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(54)OLEFIN POLYMERISATION CATALYST

(71) We, PHILLIPS PETROLEUM COMPANY, a corporation organised and existing under the laws of the State of Delaware, United States of America, of Bartlesville, Oklahoma, United States of America, 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:-

This invention relates to magnesium reduced titanium tetrahalide catalyst systems.

It is known to reduce titanium tetrahalides with Grignard reagents, that is, X compounds produced by reacting magnesium and an organic halide in the presence of ether. It is also known to produce what is termed in the art a "solventless" Grignard, which is produced by reacting magnesium metal with an organic halide in the presence of a solvent which is designated as a nonsolvating solvent (i.e. an inert noncomplexing diluent) such as a noncomplexing hydrocarbon as distinguished from an ether. True Grignard reagents, as a practical matter, present serious problems as reducing agents in the production of catalysts in view of the difficulty in removing the large amount of ether and the remaining complexed ether can reduce the effectiveness of olefin polymerization catalyst systems prepared with the thus treated Grignard reagent.

With olefin polymerizations, particularly the polymerization of ethylene or predominantly ethylene-containing olefin mixtures, it has been found to be more economical to carry out the polymerization at a temperature low enough that the resulting polymer does not go into solution in the liquid diluent used, and to recover the polymer without elaborate catalyst removal steps. This results in residual catalyst remaining in the polymer and thus requires high productivity rates in order to be practical.

The present invention seeks to provide a simplified method of producing active titanium catalyst for olefin polymerization and to provide a catalyst system capable of high productivities. This method comprises forming a magnesium reducing agent by slowly adding an organic hydrocarbyl halide to magnesium metal in the absence of any other compound capable of forming a complex with said reducing agent, mixing said reducing agent with an organoaluminum compound to form a cocatalyst mixture, and thereafter mixing the cocatalyst with a titanium tetrahalide, wherein said reducing agent, before or after mixing with the organoaluminum compound, but before addition of the titanium tetrahalide, is washed with an inert hydrocarbon. As will be seen this method is characterised by fact that the magnesium reducing agent is prepared in the absence of any other compound, e.g. diluent, which is capable of forming a complex with the reducing agent, and by washing the reducing agent, before or after mixing with the organoaluminum compound, with an inert liquid hydrocarbon.

The organic halide used in this invention will usually be a saturated or unsaturated hydrocarbyl halide of formula RX wherein R is an alkynyl, alkenyl, alkyl, aryl, cycloalkenyl or cycloalkyl radical or combinations thereof such as aralkyl, having 1 to 12 carbon atoms per molecule and X represents a halogen atom, preferably chlorine or bromine. The organic halide can also be a polyhalogenated hydrocarbyl halide of formula $R'X_2$ in which R' is a saturated divalent aliphatic hydrocarbyl radical containing from 2 to 10 carbon atoms per molecule and X is a halogen atom as set out hereinabove. Exemplary organic halides include methyl chloride, n-butyl bromide, n-pentyl chloride, n-dodecyl chloride, allyl bromide, 1,2-dibromoethane, 1,4-dichlorobutane, 1,10-dibromodecane, cyclohexyl chloride and bromobenzene. A primary alkyl halide such as n-pentyl chloride is presently

preferred.

The magnesium is in the form of the free metal, preferably in the form of a powder.

Preferably the reaction between the organic halide and the magnesium metal to form the magnesium reducing agent is carried out in the complete absence of any extraneous diluent. This can be done by simply adding the organic halide slowly (e.g. dropwise) to magnesium metal powder in a container preferably with some stirring or agitation over a relatively long period of time, for instance 1 to 10 hours. However, it is also within the scope of the invention to carry out the reaction between the organic halide and the magnesium metal in the presence of a noncomplexing diluent such as a noncomplexing hydrocarbon diluent. Suitable such diluents include pentane, hexane, cyclohexane and methylcyclopentane. The same types of inert hydrocarbons suitable for use as diluents or solvents in the polymerization of 1-olefins being suitable for use as diluents in the production of the magnesium reducing agent. In all events, a complexing diluent such as ether is avoided.

The organic halide can be added to the magnesium metal in an amount within the range of 0.25:1 to 1:0.25 (moles organic halide/gram atoms Mg). Preferably, however, about a stoichiometric amount (1/1) of halide is used.

The magnesium reducing agent is washed with a dry nonreactive (inert) normally liquid hydrocarbon 1 to 4 or more times. The hydrocarbon can be selected from among paraffins, cycloparaffins and aromatics having 2 to 20, preferably 5 to 12 carbon atoms per molecule. Exemplary compounds include n-pentane, n-hexane, n-heptane, isoctane, dodecane, cyclohexane, benzene, toluene, xylenes and mixtures thereof. Preferably the wash liquid is the same as that to be used as a diluent in the subsequent polymerization or else is compatible therewith. The treating temperature is normally accomplished at room temperature, i.e., about 25°C. although temperatures ranging from about 0° to 100°C. or higher can be used depending upon the boiling point or freezing point of the treating liquid. Generally, the wash treatment is carried out on the magnesium reducing agent/organoaluminum compound cocatalyst mixture since the mixture forms a friable mass. However, it is within the scope of this invention to wash magnesium reducing agent prior to its contact with the organoaluminum compound. It is speculated that the wash treatment removes some material that has a deleterious effect on the amount of polymer made. At any rate, the wash treatment is effective in substantially improving productivity of the catalyst system prepared with the washed product.

If exhaustive washing of the cocatalyst mixture is practiced, it is noted that it is possible to remove some or all of the organoaluminum compound. When enough is lost to adversely affect the resulting catalyst, it is necessary to replace it with additional material since in its absence an inactive catalyst system results.

The magnesium reducing agent can be washed in any manner known in the art. For instance the inert hydrocarbon can simply be added to the magnesium reducing agent and the mixture agitated and thereafter allowed to settle and the supernatant liquid decanted off. Alternatively the wash liquid can be removed by filtration or by using a centrifuge. It is frequently desirable to ball mill the magnesium reducing agent with the inert hydrocarbon wash liquid in both embodiments wherein the organoaluminum compound is already present and in the embodiments where is is not. In addition to ball milling, of course, bepple milling, rod milling and colloid milling can also be used.

A typical analysis of the magnesium reducing agent of this invention using n-pentyl chloride added dropwise to magnesium in the absence of any diluent is:

Compound	Weight Percent
Hydrocarbon Soluble Components	
Di-n-pentylmagnesium	25.0
Decane	8.2
Di-n-decylmagnesium	1.1
Magnesium n-pentoxide	0.6
Hydrocarbon Insoluble Components	
Magnesium chloride	55.2
Magnesium	4.9
Chloromagnesium hydride	2.3
n-Pentylmagnesium chloride	2.0
Magnesium n-pentoxide	0.7

This is shown for illustrative purposes and is not intended to limit the scope of the invention. Substantial variation in the exact analysis from that shown is obtained if a different halogen is used or if a different organo radical is substituted for the n-pentyl.

However, in all cases there is present a substantial amount (at least 10 weight percent) each of the diorganomagnesium and the magnesium chloride. It is the reaction mixture that is the magnesium reducing agent as defined herein.

Obviously much of the soluble portion of the magnesium reducing agent will be removed by this washing step, but the resulting insoluble portion has different characteristics from simple $Mg-Cl_2$ prepared directly.

Preferred organoaluminum compounds are hydrocarbyl aluminum compounds of formula R''_2AlZ in which R'' is the same or different and is selected from alkyl and aryl radicals containing from 1 to 12 carbon atoms per molecule and Z in a hydrogen atom or a halogen atom, preferably chlorine or bromine. Exemplary compounds include dimethylaluminum bromide, diethylaluminum chloride, diisobutylaluminum hydride, diphenylaluminum chloride, ethylphenylaluminum chloride and di-n-dodecylaluminum bromide. A presently preferred compound is diethylaluminum chloride. as noted hereinabove, the organoaluminum compound can be added either before or after the washing but in either event is added before contact of the magnesium reducing agent with the titanium tetrahalide. Compounds of the formula AlR''_3, $R''AlX_2$ and $R''AlOR''$ where R'' is as above and X is a halogen atom, preferably chlorine or bromine can also be used. Exemplary compounds are triethylaluminum, ethylaluminum dichloride and diethylaluminum ethoxide.

The titanium tetrahalide is either titanium tetrachloride, titanium tetrabromide, or titanium tetraiodide, preferably titanium tetrachloride.

It is within the scope of this invention to use one or more adjuvants, these being polar organic compounds, i.e., Lewis bases (electron donor compounds) either premixed with the organoaluminum component or as a third entity along with the magnesium reducing agent, organoaluminum compound and titanium tetrahalide or both provided that such adjuvants are not present during the formation of the reducing agent. Suitable compounds for this purpose are described in U.S. Patent 3,642,746. They include alcoholates, aldehydes, amides, amines, arsines, esters, ethers, ketones, nitriles, phosphines, phosphites, phosphoramides, sulfones, sulfoxides, and stibines. Exemplary compounds include sodium ethoxide, benzaldehyde, acetamide, triethylamine, trioctyl arsine, ethyl acetate, diethyl ether, acetone, benzonitrile, triphenyl phosphine, triphenyl phosphite, hexamethyl phosphoric triamide, dimethyl sulfone, dibutyl sulfoxide and triethyl stibine. Triethylamine and triphenyl phosphite are particularly preferred.

Presently preferred adjuvants are the C_1-C_4 alkyl esters of benzoic acid which may be additionally substituted in the para position to the carboxyl group with a monovalent radical selected from the group consisting of -F, -Cl, -Br, -I, -OH, -OR''', -OOCR''', -SH, -NH, $-NR'''_2$, -NHCOR''', $-NO_2$, -CN, -CHO, -COR''', -COOR''', $-CONH_2$, -CONR''', $-SO_2R'''$, and $-Cf_3$. The R''' group is an alkyl radical of 1 to 4 carbon atoms. Exemplary compounds include ethyl anisate (ethyl p-methoxybenzoate), ethyl benzoate, methyl benzoate, ethyl p-dimethylaminobenzoate, ethyl p-fluorobenzoate, isopropyl p-diethylaminobenzoate, butyl p-fluorobenzoate, n-propyl p-cyanobenzoate, ethyl p-trifluoromethylbenzoate, methyl p-hydroxybenzoate, methyl p-acetylbenzoate, methyl p-nitrobenzoate, ethyl p-mercaptobenzoate and mixtures thereof. Particularly preferred esters are ethyl anisate and ethyl benzoate.

Generally when polymerizing ethylene, which is the preferred utility for the catalysts of this invention, no adjuvant is used. Generally an adjuvant is used in the less preferred embodiments of this invention where the catalyst is used for propylene polymerization.

The molar ratio of organoaluminum compound(s) to adjuvant(s) is usually in the range of 1:1 to 300:1. The atom ratio of aluminum to magnesium can range from 0.1:1 to 4:1, more preferably from 0.5:1 to 2:1. The molar ratio of titanium compound to adjuvant(s) is generally in the range of 1:1 to 200:1. The atom ratio of aluminum to titanium can range from 20:1 to 10,000:1, more preferably from 75:1 to 5,000:1.

The catalyst system of this invention can be used unsupported or supported on a particulate material including silica, silica-alumina, magnesia, magnesium carbonate, magnesium chloride, magnesium alkoxides such as magnesium methoxide. The weight ratio of titanium tetrahalide to support can vary from 0.05:1 to 1:1, more preferably from 0.1:1 to -0.3:1.

The catalyst system of this invention is useful for the polymerization of mono-l-olefins having 2 to 8 carbon atoms per molecule. It is of particular value in the polymerization of ethylene polymers and copolymers of ethylene and a minor amount of another mono-l-olefin such as propylene, butene-l, or hexene-l. It is possible utilizing the catalyst system of this invention which gives such high productivities to carry out such polymerizations, particularly the polymerization of ethylene and predominantly ethylene-containing 1-olefin mixtures in an inert diluent at a temperature as described hereinbelow wherein the polymer formed is insoluble in the liquid diluent and is simply separated

therefrom and utilized with no elaborate catalyst removal steps.

The polymerization conditions employed in the process are similar to other related processes in which a catalyst system comprising a titanium tetrahalide and an organoaluminum compound are used. The polymerization temperature generally falls within the range of 0 to 150°C., more preferably from 40 to 112°C. Any convenient partial pressure of ethylene is used. It generally falls within the range of 10 to 500 psig (69 to 3447 kPa). The titanium concentration can vary between 0.005 to 10, preferably between 0.001 to 2 milligram atoms per liter of diluent.

As is known in the art, control of the molecular weight of the molecular weight of the polymer can be accomplished by the presence of hydrogen in the reactor during polymerization.

In general, the charge order of the various components to the reactor consists of adding the washed magnesium reducing agent/organoaluminum compound cocatalyst mixture, then the titanium compound, the diluent and finally hydrogen, if used. The diluent is a hydrocarbon unreactive under the polymerization conditions used. Examples of suitable diluents include isobutane, n-haptane, cyclohexane and the like. The reactor and its contents are then heated to the desired polymerization temperature, monomer such as ethylene and comonomer, if used, are added and polymerization begins. Polymerization times can vary from about 0.1 to 5 hours or more.

The resulting polymers are useful for fabrication by means of conventional equipment into fibers, film, molded articles and the like.

Example

In a dry flask equipped with a dropping funnel, condenser and stirrer was placed 60 g (2.47 gram atoms) of 50 mesh magnesium powder. While gently stirring the magnesium metal under a nitrogen atmosphere, 263.5 g (2.47 moles) of dry n-pentyl chloride was slowly added through the funnel at a rate sufficient to keep unreacted alkylhalide gently refluxing. Addition time was 4 hours. At the conclusion of the reaction, 300 ml. of dry n-hexane were added to the flask and the stirred mixture was heated to boiling and refluxed for 4 hours. Following this treatment, the flask was transferred to a dry box and the hexane was removed under reduced pressure leaving behind the magnesium reducing reagent as a gray residue. Portions of the powdered solid were individually slurried with a 25 weight percent solution of diethylaluminum chloride (DEAC) dissolved in n-heptane using 3.4 ml of the DEAC solution per gram of magnesium reducing agent. In addition to this, 5 ml of dry-n-heptane was used per gram of magnesium reducing agent. Five gram portions of the magnesium reducing agent were used in preparing each cocatalyst component except in runs 4 and 5 in which a 3.7 g portion was employed. Each mixture was placed in a 12 ounce (355 ml) glass beverage bottle along with 50 g of 1/2" (1.27 cm) ceramic balls capped and ball milled for the time shown. The washing treatment, when used, consisted of diluting the ball milled slurry with 6 times its volume of n-hexane (unless otherwise specified) followed by milling for 15 minutes, allowing the mixture to settle overnight and decanting the liquid, generally the same volume as the added n-hexane. Portions of the cocatalyst were used in subsequent runs in which ethylene was polymerized in the absence of hydrogen.

A one gallon (3.87 liter) stirred reactor, purged with dry nitrogen, was charged under an isobutane flush with cocatalyst mixture, titanium tetrachloride and 2 liters of dry isobutane as diluent, in the order named. The reactor and its contents were heated to 100°C., ethylene was admitted to give a partial pressure of 100 psig (689 kPa) and polymerization commenced. Following each run, the polymer was recovered by flashing off diluent and ethylene and the weight of recovered polymer determined.

The number of wash treatments used for each cocatalyst, weight of titanium tetrachloride charged (as titanium), calculated atom ratios of Al/Mg and Al/Ti, run length in minutes, and productivity as g polymer per g titanium are presented in the table.

TABLE

Ethylene Polymerization

Run	No. of Washes	Magnesium Reducing Agent Wash Liquid(s)	Titanium Milli-gram/Atoms	Initial Atom Ratios Al/Mg	Initial Atom Ratios Al/Ti	Catalyst Productivity g/g Ti	Polymerization TIME, Minutes	Cocatalyst Mill Time Hours	Remarks
1	0	none	0.004	0.73	215	1,300,000	60	1/4	Control
2	1	n-hexane	0.001	0.73	900	3,700,000	60	1/4	Invention
3	2	n-hexane	0.001	0.73	900	6,100,000	60	1/4	Invention
4	0	none	0.002	0.73	430	2,400,000	60	6	Control
5	1	n-hexane	0.002	0.73	430	5,500,000	60	6	Invention
6	2	n-hexane	0.004	0.73	215	750,000	8	6	Invention
7	2	n-hexane	0.001	0.73	900	2,100,000	21	6	Invention, same cocatalyst as run 6
8	5	n-hexane	0.001	0.73	900	Trace	60	6	Control because of removal of cocatalyst
9	5	n-hexane	0.001	0.73[1]	900	7,200,000	25	6	Invention, same cocatalyst as run 7
10	2	n-hexane	0.001	0[2]	0	4,400,000	60	6	Invention
11	2	toluene, hexane[3]	0.001	0[2]	0	4,800,000	60	6	Invention

1) Added 3.2 ml 25 wt. % DEAC solution to washed cocatalyst to replace initial DEAC removed by wash treatment.
2) No DEAC was initially added to magnesium reducing agent slurry. After wash treatment, sufficient DEAC solution was added to give a calculated Al/Mg ratio of 0.73 and Al/Ti ratio of 900.
3) Magnesium reducing agent slurry washed first with toluene, then with n-hexane.

As indicated by the groupings in the table, the source of the magnesium reducing agent used in the preparation of the cocatalyst used in the runs group d together was the same. Identical preparative methods for the production of each magnesium reducing agent prepared was employed, however. Thus, the results in each group are fairly compared with one another, i.e., runs 1-3 by themselves, runs 4-5 by themselves, runs 6-9 by themselves and runs 10-11 by themselves.

Control runs 1 and 4 are representative of productivity results obtained using a ball milled cocatalyst which is not washed with a hydrocarbon following milling and at the metal atom ratios employed. Runs 2, 3, 5, 6, 7, and 9 show increased production of polyethylene when the cocatalyst is washed 1 to 2 times with a suitable hydrocarbon. The catalyst systems of runs 6, 7, and 9 were so active that it was necessary to prematurely terminate each run prior to 60 minutes because it was not possible to control the polymerization temperature at or near 100°C. Run 8 indicates that washing the cocatalyst 5 times with the volume of hydrocarbon used per wash (about 6 times the volume of cocatalyst) has substantially removed all the DEAC initially present in the cocatalyst. Since the cocatalyst is inactive in the absence of a suitable organoaluminum compound it was necessary to replace it to obtain an active system as exemplified by run 9. Runs 10 and 11 show that when only the magnesium reducing agent portion of the cocatalyst mixture is washed with a hydrocarbon a very active cocatalyst is obtained when DEAC is added to the treated magnesium reducing agent. Run 11 shows that washing with an aromatic hydrocarbon followed by a wash with a paraffin gives results comparable to a paraffin wash only.

In conclusion, attention is directed to our copending application Nos. 20260/77 (serial No. 1568786) and 20262/77 (serial No. 1568788) in which methods closely related to the present method are disclosed for the production of olefin polymerisation catalysts.

WHAT WE CLAIM IS

1. A process for the preparation of olefin polymerisation catalysts which comprises forming a magnesium reducing agent by slowly adding an organic hydrocarbyl halide to magnesium metal in the absence of any other compound capable of forming a complex with said reducing agent, mixing said reducing agent with an organoaluminum compound to form a cocatalyst mixture, and thereafter mixing the cocatalyst with a titanium tetrahalide, wherein said reducing agent, before or after mixing with the organoaluminum compound, but before addition of the titanium tetrahalide, is washed with an inert hydrocarbon.

2. A process according to claim 1, wherein the reducing agent is washed with said hydrocarbon after mixing with the organoaluminum compound and additional organoaluminum compound is added to the mixture after washing but before addition of the titanium tetrahalide.

3. A process according to claim 1 or 2, wherein the hydrocarbon wash liquid is a paraffin, cycloparaffin or aromatic hydrocarbon of up to 20 carbon atoms.

4. A process according to claim 3, wherein the hydrocarbon wash liquid is n-pentane, n-hexane, n-heptane, isoctane, dodecane, cyclohexane, benzene, toluene or xylene.

5. A process according to any one of the preceding claims, wherein the organic halide is added to the magnesium metal in the complete absence of any extraneous diluent.

6. A process according to any one of the preceding claims, wherein the reducing agent, or the mixture of reducing agent and organoaluminum compound is milled in the presence of the wash liquid.

7. A process according to any one of the preceding claims, wherein the washing is conducted at a temperature in the range 0-100°C.

8. A process according to claim 7, wherein the washing is performed at room temperature.

9. A process according to any one of the preceding claims, wherein the organic halide and magnesium metal are reacted at a molar/gram atom ratio in the range 0.25:1 to 1:0.25.

10. A process according to claim 9, wherein said ratio is about 1:1.

11. A process according to any one of the preceding claims, wherein the organic halide is of the formula RX wherein X represents chlorine or bromine and R is an alkynyl, alkenyl, alkyl, aryl, cycloalkenyl, or cycloalkyl radical having from 1 to 12 carbon atoms.

12. A process according to any one of the preceding claims, wherein the organoaluminum compound is of the formula R''_2AlX wherein X is a hydrogen or halogen atom and R'' is an alkyl or aryl radical having from 1 to 12 carbon atoms.

13. A process according to any one of the preceding claims, wherein the titanium tetrahalide is titanium tetrachloride.

14. A process according to any one of the preceding claims, wherein the specified reactants are mixed in such quantities as to provide, in the final product, an atomic ratio of aluminum to titanium within the range 75:1 to 5,000:1, and an atomic ratio of aluminum to magnesium within the range 0.5:1 to 2:1.

15. A process according to any one of the preceding claims, wherein the organic halide

is n-pentylchloride and the organoaluminum compound is diethylaluminum chloride.

16. A process according to any one of the preceding claims, wherein there is added to the cocatalyst mixture, or to said titanium tetrahalide, or during the mixing thereof a Lewis base in such an amount as to provide a molar ratio of organolaluminimum compound to Lewis base in the range 1:1 to 300:1 and a molar ratio of titanium tetrahalide to Lewis base in the range 1:1 to 200:1.

17. A process according to claim 16, wherein the Lewis base is a C_1-C_4 alkyl benzoate optionally containing a para-substituent selected from halogen, OH, OR‴, OOCR‴, SH, NH, -NR_2‴, -NHCOR‴, NO_2, CN, CHO, COR‴, COOR‴, $CONH_2$, $CONR_2$‴, SO_2R and CF_3, where R⅛7⅛? IS C_1-C_4 alkyl.

18. A process according to claim 1, substantially as hereinbefore described in the Example.

19. An olefin polymerisation catalyst, when prepared by a process claimed in any one of the preceding claims.

20. A process for the preparation of olefin polymers, which comprises polymerising a 1-olefinf or 1-olefin mixture in the presence of a catalyst according to claim 19.

21. A process according to claim 20, wherein said olefin is or comprises ethylene as the major component.

22. A process according to claim 20 or 21, wherein the polymerisation is carried out in the presence of an inert hydrocarbon diluent in which, under the conditions of the polymerisation process, the product polymer is insoluble.

23. A process according to claim 20, 21 or 22, wherein the polymerisation is effected at a temperature in the range 40-112°C.

24. A process according to claim 20, substantially as hereinbefore described in the Example.

25. Olefin polymers when prepared by a process claimed in any one of claims 20-24.

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