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P/00/001 28/5/91
Section 29

Patents Act 1990

PATENT REQUEST: STANDARD PATENT/PATENT OF ADDITION

I/We, being the person(s) identified below as the Applicant, request the grant of a patent to the person identified below as the Nominated Person, for an invention described in the accompanying standard complete specification.

Full application details follow.

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Address: D-6230 Frankfurt/Main 80, Federal Republic of Germany

[70] Nominated Person: HOECHST AKTIENGESELLSCHAFT
Address: D-6230 Frankfurt/Main 80, Federal Republic of Germany

[54] Invention Title: CATALYST AND PROCESS FOR THE PREPARATION OF HIGH-MOLECULAR-WEIGHT POLYOLEFINS

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[74] Address for service in Australia: c/o WATERMARK PATENT & TRADEMARK ATTORNEYS, of The Atrium, 290 Burwood Road, Hawthorn, Victoria 3122, Australia Attorney Code: WM

BASIC CONVENTION APPLICATION(S) DETAILS

[31] Application Number	[33] Country	Country Code	[32] Date of Application
P41 21 368.8	Germany	DE	28th June 1991

Drawing number recommended to accompany the abstract .....

By my/our Patent Attorneys,
WATERMARK PATENT & TRADEMARK ATTORNEYS

.....
D. B. Mischlewski

Registered Patent Attorney
F034963 26/06/92

25th June 1992
(Date)

P/00/008b 12/11/91
Section 29 (1)
Regulation 3.1 (2)

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NOTICE OF ENTITLEMENT

(To be filed before acceptance)

We, **HOECHST AKTIENGESELLSCHAFT**, of D-6230 Frankfurt-am-Main 80, Federal Republic of Germany, being the applicant in respect of Application No. 18576/92 state the following:-

The person nominated for the grant of the patent has entitlement from the actual inventors by assignment.

The person nominated for the grant of the patent is the applicant of the basic application listed on the patent request form.

The basic application listed on the request form is the first application made in a Convention country.

By our Patent Attorneys,
WATERMARK PATENT & TRADEMARK ATTORNEYS

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Darryl B. Mischlewski
Registered Patent Attorney

Dated: 1 June 1994

AU9218576

(12) PATENT ABRIDGMENT (11) Document No. AU-B-18576/92
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 653029

(54) Title
CATALYST AND PROCESS FOR THE PREPARATION OF HIGH-MOLECULAR-WEIGHT POLYOLEFINS

International Patent Classification(s)
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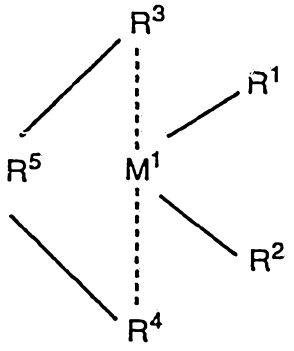
(56) Prior Art Documents
AU 648172 17134/92 C08F 4/76
AU 640559 12866/92 C08F 4/76
AU 625601 43296/89 C08F 4/76

(57) Claim

1. A supported catalyst component for olefin polymerization, consisting essentially of an inorganic support material and a metallocene, said metallocene alone being supported on said inorganic support material.

2. A catalyst component as claimed in claim 1, wherein the inorganic support material is an oxide of a metal from main group II-IV or sub-group IV of the Periodic Table of the Elements, or iron oxide or a mixture thereof.

4. A catalyst component as claimed in one or more of claims 1-3, wherein the metallocene is a compound of the formula I



(I)

.../2

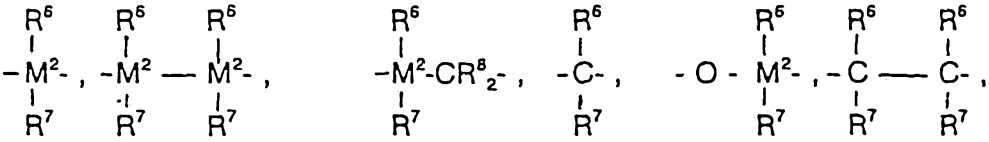
in which

M^1 is titanium, zirconium, vanadium, niobium or tantalum,

R^1 and R^2 are identical or different and are a hydrogen atom, a halogen atom, a C_1-C_{10}-alkyl group, a C_1-C_{10}-alkoxy group, a C_6-C_{10}-aryl group, a C_6-C_{10}-aryloxy group, a C_2-C_{10}-alkenyl group, a C_7-C_{40}-alkylaryl group or a C_8-C_{40}-arylalkenyl group,

R^3 and R^4 are identical or different and are a monocyclic or polycyclic hydrocarbon radical which can form a sandwich structure with the central atom M^1,

R^5 is



$=AlR^6$, $-O-$, $=NR^6$, $=CO$, $=PR^6$ or $=P(O)R^6$, where R^6, R^7 and R^8 are identical or different and are a hydrogen atom, a halogen atom, a C_1-C_{10}-alkyl group, a C_1-C_{10}-fluoroalkyl group, a C_6-C_{10}-fluoroaryl group, a C_6-C_{10}-aryl group, a C_1-C_{10}-alkoxy group, a C_2-C_{10}-alkenyl group, a C_7-C_{40}-arylalkyl group, a C_8-C_{40}-arylalkenyl group or a C_7-C_{40}-alkylaryl group, or R^6 and R^7 or R^6 and R^8, in each case together with the atoms connecting them, form a ring, and

M^2 is silicon, germanium or tin.

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Regulation 3.2(2)

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653029

ORIGINAL
COMPLETE SPECIFICATION
STANDARD PATENT

Application Number:

Lodged:

Invention Title: CATALYST AND PROCESS FOR THE PREPARATION OF HIGH-MOLECULAR-WEIGHT POLYOLEFINS

The following statement is a full description of this invention, including the best method of performing it known to :- us

HOE 91/F 199

Abstract of the disclosure:

Catalyst and process for the preparation of high-molecular-weight polyolefins

High-molecular-weight polyolefins, in particular those of propylene, which have high tacticity are obtained by polymerization of copolymerization of α-olefins using a catalyst system comprising an aluminoxane and a supported catalyst component, the latter being prepared from an inorganic support material, preferably SiO_2, and a metallocene.

HOECHST AKTIENGESELLSCHAFT HOE 91/F 199 Dr. LO/pe

Description

Catalyst and process for the preparation of high-molecular-weight polyolefins

The present invention relates primarily to a supported catalyst component which, together with an aluminoxane as cocatalyst, is suitable for the preparation of high-molecular-weight polyolefins.

High-molecular-weight polyolefins (such as, for example, polypropylene having an M_w of $\geq$ 500,000) are particularly suitable for the production of films, sheets or large-cavity articles, such as, for example, tubes or moldings for automobile manufacture.

It is known that metallocene catalysts are able to polymerize olefins to give polyolefins having a narrow molecular weight distribution (M_w/M_n = 2-3) and high stereoregulatory (isotactic and syndiotactic polymers) (EP-A 185,918). Compared with polymers prepared using classical Ziegler catalysts, however, they have the disadvantage, with the exception of polyethylene, of a lowered melting point and an excessively low molecular weight (Angew. Chem. Int. Ed. Engl., 29 (1990) 279; Chem. Lett. (1989) 1853).

EP-A 232 595 describes a supported catalyst component which is obtained by reacting (inorganic) support material with at least one metallocene and at least one transition-metal compound containing no cyclopentadienyl radical. This catalyst component is employed exclusively for the polymerization or copolymerization of ethylene. It is said to give polyethylene having improved bulk density and at the same time ensure that the amount of aluminoxane as cocatalyst is reduced compared with conventional metallocene catalyst components.

The object of the present invention was thus to find a catalyst system or a polymerization process which makes it possible to prepare, in particular, polypropylene or copolymers of propylene of high molecular weight and high melting point, the products additionally having high stereoregularity and a narrow molecular weight distribution.

The invention relates to a supported catalyst component essentially consisting of ~~obtainable from~~ an inorganic support material and a metallocene.

Preferred ~~Suitable~~ inorganic support materials are oxides of the metals of main groups II-IV or sub-group IV of the Periodic Table of the Elements and iron oxides, or mixtures thereof. Preference is given to the oxides of the metals magnesium, calcium, aluminum, silicon, titanium and iron, and mixtures thereof. Particular preference is given to commercially available silicon dioxides, especially "Silica Davison Grade 952".

The oxides to be used according to the invention preferably have a BET surface area (cf. J. Am. Chem. Soc. 60 (1938) 309) of 10-1000 m^2/g, preferably 100-500 m^2/g, a water content of 10^{-8}-6% by weight, preferably less than 0.1% by weight, and a particle size of between 10 and 200 μm.

Thermal pretreatment of the inorganic support in a stream of inert gas or in vacuo at temperatures of 30-1000°C for 1-50 hours is advantageous.

This thermal pretreatment is preferably carried out in a fluidized bed under a nitrogen atmosphere at temperatures of 200-800°C for a time matched to the amount of material, but for at least 2 hours.

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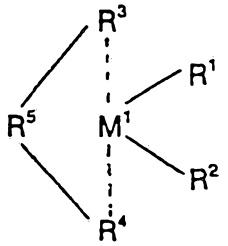
It is furthermore expedient, when the pretreatment is complete, to separate the absorbed gases from the support material in a subsequent step by pumping in vacuo at temperatures above 80°C (time requirement about 10 hours).

The metallocenes to be used according to the invention are preferably those of the formula I



(I)

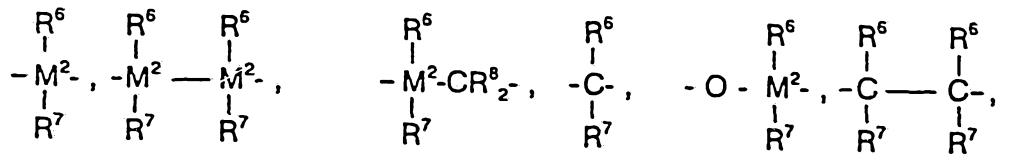
in which

M^1 is titanium, zirconium, vanadium, niobium or tantalum,

R^1 and R^2 are identical or different and are a hydrogen atom, a halogen atom, a C_1-C_{10}-alkyl group, a C_1-C_{10}-alkoxy group, a C_6-C_{10}-aryl group, a C_6-C_{10}-aryloxy group, a C_2-C_{10}-alkenyl group, a C_7-C_{40}-arylalkyl group, a C_7-C_{40}-alkylaryl group or a C_8-C_{40}-arylalkenyl group,

R^3 and R^4 are identical or different and are a monocyclic or polycyclic hydrocarbon radical which can form a sandwich structure with the central atom M^1,

R^5 is



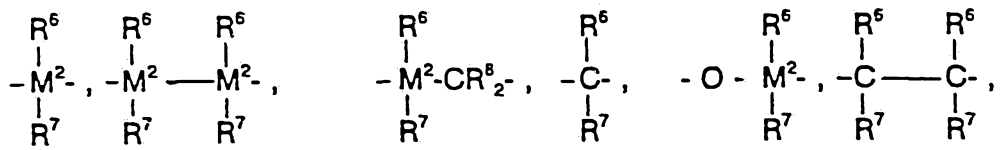
$=AlR^6$, $-O-$, $=NR^6$, $=CO$, $=PR^6$ or $=P(O)R^6$, where R^6, R^7 and R^8 are identical or different and are a hydrogen atom, a halogen atom, a C_1-C_{10}-alkyl group, a C_1-C_{10}-fluoroalkyl group, a C_6-C_{10}-fluoroaryl group, a C_6-C_{10}-aryl group, a C_1-C_{10}-alkoxy group, a C_2-C_{10}-alkenyl group, a C_7-C_{40}-arylalkyl group, a C_8-C_{40}-arylalkenyl group or a C_7-C_{40}-alkylaryl group, or R^6 and R^7 or R^6 and R^8, in each case together with the atoms connecting them, form a ring, and

M^2 is silicon, germanium or tin.

In the formula I, M^1 is a metal from the group consisting of titanium, zirconium, vanadium, niobium and tantalum, preferably zirconium.

R^1 and R^2 are identical or different and are a hydrogen atom, a C_1-C_{10}-, preferably C_1-C_3-alkyl group, a C_1-C_{10}-, preferably C_1-C_3-alkoxy group, a C_6-C_{10}-, preferably C_6-C_8-aryl group, a C_6-C_{10}, preferably C_6-C_8-aryloxy group, a C_2-C_{10}-, preferably C_2-C_4-alkenyl group, a C_7-C_{40}-, preferably C_7-C_{10}-arylalkyl group, a C_7-C_{40}-, preferably C_7-C_{12}-alkylaryl group, a C_8-C_{40}-, preferably C_8-C_{12}-arylalkenyl group, or a halogen atom, preferably chlorine.

R^5 is a single-membered or multimembered bridge which links the radicals R^3 and R^4 and is



$=AlR^6$, $-O-$, $=NR^6$, $=CO$, $=PR^6$ or $=P(O)R^6$, where R^6, R^7 and R^8 are identical or different and are a hydrogen atom, a halogen atom, preferably chlorine, a C_1-C_{10}-, preferably a C_1-C_3-alkyl group, in particular a methyl group, a

C_1-C_{10}-fluoroalkyl group, preferably a CF_3 group, a C_6-C_{10}-fluoroaryl group, preferably a pentafluorophenyl group, a C_6-C_{10}-, preferably C_6-C_8-aryl group, a C_1-C_{10}-, preferably C_1-C_4-alkoxy group, in particular a methoxy group, a C_2-C_{10}-, preferably C_2-C_4-alkenyl group, a C_7-C_{40}-, preferably C_7-C_{10}-arylalkyl group, a C_8-C_{40}-, preferably C_8-C_{12}-arylalkenyl group or a C_7-C_{40}-, preferably C_7-C_{12}-alkylaryl group, or R^6 and R^7 or R^6 and R^8, in each case together with the atoms connecting them, form a ring.

M^2 is silicon, germanium or tin, preferably silicon or germanium.

R^5 is preferably $=CR^6R^7$, $=SiR^6R^7$, $-O-$, $=PR^6$ or $=P(O)R^6$.

To prepare syndiotactic polyolefins, metallocenes I are employed in which R^3 and R^4 are different. In this case, R^3 and R^4 are preferably fluorenyl or cyclopentadienyl, it being possible for these parent structures to contain additional substituents as defined for R^1. These substituents, together with the atoms connecting them, may form additional - substituted - rings.

Isotactic polymers are prepared using metallocenes I in which R^3 and R^4 are identical or different. R^3 and R^4 are then preferably indenyl, tetrahydroindenyl, cyclopentadienyl or fluorenyl, it being possible for these parent structures to carry additional substituents as defined for R^1. These substituents, together the atoms connecting them, may form additional - substituted - rings.

Preferred metallocenes for the preparation of syndiotactic polymers are (arylalkylidene)-(9-fluorenyl)(cyclopentadienyl)zirconium dichloride, (diarylmethylene)-(9-fluorenyl)(cyclopentadienyl)zirconium dichloride and (dialkylmethylene)(9-fluorenyl)(cyclopentadienyl)-zirconium dichloride.

Particular preference is given to (methyl(phenyl)-methylene)-(9-fluorenyl)(cyclopentadienyl)zirconium dichloride, (diphenylmethylene)(9-fluorenyl)(cyclopentadienyl)zirconium dichloride and (dimethylmethylene)-(9-fluorenyl)(cyclopentadienyl)zirconium dichloride.

Preferred metallocenes for the preparation of isotactic polyolefins are:
rac-dimethylsilyl-bis-(1-indenyl)zirconium dichloride,
rac-diphenylsilyl-bis-(1-indenyl)zirconium dichloride,
rac-dimethylsilyl-bis-(tetrahydro-1-indenyl)zirconium dichloride,
rac-diphenylsilyl-bis-(tetrahydro-1-indenyl)zirconium dichloride,
rac-ethylene-bis-(tetrahydro-1-indenyl)zirconium dichloride,
rac-ethylene-bis-(1-indenyl)zirconium dichloride,
rac-dimethylsilyl-bis-(2-methyl-4,6-diisopropylindenyl)-zirconium dichloride,
rac-dimethylsilyl-bis-(2,4,6-trimethylindenyl)zirconium dichloride and
rac-dimethylsilyl-bis-(2-methyl-4,5-benzoindenyl)-zirconium dichloride.

Unbridged metallocenes, such as, for example (cyclopentadienyl)$_2$ZrCl$_2$, can also be converted to a supported catalyst component by the process according to the invention, this component being particularly suitable for the preparation of high-molecular-weight atactic polyolefins or high-molecular-weight polyethylene.

Said metallocenes I are known and processes for their preparation are described in the literature (cf. J. Organomet. Chem. 288 (1985) 63-67, EP-A 320 762, EP-A 336 127, EP-A 387 590 and EP-A 302 424).

The reaction of the metallocene of the formula (I) with the pretreated inorganic support material is carried out

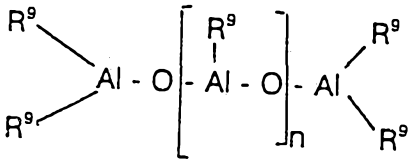
by vigorous stirring under inert gas in a solvent, which may be aromatic, aliphatic or additionally halogenated, by adding the metallocene to the pretreated support material in the form of a solid or suspension or metering the latter into a solution of the metallocene to be supported, in both cases at temperatures of -30°C to 120°C. Examples of suitable solvents are toluene, dichloromethane and hexane, in which the metallocene is reacted in a ratio of from 1×10^{-6} to 5×10^{-2} mol, preferably from 1×10^{-5} to 1×10^{-3} mol, of M^1/g of support. The metallocene concentration in the solvent is between 0.1 and 10^{-6} mol/l, preferably between 0.01 and 10^{-5} mol/l, it also being possible for some of the organometallic compound to be in undissolved form as a suspension.

The reaction duration is between 15 minutes and 48 hours, preferably between 1 hour and 20 hours.

This process is distinguished by a high degree of immobilization of the metallocene on the support used.

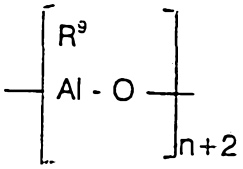
It is advantageous, in order to remove small, adhering residual amounts of non-immobilized metallocene, to wash the catalyst component prepared in this way with a suitable solvent, such as, for example, anhydrous and oxygen-free toluene, under inert conditions, it being possible to use an extractor (for example a Soxhlet extractor) in order to avoid large amounts of solvents.

The cocatalyst used in the process according to the invention for the preparation of high-molecular-weight polyolefins is an aluminoxane of the formula II



(II)

for the linear type and/or of the formula III



(III)

for the cyclic type, where, in the formulae II and III, the radicals R^9 may be identical or different and are a C_1-C_6-alkyl group, a C_1-C_6-fluoroalkyl group, a C_6-C_{18}-aryl group, a C_6-C_{18}-fluoroaryl group or hydrogen, and n is an integer from 2 to 50. n is preferably an integer from 10 to 35.

The radicals R^9 are preferably identical and are methyl, isobutyl, phenyl or benzyl, particularly preferably methyl.

If the radicals R^9 are different, they are preferably methyl and hydrogen or alternatively methyl and isobutyl, it being preferred for hydrogen or isobutyl to be present to the extent of 0.01-40% (number of radicals R^9).

It is also possible to replace the aluminoxane by a mixture comprising aluminoxane and AlR^9_3. The aluminoxane can be prepared by various methods by known processes. One of the methods is, for example, to react an aluminum hydrocarbon compound and/or a hydridoaluminum hydrocarbon compound with water (in gas, solid, liquid or bonded form - for example as water of crystallization) in an inert solvent (such as, for example, toluene). To prepare an

aluminoxane containing different alkyl groups R^9, two different trialkylaluminum compounds ($AlR_3 + AlR'_3$), corresponding to the desired composition, are reacted with water (cf. S. Pasynkiewicz, Polyhedron 9 (1990) 429 and EP-A 302 424).

The precise structure of the aluminoxanes II and III is unknown.

Irrespective of the preparation method, all aluminoxane solutions have in common a varying content of unreacted aluminum starting compound, which is present in free form or as an adduct.

It is possible to preactivate the supported catalyst component with an aluminoxane of the formula (II) and/or (III) before use in the polymerization reaction. This significantly increases the polymerization activity and improves the particle morphology. In this case, the supported catalyst is preferably added as a solid to a solution of an aluminoxane in an inert hydrocarbon. Suitable inert hydrocarbons are aliphatic or aromatic hydrocarbons. Preference is given to toluene or a C_6-C_{10}-hydrocarbon.

The concentration of the aluminoxane in the solution is in the range from about 1% by weight to the saturation limit, preferably from 5 to 30% by weight, in each case based on the total solution. The metallocenes can be employed in the same concentration (values to be understood without support), but are preferably employed in an amount of from 10^{-4} to 1 mol per mol of aluminoxane. The preactivation time is from 5 minutes to 60 hours, preferably from 5 to 60 minutes. The reaction temperature is from -78°C to 100°C, preferably from 0 to 70°C.

A further possible embodiment of the process according to the invention comprises using a salt-like compound of the

formula $R_xNH_{4-x}BR'_4$ or of the formula $R_3PHBR'_4$ as cocatalyst in place of or in addition to an aluminoxane. In these formulae, x = 1, 2 or 3, R = alkyl or aryl, identical or different, and R' = aryl, which may also be fluorinated or partially fluorinated. In this case, the catalyst comprises the product of the reaction of the supported metallocene with one of said compounds (cf. EP-A 277 004).

The present invention thus also relates to a process for the preparation of high-molecular-weight polyolefins by polymerization or copolymerization of an olefin of the formula $R^aCH=CHR^b$, in which R^a and R^b are identical or different and are a hydrogen atom or an alkyl radical having 1 to 14 carbon atoms, or R^a and R^b, together with the atoms connecting them, can form a ring, at a temperature of from -60 to 200°C, at a pressure of from 0.5 to 100 bar, in solution, in suspension or in the gas phase, in the presence of a catalyst comprising a transition-metal component (metallocene) and an aluminoxane, wherein the transition-metal component is the above-described supported metallocene I.

The polymerization or copolymerization is carried out in a known manner in solution, in suspension or in the gas phase, continuously or batchwise, in one or more steps, at a temperature of from -60 to 200°C, preferably from 20 to 80°C. Olefins of the formula $R^a-CH=CH-R^b$ are polymerized or copolymerized. In this formula, R^a and R^b are identical or different and are a hydrogen atom or an alkyl radical having from 1 to 14 carbon atoms. However, R^a and R^b, together with the carbon atoms connecting them, may also form a ring. Examples of such olefins are ethylene, propylene, 1-butene, 1-hexene, 4-methyl-1-pentene, 1-octene, norbornene and norbornadiene. In particular, propylene and ethylene are polymerized.

As molecular weight regulator, hydrogen is added if necessary. The overall pressure in the polymerization system is from 0.5 to 100 bar. The polymerization is preferably carried out in the industrially particularly interesting pressure range of from 5 to 64 bar.

The metallocenes are used in a concentration, based on the transition metal, of from 10^{-3} to 10^{-8}, preferably from 10^{-4} to 10^{-7}, mol of transition metal per dm^3 of solvent or per dm^3 of reactor volume. The aluminoxane or the aluminoxane/AlR^9_3 mixture is used in a concentration of from 10^{-5} to 10^{-1} mol, preferably from 10^{-4} to 10^{-2} mol, per dm^3 of solvent or per dm^3 of reactor volume. In principle, however, higher concentrations are also possible.

The process according to the invention for supporting the metallocenes enables, irrespective of the type, surface area and pretreatment of the support, an incorporation rate of from 1×10^{-6} to 1×10^{-2} mol of M^1/g of support, preferably from 1×10^{-5} to 1×10^{-3} mol of M^1/g of support.

If polymerization is carried out as a suspension or solution of polymerization, an inert solvent which is customary for the Ziegler low-pressure process is used. For example, the polymerization is carried out in an aliphatic or cycloaliphatic hydrocarbon; examples of these which may mentioned are butane, pentane, hexane, heptane, decane, isooctane, cyclohexane and methylcyclohexane.

It is furthermore possible to use a gasoline or hydrogenated diesel oil fraction. Toluene can also be used. The polymerization is preferably carried in the liquid monomer.

If inert solvents are used, the monomers are metered in gas or liquid form.

The polymerization can be carried out for as long as desired, since the catalyst system to be used according to the invention only exhibits a slight time-dependent drop in polymerization activity.

The supported catalyst component according to the invention is particularly suitable for the preparation of highly isotactic or highly syndiotactic polypropylene having a narrow molecular weight distribution, and of corresponding copolymers of propylene with ethylene or other C_4-C_{16}-α-olefins, it still being possible to achieve molecular weights of greater than 10^6 g/mol in said cases, even at high polymerization temperatures.

The polymerization process according to the invention thus enables for the first time, for example, general access to isotactic or syndiotactic polypropylene having a molecular weight of greater than 500,000 g/mol and having a narrow molecular weight distribution. The material prepared in this way has a melting point of about 160°C.

For a large range of various metallocenes, the catalyst system according to the invention thus generally solves the problem, known in particular for polypropylene, of the excessively low melting point and enables metallocenes which can be prepared in a simple manner to be used for said purpose.

Example 1 Preparation of the supported catalyst components

The support material used was Silica Davison Grade 952. The surface area of the material used, according to BET measurements, was 350 m^2/g, and the pore diameter was 15 nm (from the N_2 desorption curve). The particle size was in the range from 50 to 100 μm. Before use, the material was ignited at 500°C for 3 hours and degassed in

vacuo at 100°C for 16 hours.

60 cm^3 of a 10^{-3} molar solution of ethylene(indenyl)-zirconium dichloride in toluene were added to 2.7 g of Silica Davison Grade 952. The suspension was stirred at 55°C for 16 hours. Subsequent Soxhlet extracted for 2 days was intended to ensure that the support was free from homogeneous components. Filtration with suction and drying in vacuo to constant weight gave a pale yellow solid.

In order to determine the zirconium content, samples of 300 mg were weighed out, digested for one day at 220°C in a mixture of 4 ml of HNO_3 (65% strength), 2 ml of $HClO_4$ (70% strength) and 1 ml of HF (40% strength), and, when the acid had stopped fuming, the mixture was taken up in 10 ml of distilled H_2O. The measurement was carried out on a Perkin Elmer ICP-OES spectrometer. For Example 1, a zirconium content of 1.9×10^{-5} mol of Zr/g of support was obtained. Further data are given in Table 1.

Examples 2-4

The supported catalysts of Examples 2-4 were prepared analogously to Example 1, the reaction conditions selected being 85°C/16 hours (Example 2), 25°C/2 hours (Example 3) and 55°C/2 hours (Example 4). The work-up and characterization were carried out analogously to Example 1. The changes in amount of catalyst employed and Zr content found compared with Example 1 are shown in Table 1.

Example 5

Ethylene(tetrahydroindenyl)zirconium dichloride was used as a further starting compound. In a modification of the examples above, the compound, which is more soluble in toluene, particularly at elevated temperatures, than is

the unhydrated zirconocene, was added as a solid.

4.22 g of Silica Davison Grade 952 and 323 mg (0.75 mmol) of the metallocene were stirred at 70°C for 2 hours in 50 ml of toluene. The sample contained 8.4×10^{-5} mol of Zr/g of support. Further data are shown in Table 1.

Example 6

The same stoichiometry as in Example 5 was selected, but the batch was increased in size.

14.4 g of Silica Davison Grade 952 were stirred at 70°C for 2 hours with 1.06 g (2.47 mmol) of said metallocene in 175 ml of toluene. The work-up and characterization were carried out analogously to Example 1. In excellent agreement with Example 5, the sample likewise contained 8.4×10^{-5} mol of Zr/g of support.

Example 7

315 mg of Silica Davison Grade 952 were stirred at 70°C for 16 hours with 227 mg (0.53 mmol) of ethylenebis-(tetrahydroindenyl)zirconium dichloride in 10 ml of toluene. The work-up and characterization were carried out analogously to Example 1. The sample contained 4.5×10^{-4} mol of Zr/g of support.

Table 1

Example	Employed	Found	Found
	mol of Zr/g of support	mol of Zr/g of support	mg of Zr/g of support
1	2.2×10^{-5}	1.9×10^{-5}	1.8
2	2.3×10^{-5}	2.1×10^{-5}	2.0
3	3.8×10^{-5}	3.3×10^{-5}	3.1
4	5.8×10^{-5}	5.5×10^{-5}	5.1
5	1.7×10^{-4}	8.4×10^{-5}	7.6
6	1.7×10^{-4}	8.4×10^{-5}	7.6
7	1.7×10^{-3}	4.5×10^{-4}	40.7

Polymerization examples

Example 8

A 1 dm^3 reactor which had been dried by heating in vacuo, had been flushed several times and was held at 50°C by means of a thermostat, was filled in a counter stream of argon with 100 ml of toluene, 600 mg of aluminoxane and 310 mg of the supported metallocene in Example 1. After a prereaction time of one hour with stirring, 2 bar of propene were injected. After a reaction time of 16 hours, the excess pressure was released, and the batch was quenched by means of ethanol. In order to remove catalyst residues, the mixture was stirred in ethanolic HCl for one day. After subsequent drying the polypropylene was

separated from the support by extraction with decalin at 140°C. After precipitation of the hot decalin solution in ethanol, filtration with suction and drying in vacuo at 70°C, silica-free polypropylene was obtained as a white material in a yield of 2.1 g.

The viscosity average molecular weight of the sample was determined in decalin (135°C) for a sample weight of 15 mg in 50 ml. For evaluation, the values $K = 1 \times 10^{-4}$ and $\alpha = 0.8$ were used. A viscosity average molecular weight M_v of 958,000 was obtained. DSC measurements gave a melting point of 160.1°C.

Examples 9-11

The polymerizations were carried out analogously to Example 8. The catalyst amounts employed were 587 mg (Example 9), 460 mg (Example 10) and 340 mg (Example 11). Further data and the characterization of the products are shown in Table 2.

Example 12

In a modification of the examples above, the heterogenized form of the hydrogenated zirconocene of Example 5 was employed here. The polymerization was carried out analogously to Example 8 using 328 mg of supported catalyst components. Further data and the characterization of the product are given in Table 2.

Examples 13 and 14

The polymerizations were carried out analogously to Example 8 using 262 mg of the catalyst of Example 5 at 30°C in Example 13 and using 323 mg at 70°C in Example 14. Further data and the characterization of the products are given in Table 2.

Example 15

The polymerization was carried out analogously to Example 8. In order to be able to determine the activity more precisely, 963 mg of the catalyst of Example 6 and 2.0 g of aluminoxane were employed. After polymerization for 2 hours at 50°C and a propene pressure of 2 bar, 8.7 g of product were obtained after work-up. The activity was 28.2 kg of PP/mol of Zr·h·bar.

Example 16

In this example, ethene was employed as the monomer. The polymerization was carried out analogously to Example 8. Using 205 mg of the catalyst component of Example 5, 1.7 g of product were obtained in 10 minutes at 50°C and an ethene pressure of 4 bar.

Table 2

Example No.	Cat. of Example No.	T(°/C) [1]	M_v (g/mol)	m.p. (°C) of product (PP)
8	1	50	958,000	160.1
9	2	50	1,096,000	158.4
10	2	50	1,333,000	158.4
11	3	50	1,171,000	155.2
12	5	50	1,217,000	155.6
13	5	30	1,145,000	153.6
14	5	70	1,352,000	156.4

[1] Polymerization temperature

Example 17

The polymerization was carried out using 582 mg of aluminoxane and 986 mg of the catalyst component of Example 6 at 50°C, a propene pressure of 2 bar and a polymerization time of eight hours.

Yield:	2.0 g
Activity:	773 g of PP/mol of Zr·h·bar
Melting point:	155.8°C
Isotacticity:	90.2%
Isotactic block length:	18.4
M_v:	911,000 g/mol

Example 18

The polymerization was carried out using 566 mg of aluminoxane and 246 mg of the catalyst component of Example 6 at 50°C, a propene pressure of 2 bar and a polymerization time of three hours, after prereaction of the catalyst component in 10 ml of toluene at room temperature for one hour.

Yield:	0.37 g
Activity:	1000 g of PP/mol of Zr · h · bar
Melting point:	158.2°C
Isotacticity:	96.5%
Isotactic block length:	49.5
M_v:	921,000 g/mol

The isotacticity was determined by means of ^{13}C-NMR spectroscopy.

Example 19

Preparation of the supported catalyst component

4.23 g of Silica Davison 952 and 300.6 mg of ethylenebis-(indenyl)zirconium dichloride were stirred at 70°C for 16 hours in 50 ml of toluene. A slight red coloration of the support material was observed after a few minutes. When the reaction time was complete, the supernatant solution had become virtually colorless. After extraction for one day and drying for 12 hours in vacuo at 40°C, the supported catalyst $SiBi_6$ was obtained as a reddish solid.

Zirconium concentration employed:	1.7×10^{-4} mol of Zr/g of silica
Zirconium concentration found:	1.6×10^{-4} mol of Zr/g of silica
Degree of immobilization:	94%

Polymerization examples

Example 20

The polymerization was carried out analogously to Example 8 using 431 mg of the catalyst from Example 19 and 0.46 g of methyl aluminoxane (MAO) at a propene pressure of 2 bar, a polymerization temperature of 50°C and a polymerization time of 2 hours.

The yield was 1.20 g, this corresponds to an activity of 11.2 kg/mol of [Zr]. ^{13}C-NMR studies gave an isotacticity of 96.8% ([mm] = 94.6). Compared with polypropylene prepared under otherwise identical conditions using the corresponding homogenous catalyst system, the percentage of [mm] triads in the product obtained here was 9% higher (^{13}C-NMR). Further data on the characterization are given in Table 3.

Example 21

The polymerization was carried out analogously to Example 20 using 237 mg of the catalyst from Example 19 and 0.35 g of MAO at a polymerization temperature of 75°C. DSC measurements of the products gave a melting point of 162.2°C. Further data and the characterization are given in Table 3.

Examples 22 and 23

The polymerizations were carried out analogously to Example 21, using 319 mg and 279 mg of the catalyst from Example 19 and 0.36 g and 0.37 g of MAO. Further data and the characterization are given in Table 3.

Table 3

Example No.	Yield in g	Activity in kg/mol of [Zr]	M_v [$\times 10^3$]	m.p. (0°C) of Product (PP)	[mm] in %
20	1.20	11.2	518	159.2	94.6
21	0.51	7.0	675	162.1	
22	0.80	9.4	632	161.3	
23	0.62	7.0	758	162.1	

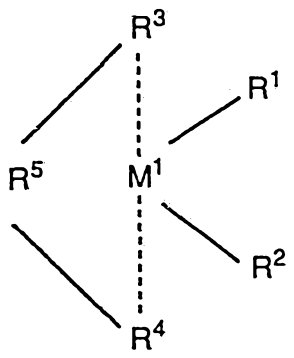
THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A supported catalyst component for olefin polymerization, consisting essentially of an inorganic support material and a metallocene, said metallocene alone being supported on said inorganic support material.

2. A catalyst component as claimed in claim 1, wherein the inorganic support material is an oxide of a metal from main group II-IV or sub-group IV of the Periodic Table of the Elements, or iron oxide or a mixture thereof.

3. A catalyst component as claimed in claim 1 or 2, wherein the inorganic support material is silicon dioxide.

4. A catalyst component as claimed in one or more of claims 1-3, wherein the metallocene is a compound of the formula I



(I)

in which

M^1 is titanium, zirconium, vanadium, niobium or tantalum,

R^1 and R^2 are identical or different and are a hydrogen atom, a halogen atom, a C_1-C_{10}-alkyl group, a C_1-C_{10}-alkoxy group, a C_6-C_{10}-aryl group, a C_6-C_{10}-aryloxy group, a C_2-C_{10}-alkenyl group, a C_7-C_{40}-alkylaryl group or a C_8-C_{40}-arylalkenyl group,

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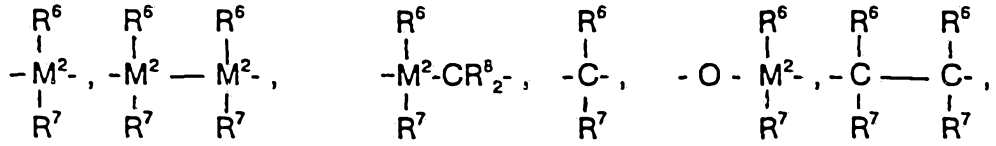
R^3 and R^4 are identical or different and are a monocyclic or polycyclic hydrocarbon radical which can form a sandwich structure with the central atom M^1,

R^5 is



$=AlR^6$, $-O-$, $=NR^6$, $=CO$, $=PR^6$ or $=P(O)R^6$, where R^6, R^7 and R^8 are identical or different and are a hydrogen atom, a halogen atom, a C_1-C_{10}-alkyl group, a C_1-C_{10}-fluoroalkyl group, a C_6-C_{10}-fluoroaryl group, a C_6-C_{10}-aryl group, a C_1-C_{10}-alkoxy group, a C_2-C_{10}-alkenyl group, a C_7-C_{40}-arylalkyl group, a C_8-C_{40}-arylalkenyl group or a C_7-C_{40}-alkylaryl group, or R^6 and R^7 or R^6 and R^8, in each case together with the atoms connecting them, form a ring, and

M^2 is silicon, germanium or tin.

5. A catalyst component as claimed in one or more of claims 1-4, wherein the metallocene is (arylalkylidene)-(9-fluorenyl)(cyclopentadienyl)zirconium dichloride, (diarylmethylene)(9-fluorenyl)(cyclopentadienyl)zirconium dichloride or (dialkylmethylene)(9-fluorenyl)(cyclopentadienyl)zirconium dichloride.

6. A catalyst component as claimed in one or more of claims 1-5, wherein the metallocene is (methyl(phenyl)methylene)-(9-fluorenyl)(cyclopentadienyl)-zirconium dichloride, (diphenylmethylene)-

(9-fluorenyl)(cyclopentadienyl)zirconium dichloride or (dimethylmethylene)(9-fluorenyl)(cyclopentadienyl)zirconium dichloride.

7. A catalyst component as claimed in one or more of claims 1-6, wherein the metallocene is rac-dimethylsilyl-bis-(1-indenyl)zirconium dichloride, rac-diphenylsilyl-bis-(1-indenyl)zirconium dichloride, rac-dimethylsilyl-bis-(tetrahydro-1-indenyl)-zirconium dichloride, rac-diphenylsilyl-bis-(tetrahydro-1-indenyl)-zirconium dichloride, rac-ethylene-bis-(tetrahydro-1-indenyl)zirconium dichloride or rac-ethylene-bis-(1-indenyl)zirconium dichloride.

8. A process for the preparation of a supported catalyst component as claimed in one or more of claims 1-7, which comprises reacting the inorganic support material in a solvent with the metallocene.

9. The process as claimed in claim 8, wherein the solvent is toluene.

10. A process for the preparation of a high-molecular-weight polyolefin by polymerization or copolymerization of an olefin of the formula $R^aCH=CHR^b$, in which R^a and R^b are identical or different and are a hydrogen atom or an alkyl radical having 1 to 14 carbon atoms, or R^a and R^b, together with the atoms connecting them, can form a ring, at a temperature of from -60 to 200°C, at a pressure of from 0.5 to 100 bar, in solution, in suspension or in the gas phase, in the presence of a catalyst comprising a transition-metal component (metallocene) and an aluminoxane, wherein the transition-metal component

is a supported catalyst component as claimed in one or more of claims 1-7.

11. The process as claimed in claim 10, wherein propylene is polymerized or copolymerized.

12. Polypropylene obtainable by the process as claimed in claim 10 or 11.

DATED this 25th day of June 1992.

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