producing a heterogeneous chromium catalyst system for the polymerisation of ethylene and/or alpha olefins.

In the present invention, polymerisation means a chemical process that combines two or more monomers to form a polymer.

In the present invention, hexene includes 1-hexene.

The present inventors have found a method for producing such heterogeneous chromium catalyst system, said method comprising the steps of:

- a) providing a silica-containing support,
- b) treating the silica-containing support with a chromium compound to form a chromium-based silica-containing support,
- c) activating the chromium-based silica-containing support,
- 10 d) chemically reducing the activated chromium-based silica-containing support to produce a precursor catalyst,
- e) reacting the reduced precursor catalyst with a tridentate ligand compound to obtain a catalyst and
- f) optionally activating the catalyst issued from step e) with a cocatalyst.

15

The present inventors have found that the method according to the invention solves the object of the invention.

The present invention further provides heterogeneous chromium catalysts.

20

Finally, the present invention provides a process for the polymerisation of ethylene and/or alpha olefins, preferably for the polymerisation of ethylene to hexene, by passing the ethylene and /or alpha olefins over the heterogeneous chromium catalyst system of the invention and by further recovering the polymer produced. The inventors have surprisingly found that the heterogeneous chromium catalyst system has an improved activity by catalytic site.

25

The silica-containing support material used in the catalyst of the invention may be composed of 5 to 100 weight percent silica, the remainder if any being

30

selected from aluminium oxide, magnesium oxide, titanium oxide, zirconium oxide, or mixtures thereof. Preferably, the support is silica.

5 The specific surface area of the silica-containing support is preferably larger than  $200 \text{ m}^2/\text{g}$  and its pore volume greater than  $1 \text{ cm}^3/\text{g}$ .

10 The particles size of the silica-containing support preferably ranges from 0.020 to 2 millimetres. More preferably, the silica-containing support is sieved to achieve size fractions between 0.2 and 0.4 millimetres. The required size fraction can be obtained by any method known in the art. As an example, to obtain size fractions between 0.2 and 0.4 millimetres, the silica-containing support is first pressed into a wafer, then grained and sieved using size sieves with 0.425 mm and 0.212 mm aperture. This may be done either before the treatment of the silica-containing support with the chromium compound or after  
15 it.

The silica-containing support is then treated with a chromium compound. The chromium compound used in the present invention is preferably chromium trioxide. Preferably, the resultant catalyst precursor contains between 0.01 and  
20 2 weight percent of chromium, preferably between 0.1 and 1 weight percent of chromium, based on the total weight of the chromium and support. Most preferably, the catalyst contains 1 weight percent of chromium, based on the total weight of the chromium and support.

25 The catalyst precursor is then subjected to an activation step in air, at an elevated temperature, for at least 6 hours. The activation temperature preferably ranges from 400 to 900°C. Most preferably, the activation temperature is about 720°C.

After activation, a chemical reduction process occurs at a temperature of from 200°C to 600°C, preferably at a temperature from 350 to 450°C, and more preferably at a temperature of about 400°C, in either carbon monoxide or hydrogen.

5

After reduction, the catalyst precursor is treated with a tridentate ligand compound that has been dissolved in a solvent such as chlorinated solvents, one can cite dichloromethane. Preferably, the tridentate ligand compound is a cyclic tridentate ligand with electron donating atoms in the cycle, substituted or  
10 unsubstituted, more preferably, the tridentate ligand compound is a neutral cyclic tridentate ligand with electron donating atoms in the cycle, substituted or unsubstituted, most preferably the tridentate ligand compound is the 1,3,5-triazacyclohexane, wherein each of the nitrogen atoms of the 1,3,5-triazacyclohexane may independently be substituted or not. When substituted,  
15 the substituents may be hydrocarbon radicals. Preferably the substituents are benzyl. In the present invention, the 1,3,5-tribenzyl 1,3,5-triazacyclohexane is preferably used.

After treatment with the tridentate ligand compound, the catalyst is optionally  
20 activated. Depending on the tridentate ligand compound used, the man in the art has to test if the catalyst has to be activated, or not, with a cocatalyst. When the catalyst has to be activated, the activation compound is preferably a fluorinated boron compound and /or an aluminium compound.

25 When 1,3,5-triazacyclohexane substituted or unsubstituted is used as tridentate ligand compound, the catalyst is activated with a cocatalyst. Preferably the catalyst is first activated with a fluorinated boron compound and then with an aluminium compound. In the present invention, the aluminium compound is preferably triisobutylaluminium and the fluorinated boron compound is  
30 preferably N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate.

The heterogeneous chromium catalyst obtainable according to the method of the invention is novel over that disclosed by the Chemical abstract of JP 10 130319. Indeed, the Chemical abstract of JP 10 130319 does not disclose an activation step of a chromium based silica support at a temperature from 400°C to 900°C. Moreover it does not disclose a chromium multi-dentate coordination complex as the invention does. Indeed, the Chemical abstract of JP 10 130319 discloses a chromium multi-dentate coordination complex, which is treated with a silylamide salt. This is not the case in the invention.

10 Examples:

Example 1: preparation of the heterogeneous catalyst according to the invention.

15 10 g silica support was introduced in a 50 ml flask. A solution of chromium trioxide prepared by dissolving 0.2 g of chromium trioxide in 20 ml water was added to the support at room temperature in order to get a chromium content of 1 weight percent of chromium based on the total weight of the chromium and the support. After impregnation, the chromium silica-containing support is dried  
20 in air at around 150 °C, then sieved in order to achieve fractions from 0.2 to 0.4 mm and loaded in a sealed vessel where the activation treatment took place under dry air for 6 hours at 720°C. After the activation step, the chromium silica-containing support was further reduced under carbon monoxide for thirty minutes at 400°C. In a glove box under inert atmosphere, 1.2 g of the reduced  
25 precursor catalyst was placed in a 5 ml flask to which were added 2 ml solution of 0.04 M 1,3,5-tribenzyl 1,3,5-triazacyclohexane ligand prepared by dissolving 1.43 g of 1,3,5-tribenzyl 1,3,5-triazacyclohexane ligand in 100 ml of extra dry dichloromethane. The reduced precursor catalyst and the ligand reacted for 10 minutes at room temperature. In order to remove the un-reacted ligand, the  
30 catalyst was washed at room temperature with 10 to 15 ml of dichloromethane.

The dichloromethane was further removed by evaporation at 40°C. A light purple catalyst powder was produced. The catalyst was further activated with 1.3 to 2 equivalents of N,N-dimethylanilinium tetrakis(pentafluorophenyl) borate prepared by adding 5 mg of said fluorinated boron compound to 2.5 ml of dichloromethane. The solvent was removed from the catalyst by evaporation at 40°C. Afterwards, the catalyst was still activated with 25 to 50 equivalents of triisobutylaluminium.

Before activation with the N,N-dimethylanilinium tetrakis(pentafluorophenyl) borate, the heterogeneous catalyst produced according to the invention and identified in the description as catalyst  $(\text{Bz})_3\text{TAC-Cr/SiO}_2$  (with Bz = benzyl) was characterised by using ultraviolet-visible spectroscopy. The UV-Vis absorption bands of the catalyst according to the invention, as well as of the homogeneous complex 1,3,5-tribenzyl 1,3,5-triazacyclohexane chromium trichloride reported in the literature by Köhn et al., identified as homogeneous  $(\text{Bz})_3\text{TAC-CrCl}_3$  in the description, and of the reduced precursor catalyst not yet treated with the 1,3,5-tribenzyl 1,3,5-triazacyclohexane ligand were also determined. The values are displayed in Table I.

**Table I**

Sample	$\text{Cr}^{2+}$ ( $\text{cm}^{-1}$ )	$\text{Cr}^{3+}$ ( $\text{cm}^{-1}$ )		
Catalyst $(\text{Bz})_3\text{TAC-Cr/SiO}_2$	-	13500	20700	30500
Homogeneous $(\text{Bz})_3\text{TAC-CrCl}_3$	-	13900	19600	29900
Precursor catalyst not treated with the ligand	10300	14000	20000	28700



The UV-Vis spectrum of the catalyst according to the invention showed three major maxima located respectively at 13500  $\text{cm}^{-1}$ , 20700  $\text{cm}^{-1}$  and 30500  $\text{cm}^{-1}$ . These positions are characteristic for the chromium trivalent d-d transitions that occur in the complex. These positions are not present in the spectrum of the reduced precursor catalyst that has not been treated with the ligand. In the catalyst  $(\text{Bz})_3\text{TAC-Cr/SiO}_2$ , the maxima are shifted comparing with the homogeneous  $(\text{Bz})_3\text{TAC-CrCl}_3$  complex because the silica lattice replaced the chlorine ligands from the homogeneous complex. The UV-Vis spectrum of the homogeneous  $(\text{Bz})_3\text{TAC-CrCl}_3$  complex presented also the characteristic 3 d-d transitions of  $\text{Cr}^{3+}$  in Cr complexes with nitrogen ligands.

Some reagents such as water or mineral acids, in particular hydrochloric acid (HCl), can affect the stability of the catalyst according to the invention. This was tested by treating the catalyst with hydrochloric acid or water by injecting 2 ml of hydrochloric acid or water inside the spectroscopic cell. After 10 min contacting time, the UV-Vis spectra were determined. The UV-Vis absorption bands of the catalyst of the invention after treatment with HCl and  $\text{H}_2\text{O}$  as well as of the homogeneous catalyst values are displayed in Table II.

20

Table II

Sample	$\text{Cr}^{3+}$ ( $\text{cm}^{-1}$ )		
Catalyst $(\text{Bz})_3\text{TAC-Cr/SiO}_2$	13500	20700	30500
Catalyst $(\text{Bz})_3\text{TAC-Cr/SiO}_2$ treated with HCl	14520	20100	28000
Catalyst $(\text{Bz})_3\text{TAC-Cr/SiO}_2$ treated with $\text{H}_2\text{O}$	16400	24500	27800
Homogeneous $(\text{Bz})_3\text{TAC-CrCl}_3$	13900	19600	29900

The new maxima positions of the catalyst of the invention treated with HC I were closer to the positions of the homogeneous complex  $(\text{Bz})_3\text{TAC-CrCl}_3$ . Indeed, after the treatment, the Cr-O bond of the catalyst of the invention was broken and the supported complex was converted into the homogeneous complex. The colour of the treated catalyst intensified from light purple to dark purple, which is the colour of the homogeneous complex. The spectrum of the catalyst of the invention treated with water differed also widely from those of the untreated catalyst indicating the presence of new species.

10

In a first step, to elucidate the structure of the catalyst of the invention fluorescence Extended X-ray Absorption Fine Structure Spectroscopy (EXAFS) data were recorded. The EXAFS measurements involved synchrotron radiation provided by HASYLAB, Hamburg, Germany. The results were compared with the results for a comparable homogeneous catalyst provided by X-ray diffraction (XRD), that were furnished by CSD database, Cambridge University.

The EXAFS pattern of the heterogeneous chromium catalyst, shown in figure 1 indicated a very good fit of the theoretical curve (dashed line) with this related to the catalyst of the invention (unbroken line). The Fourier transform plot illustrated in figure 2, wherein the dashed and unbroken lines have the same meaning as in figure 1, gave indications about the atom position distribution. Short-range distances were selected in order to visualize the closest atoms around the Cr centre. The distance evaluation is in agreement with data reported by XRD. Table III presents the molecular structure of the catalyst of the invention obtained by EXAFS and the molecular structure reported for the homogeneous catalyst  $(\text{Bz})_3\text{TAC-CrCl}_3$ .

Table III

Coordination Shell	Atom	Coordination number	R <sub>EXAFS</sub> (Å) for catalyst of the invention	R <sub>XRD</sub> (Å) for the homogeneous catalyst
1 <sup>st</sup> shell	O	0.9	1.908	-
2 <sup>nd</sup> shell	N	2.8	2.091	2.095
3 <sup>rd</sup> shell	C	3.4	2.601	2.615
4 <sup>th</sup> shell	Si	1.0	3.217	-

5 Å: Angstroms

A first analysis of the structure of the catalyst of the invention according to EXAFS data makes us suppose that the closest atom to the Cr centre is one oxygen atom, at a very short distance, which implies a very strong bond. Consequently, the anchored complex is linked via one oxygen atom with the silica surface. Three nitrogen atoms are found also around Cr centre at the same distance reported for the reference catalyst as well as for the carbon atoms. Further, a silicon atom is present, in fact the linkage of oxygen with the surface. According to these data, we can conclude that an anchored complex was formed on the silica surface and makes us suppose that the molecular structure of the heterogeneous chromium catalyst of the invention is the structure illustrated in figure 3.

In a second step, a more precise analysis of the structure of the catalyst of the invention took into account the data recorded by the X-ray absorption near edge spectroscopy (XANES) and by the fluorescence Extended X-ray Absorption Fine Structure Spectroscopy (EXAFS). Table IV presents the molecular structure of the catalyst of the invention taking into account the

XANES and EXAFS datas and the molecular structure reported for the homogeneous catalyst  $(\text{Bz})_3\text{TAC-CrCl}_3$ .

5

Table IV

Coordination Shell	Atom	Coordination number	$R_{\text{EXAFS}}(\text{\AA})$ for catalyst of the invention	$R_{\text{XRD}}(\text{\AA})$ for the homogeneous catalyst
1 <sup>st</sup> shell	O	2.0	1.908	-
2 <sup>nd</sup> shell	N	2.8	2.091	2.095
3 <sup>rd</sup> shell	Cl	1.0	2.285	2.288
4 <sup>th</sup> shell	C	3.0	2.640	2.615
5 <sup>th</sup> shell	Si	1.0	3.217	-

The analysis of the XANES and EXAFS datas disclosed that the the closest atoms to the Cr centre are two oxygen atoms, at a short distance, which implies very strong bonds. Consequently, the anchored complex is linked via two oxygen atoms with the silica surface. Three nitrogen atoms are found also around Cr centre at the same distance reported for the reference catalyst as well as for the carbon atoms. A chlorine atom originating from chlorinated ligand completes the first coordination sphere to an octahedron (coordination number 6). Further, silicon atoms are present, in fact the linkage of the oxygens with the surface. According to these data, we can conclude that an anchored complex was formed on the silica surface via reaction with two silanol groups. The molecular structure of the heterogeneous chromium catalyst of the invention is illustrated in figure 4.

20

In order to confirm that the heterogeneous complex was well anchored onto the surface of the silica with the method described by this invention, a polymerisation was conducted by using two reactors. The catalyst prepared as described hereabove was introduced in a first reactor. Toluene was used as diluent in the reactor and ethylene was continuously added in the reactor at a rate of 30 ml/min. The polymerisation was performed under slurry conditions at normal pressure and at room temperature for 30 minutes. After 30 minutes, the solid phase was separated from the liquid phase. The separation was fulfilled with a double pointed needle and the liquid phase was transferred from the first reactor to a second one. In the second reactor, ethylene was added at a rate of 30 ml/min. No more catalyst was added in the second reactor. After 30 minutes, no catalytic activity occurred in the second reactor indicating the absence of any active homogeneous complex in the solution, which was transferred from the first reactor to the second reactor. This was confirmed by the atomic absorption spectroscopy of the liquid solution. Indeed, no significant traces of chromium were detected in the liquid solution.

Example 2: Catalysis of the heterogeneous catalyst according to the invention at normal pressure.

Example 2.1

The catalyst of the invention prepared according to example 1 was carried out under slurry conditions at normal pressure and at a temperature of 90°C during 60 min. The polymerisation was performed in a slurry reactor connected to a bubbler. The catalyst of the invention was introduced into the reactor. Toluene was used as diluent in the reactor and in the bubbler. Ethylene was continuously added in the reactor at a rate of 30 ml/min. Hexene was determined in the liquid phase of the reactor and of the bubbler as well as in the gas phase coming out from the bubbler by gas chromatography and gas chromatograph-mass spectrometry. The distribution of the hexene (g) in the reactor, bubbler and gas phase are shown in Table IV.

**Example 2.2**

In this example, the polymerisation of ethylene to hexene was conducted in the same conditions as in example 2.1, except that the temperature was at room temperature. The distribution of the hexene (g) in the reactor, bubbler and gas phase are shown in Table IV.

**Example 3: comparative example**

10

In this example, the polymerisation of ethylene to hexene was conducted in the same conditions as in example 2.2 excepted that the polymerisation occurred in the presence of the homogeneous complex  $(Bz)_3TAC-CrCl_3$  used for comparison. The distribution of the hexene (g) in the reactor, bubbler and gas phase are shown in Table IV. The activity of the catalyst of the invention was determined through the turnover number (TON), defined as the number of moles of hexene divided by the number of moles of chromium. TON represents the number of molecules of hexene formed on a chromium site. The amount of hexene formed, and the TON for the different Cr complexes are given in Table IV.

20

**Table IV**

<b>Example</b>	<b>2.1 (Invention)</b>	<b>2.2 (Invention)</b>	<b>3 (Comparative)</b>
Reactor	0.18	0.19	0.25
Bubber	0.010	0.035	0.014
Gas phase	0.00021	0.00013	0.00017
hexene (g)	0.19	0.22	0.24
TON	7.9	9.6	2.9

Table IV showed that the heterogeneous catalyst of the invention has a higher polymerisation activity per catalyst site than those of the homogeneous catalyst according to Köln et al. used herein as comparative. This result was  
5 unexpected.

Example 4: Catalysis of the heterogeneous catalyst according to the invention under pressure.

- 10 In this example, the polymerisation of ethylene was carried out under slurry conditions at room temperature and at 3 MPa ethylene pressure with a maximal incoming flow of 100 ml/min. The stirring rate was 700 rpm.  
A solid polymer was formed with a polymerisation activity of 192 g polyethylene/mole Cr/h.
- 15 The distribution of hexene (g) in the reactor is given in table IV.

**Table IV**

Reactor	0.02
Bubbler	not detectable
Gas phase	not detectable-
Hexene	0.02
TON	0.3

In this example, the reaction at 3 MPa resulted in a significant increase in the  
20 formation of polyethylene, while the amount of unbounded 1 -hexene decreases in the reaction mixture. It is clear that most of the 1 -hexene formed has been incorporated into the growing polyethylene chain, resulting in a decrease of the TON.

**Claims**

1. A method for producing a heterogeneous chromium catalyst system,  
5 said method comprising the steps of:
- a) providing a silica-containing support,
  - b) treating the silica-containing support with a chromium compound to form a chromium-based silica-containing support,
  - c) activating the chromium-based silica-containing support at a  
10 temperature from 400 to 900°C,
  - d) chemically reducing the activated chromium-based silica-containing support to produce a precursor catalyst,
  - e) reacting the reduced precursor catalyst with a tridentate ligand compound to obtain a catalyst and  
15 f) optionally activating the catalyst issued from step e) with a cocatalyst.
2. A method according to claim 1 wherein the chromium content of the  
20 catalyst is 1 weight percent based on the total weight of the chromium and support.
3. A method according to any foregoing claims wherein the reduction occurs under carbon monoxide at a temperature of from 200°C to 600°C.  
25
4. A method according to any foregoing claims wherein the tridentate ligand compound is a cyclic tridentate ligand with electron donating atoms in the cycle, substituted or unsubstituted.



5. A method according to claim 4 wherein the tridentate ligand compound is a neutral cyclic tridentate ligand with electron donating atoms in the cycle, substituted or unsubstituted.
- 5 6. A method according to any foregoing claims wherein the tridentate ligand compound is the 1,3,5-triazacyclohexane substituted or unsubstituted and the catalyst is further activated with a cocatalyst.
7. A method according to claim 6 wherein the triazacyclohexane is 1,3,5 -  
10 triazacyclohexane wherein each of the nitrogen atoms is independently substituted with hydrocarbon radicals.
8. A method according to claim 7 wherein the hydrocarbon radicals are benzyl  
15
9. Heterogeneous chromium catalyst system obtainable according to claim 1 characterised in that the tridentate ligand is the 1,3,5 - triazacyclohexane substituted or unsubstituted and that after treatment with said triazacyclohexane, the catalyst is further activated with a  
20 cocatalyst.
10. Heterogeneous chromium catalyst system according to claim 9 characterised in that the tridentate ligand is 1,3,5 triazacyclohexane wherein each of the nitrogen atoms is independently substituted with  
25 hydrocarbon radicals.
11. Heterogeneous chromium catalyst system according to claim 10 characterised in that hydrocarbon radicals are benzyl.

12. A process for the polymerisation of ethylene and/or alpha olefins comprising the steps of passing the ethylene and/or alpha olefins over the heterogeneous chromium catalyst system according to any one of claims 9 to 11 and further recovering the polymer.

5

13. A process according to claim 12 for the polymerisation of ethylene to hexene.

10

15

20

25

30

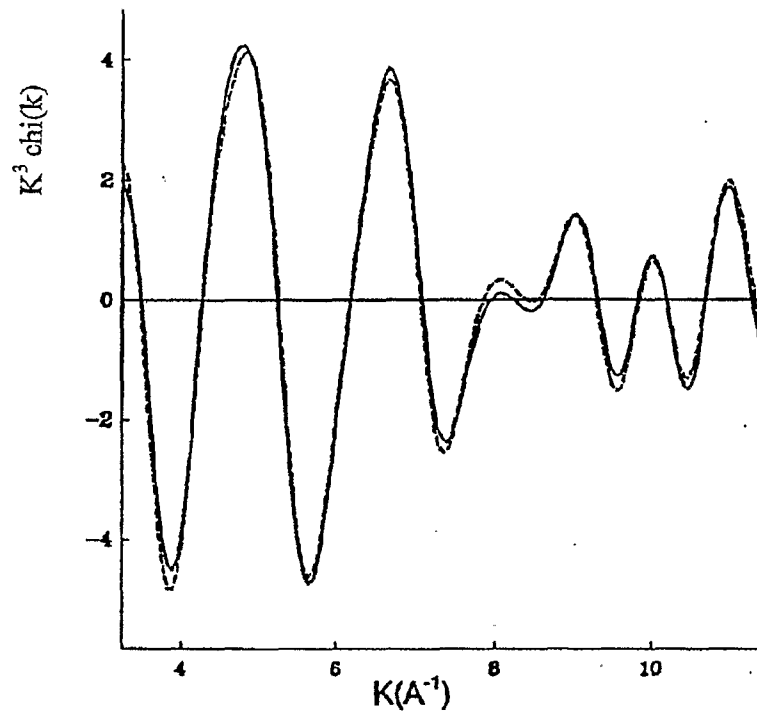


Figure 1

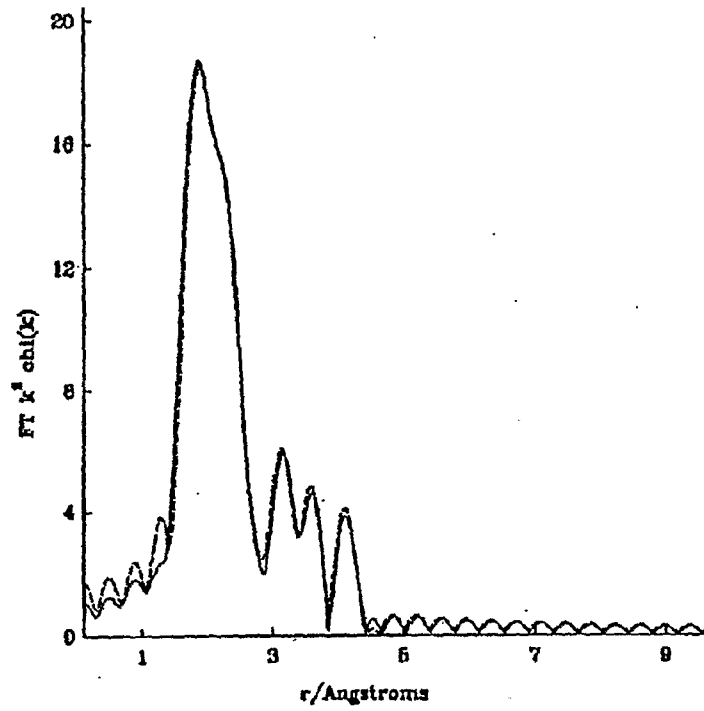
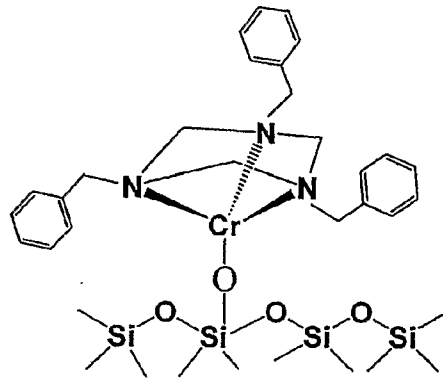
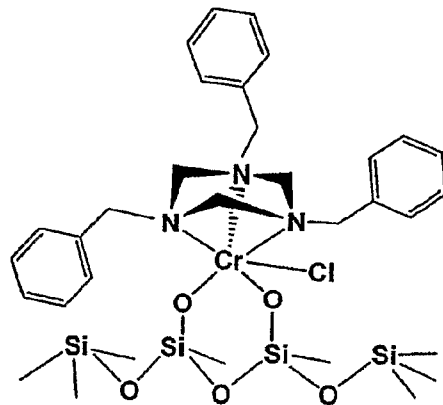


Figure 2



**Figure 3**



**Figure 4**

## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP2005/050565

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC 7 C07C2/32 C08F10/02 C08F4/69 C08F4/00 C08F110/02		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b>		
Minimum documentation searched (classification system followed by classification symbols) IPC 7 C08F C07C		
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		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>DATABASE CAPLUS 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US; MONOI, HISASHI ET AL MONOI, HISASHI ET AL: "Manufacture of catalysts for ethylenic polymers and manufacture of polymers with wide molecular weight distribution Manufacture of catalysts for ethylenic polymers and manufacture of polymers with wide molecular weight distribution" XP002288104 retrieved from STN Database accession no. 1998:314739 abstract &amp; JP 10 130319 A (NIPPON POLYOLEFIN K. K., JAPAN NIPPON POLYOLEFIN K. K., JAPAN) 19 May 1998 (1998-05-19)</p> <p style="text-align: center;">----- -/--</p>	1,3-7, 9-12
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
° Special categories of cited documents :		
"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention	
"E" earlier document but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone	
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.	
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family	
"P" document published prior to the international filing date but later than the priority date claimed		
Date of the actual completion of the international search	Date of mailing of the international search report	
25 May 2005	01/06/2005	
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer  Parry, J	

## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP2005/050565

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 00/34211 A1 (BP CHEMICALS LIMITED, UK) 15 June 2000 (2000-06-15) page 8; table 2 -----	1-13
Y	WO 01/32307 A (PHILLIPS PETROLEUM CO ; GEERTS ROLF L (US); SMITH JAMES L (US); MCDANI) 10 May 2001 (2001-05-10) page 13; example 1 -----	1-13
A	GASPAR, A. B. ET AL GASPAR, A. B. ET AL: "The influence of Cr precursors in the ethylene polymerization on Cr/SiO <sub>2</sub> catalysts The influence of Cr precursors in the ethylene polymerization on Cr/SiO <sub>2</sub> catalysts" APPLIED CATALYSIS, A: GENERAL , 227(1-2), 241-254, 2002, XP004340867 the whole document -----	1-13
A	EP 0 967 234 A (FINA RESEARCH) 29 December 1999 (1999-12-29) page 2, paragraph 9 - page 4, paragraph 27 -----	1-13
A	KOEHN R D ET AL: "SELECTIVE TRIMERIZATION OF ALPHA-OLEFINS WITH TRIAZACYCLOHAXANE COMPLEXES OF CHROMIUM AS CATALYSTS" ANGEWANDTE CHEMIE. INTERNATIONAL EDITION, VERLAG CHEMIE. WEINHEIM, DE, vol. 39, no. 23, 4 December 2000 (2000-12-04), pages 4337-4339, XP000975912 ISSN: 0570-0833 the whole document -----	1-13



**INTERNATIONAL SEARCH REPORT**  
 Information on patent family members

International Application No  
 PCT/EP2005/050565

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
JP 10130319	A	19-05-1998	NONE	
WO 0034211	A1	15-06-2000	AU 1399200 A	26-06-2000
WO 0132307	A	10-05-2001	US 6828268 B1 AU 3792201 A CA 2389654 A1 CN 1391498 A EP 1235645 A1 HU 0203283 A2 NO 20022099 A WO 0132307 A1 US 2005090629 A1	07-12-2004 14-05-2001 10-05-2001 15-01-2003 04-09-2002 28-01-2003 24-06-2002 10-05-2001 28-04-2005
EP 0967234	A	29-12-1999	EP 0967234 A1 AU 4267099 A WO 9967306 A1 EP 1179027 A1 JP 2000026524 A US 6245869 B1	29-12-1999 10-01-2000 29-12-1999 13-02-2002 25-01-2000 12-06-2001