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- (21) Application No. 8031/76
- (22) Filed 1 Mar. 1976
- (32) Complete Specification Filed 23 Feb. 1977
- (44) Complete Specification Published 16 Jul. 1980
- (51) INT. CL.³ CO8F 4/64 10/02
- (52) Index at Acceptance
C3P 404 438 452 464 474 538 574 582
590 594 602 GA
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(19)



(54) SUPPORTED ZIEGLER POLYMERISATION CATALYST AND COMPONENTS THEREOF

(71) We, BP CHEMICALS LIMITED, of Britannic House, Moor Lane, London, EC2Y 9BU, a British company, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:-

5 The present invention relates to a process for the production of a supported Ziegler catalyst component and to the use thereof in the polymerisation of olefins. 5

10 It has long been known that olefins such as ethylene can be polymerised by contacting them under polymerisation conditions with a catalyst comprising (1) a transition metal compound, e.g. titanium tetrachloride and (2) a co-catalyst or activator, e.g. an organometallic compound such as triethylaluminium. Catalysts of this type are generally referred to as Ziegler catalysts and will be so referred to throughout this specification. It is also known to deposit the transition metal compounds on support materials such as silicon carbide, calcium phosphate and magnesium or sodium carbonate. 10

15 The present invention provides a process for the production of a supported Ziegler catalyst component comprising forming a support material by heating the magnesium salt of an organic carboxylic acid under conditions so that at least part thereof is converted to magnesium oxide, and impregnating the support material with the reaction mixture obtained by reacting together titanium tetrachloride and isopropanol. 15

20 The magnesium salt employed in the process of the present invention can be the salt of a mono- or polycarboxylic acid, for example, magnesium formate, magnesium acetate, magnesium oxalate, magnesium malonate, magnesium maleate, or magnesium benzoate. The salt can be anhydrous, hydrated or solvated. 20

25 The heating of the magnesium salt must be carried out under conditions such that at least part, for example 5%, preferably at least 50 wt %, most preferably at least 60% is converted to magnesium oxide. The degree of conversion to magnesium oxide can be determined satisfactorily by elementary analysis or by x-ray diffraction. The temperature at which a magnesium salt of an organic carboxylic acid commences to decompose to magnesium oxide will, of course, depend on the given salt, and may be for instance in the range 300° to 700°C. The decomposition temperature for any particular salt may be determined by trial and error. The heating is preferably carried out at a temperature only marginally above the decomposition temperature of the salt, for example between 5 and 100°C above the decomposition temperature. The heating can be carried out, for example, 'in vacuo', in an inert gas such as steam or nitrogen or in air. It is preferred to carry out the heating in air. If desired, a stream of gas, e.g. steam or nitrogen, can be used to fluidise the powdered salt during the heating. 30 35

40 The product of heating the magnesium salt of the carboxylic acid is preferably sieved or screened before impregnating it with the reaction mixture obtained by reacting together the titanium tetrachloride and isopropanol. If the product of the heating contains lumps it can, for example, be sieved to separate the product having the desired particle size and the lumps may be ground and sieved again. Preferably the product used as the support material has a particle size in the range 1 µm to 500 µm (mean particle diameter) and most preferably in the range 50 µm to 250µm. 40

45 The reaction mixture obtained by reacting together titanium tetrachloride and isopropanol - hereinafter referred to as "the Ti-reaction mixture" - is believed to comprise compounds of titanium having the general formula $Ti(OR)_n(Cl)_{4-n}$ wherein n has any value 45

from 0.4 inclusive and R is an isopropyl group, for example, titanium tetrakispropylate, $Ti(OiPr)_2Cl_2$ or mixtures thereof.

5 The quantity of titanium tetrachloride employed is suitably sufficient to give a concentration of titanium in the catalyst in the range 0.5 to 15 wt %, preferably 1.5 to 9 wt % based on the total weight of catalyst component. 5

10 The impregnation of the support material of the present invention with the Ti-reaction mixture may be carried out using any convenient technique. Suitably the support material is treated with the Ti-reaction mixture at a temperature in the range -40° to $150^\circ C$, and preferably between 20° to $100^\circ C$. This can be carried out, for example, by mixing the support material and the Ti-reaction mixture with or without an inert diluent or a solvent for the said reaction mixture. It is preferred to heat the support material and the Ti-reaction mixture together at a temperature in the range 70 to $100^\circ C$ for $\frac{1}{2}$ to 5 hours in the presence of an inert diluent or a solvent for the said reaction mixture. Suitable inert diluents (which are in some cases also solvents for the Ti-reaction mixture) are, for example, saturated aliphatic hydrocarbons such as petroleum ether, butane, pentane, hexane, heptane, methylcyclohexane and cyclohexane and aromatic hydrocarbons such as benzene, toluene and xylene. 15

20 Any excess titanium compound remaining in the catalyst after the impregnation step is preferably removed from the catalyst, for example, by solvent washing, distillation or other convenient techniques which do not have a deleterious effect on the catalyst. 20

The preparation and impregnation of the Ti-reaction mixture is preferably carried out in the absence of oxygen or moisture.

25 The present invention further provides a process for polymerising 1-olefins comprising contacting the monomer under polymerisation conditions with the supported Ziegler catalyst component of the present invention in the presence of a Ziegler catalyst activator. 25

30 The polymerisation process according to the present invention can be applied to the polymerisation of 1-olefins e.g. ethylene or propylene or mixtures of olefins, e.g. ethylene with other 1-olefins, for example, propylene, 1-butene, 1-pentene, 1-hexene, 4-methylpentene-1, 1-3-butadiene or isoprene. The process is particularly suitable for the polymerisation of ethylene or copolymerisation of ethylene with up to 40 weight % (based on total monomer) of comonomers i.e. one or more other 1-olefins. 30

35 Ziegler catalyst activators and the methods by which they are used to activate Ziegler catalysts are well-known. Examples of Ziegler catalyst activators are organic derivatives or hydrides of metals of Groups I, II, III and IV of the Periodic Table. Particularly preferred are the trialkylaluminiums, e.g. triethyl- or tributylaluminium, or alkylaluminium halides. 35

40 The polymerisation conditions can be in accordance with known techniques used in supported Ziegler polymerisation. The polymerisation can be carried out in the gaseous phase or in the presence of a dispersion medium in which the monomer is soluble. As a liquid dispersion medium use can be made of an inert hydrocarbon which is liquid under the polymerisation conditions, or of the monomer or monomers themselves maintained in the liquid state under their saturation pressure. The polymerisation can, if desired, be carried out in the presence of hydrogen gas or other chain transfer agent to vary the molecular weight of the produced polymer. 40

45 The polymerisation is preferably carried out under conditions wherein the supported Ziegler catalyst component is suspended in a liquid diluent in the presence of a Ziegler catalyst activator so that the polymer is formed as solid particles suspended in the liquid diluent. Suitable diluents are, for example, selected from paraffins and cycloparaffins having from 3-30 carbon atoms per molecule. Examples of diluents include isopentane, isobutane, and cyclohexane. Isobutane is preferred. 45

50 The polymerisation can be carried out under continuous or batch conditions. 50

Methods of recovering the product polyolefin are well-known in the art.

55 The polymerisation catalyst of the present invention can be used to make high density ethylene polymers and copolymers at high productivity having properties which render them suitable for injection moulding. 55

The invention is illustrated by the following examples:-

In the Examples the melt index ($MI_{2.16}$) and high load melt index ($MI_{21.6}$) were determined according to ASTM method 1238 using 2.16 kg and 21.6 kg loads respectively: the units are grammes per 10 minutes. "MIR" is the melt index ratio $MI_{21.6}/MI_{2.16}$.

60 Example 1A 60

65 80 g of dried magnesium acetate (BDH laboratory Reagent) were placed in an oven at $200^\circ C$. The oven was rapidly heated to $375^\circ C$ and maintained at that temperature for 20 hours to convert at least part of the acetate to oxide. The oven was purged with nitrogen for the first six hours. 21.3 g of a rough pale grey powder were obtained. The powder was ground with a mortar and pestle to produce a support material of the desired particle size. 65

Before use, 10 g of the support were placed in an oven at 150°C under vacuum for 2 hours to ensure dryness. No further weight loss was observed.

57 ml of isopropanol and 150 ml of cyclohexane were stirred under an atmosphere of dry nitrogen and 36.4 ml of TiCl_4 were slowly added. The resultant yellow solution was refluxed for 2 hours. The solution was allowed to cool to 55°C and 10 g of the support, prepared as described above, were added. The mixture was refluxed for 3 hours and the catalyst component slurry washed seven times with cyclohexane to ensure that the concentration of titanium in the solvent was less than 1g/litre. The volume was made up to 500 ml with dry cyclohexane and the catalyst component handled as a slurry with a solids content of 51 mg/ml. Analysis of the catalyst component yielded (w/w) - Ti 4.77%, Cl 34.26%.

Example 1B

70 g of dried magnesium acetate (BDH Laboratory Reagent) were placed in an oven at 200 °C. The temperature was quickly raised to 600°C. No gas purge was employed. This temperature was maintained for 16 hours and 18.7g of a rough grey powder (similar to that formed in the first example) were obtained. This was ground in a mortar and pestle and the catalyst component prepared as in Example 1A. The solids content of this catalyst component was 60.5 mg/ml. Analysis of the catalyst component yielded (w/w) - Ti 5.60%, Cl - 25.90%.

Example 2

80 g of hydrated magnesium oxalate, $\text{MgC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (BDH Laboratory Reagent) were placed in an oven at 125°C. The oven was rapidly heated to 600°C and maintained at that temperature for 17 hours. The oven was purged with nitrogen for the first six hours to prevent a dangerous build-up of carbon monoxide. The produced support material was a fine white powder weighing 20.5 g. The support was predried and the catalyst prepared as described in Example 1A. Six washes were required to remove free Ti salts. The solids content of the catalyst component slurry was 79 mg/ml. Analysis of the catalyst component yielded Ti 4.86%, Cl 33.64%.

Polymerisation

Polymerisations were carried out using the catalyst components of Example 1 and 2 in a 2.3 litre stainless steel stirred autoclave. The reactor was purged with nitrogen, heated to 70°C and then 2 ml of the catalyst component slurry added with a syringe. This was followed by the triethylaluminium co-catalyst in 1 litre of isobutane. The temperature was raised to 85°C. The required pressure of hydrogen was added, followed by ethylene to bring the total pressure of the reactor contents to 41.4 bar. Ethylene was added continuously to maintain this pressure during the reaction. Polymerisation and polymer property data are shown in the Table.

TABLE

Catalyst Prep.	Catalyst component (mg)	Co-Catalyst Wt. (mg)	H ₂ Partial Pressure (bar)	Productivity (g/g hour)	MI _{2.6} (g/10 min)	MIR	Polymer Size (>500μm (w/w))	Polymer Size (<100μ (w/w))
Ex. 1A	102	251	5.2	5602	5.52	25.8	10.8	1.3
"	102	251	7.6	4156	18.48	23.9	17.4	3.2
Ex. 1B	121	251	5.2	3813	3.54	31.8	48.1	0.1
"	121	251	6.9	2975	4.38	28.2	51.9	Nil
Ex. 2	158	251	5.2	1981	3.24	26.5	96.0	Nil
"	158	251	6.9	1373	9.60	26.7	91.6	Nil

WHAT WE CLAIM IS

1. A process for the production of a supported Ziegler catalyst component comprising forming a support material by heating the magnesium salt of an organic carboxylic acid under conditions so that at least part thereof is converted to magnesium oxide, and impregnating the support material with the reaction mixture obtained by reacting together titanium tetrachloride and isopropanol.
2. A process as claimed in Claim 1 wherein the magnesium salt is magnesium formate, magnesium acetate, magnesium oxalate, magnesium malonate, magnesium maleate or magnesium benzoate.
3. A process as claimed in Claim 1 or 2 wherein at least 50 wt % of the magnesium salt is converted to magnesium oxide.
4. A process as claimed in any preceding claim wherein at least 60 wt % of the magnesium salt is converted to magnesium oxide.
5. A process as claimed in any preceding claim wherein the heating is carried out at a temperature only marginally above the decomposition temperature of the salt.
6. A process as claimed in any preceding claim wherein the quantity of titanium tetrachloride employed is sufficient to give a concentration of titanium in the catalyst in the range 1.5 to 9 wt % based on the total weight of catalyst component.
7. A process as claimed in any one of the preceding claims wherein the titanium tetrachloride and isopropanol are reacted together in the presence of a diluent.
8. A process as claimed in claim 7 wherein the diluent is a saturated aliphatic hydrocarbon.
9. A process as claimed in claim 7 wherein the diluent is cyclohexane.
10. A process for preparing a supported Ziegler catalyst component substantially as described in Example 1A, 1B, or 2.
11. A supported Ziegler catalyst component prepared by the process claimed in any one of the preceding claims.
12. A process for polymerising 1-olefins comprising contacting the monomer under polymerisation conditions with the supported Ziegler catalyst component of the present invention in the presence of a Ziegler catalyst activator.
13. A process as claimed in Claim 12 wherein the 1-olefinic monomer is ethylene or a mixture of ethylene with up to 40 wt % (based on total monomer) of one or more other 1-olefins.
14. A process as claimed in Claim 12 or 13 wherein the Ziegler catalyst activator is triethyl or tributylaluminium.
15. A process as claimed in Claim 12, 13, or 14 wherein the polymerisation process is carried out under particle form process conditions.
16. A process for polymerising ethylene substantially as described in any one of Examples 1A, 1B or 2.
17. Polyolefins when prepared by the process claimed in any one of Claims 12 to 16.

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