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PHOSPHATED ALUMINA OR ALUMINUM PHOSPHATE CHROMIUM-
CONTAINING OLEFIN POLYMERISATION CATALYST, PROCESS
FOR THE PREPARATION AND USE THEREOF

This invention relates to chromium on alumina olefin polymerization catalysts.

Supported chromium oxide catalysts can be used to prepare
5 olefin polymers in a hydrocarbon solution to give a product having
excellent characteristics from many standpoints. Supported chromium
oxide catalysts can also be used to prepare olefin polymers in a slurry
system wherein the polymer is produced in the form of small particles of
solid material suspended in a diluent. This process, frequently referred
10 to as a particle-form process, has the advantage of being less complex.
However, certain control operations which are easily carried out in the
solution process are considerably more difficult in the particle-form
process. For instance, in the solution process, control of the molecular
weight can be effected by changing the temperature, with lower molecular
15 weight (higher melt flow) being obtained at the higher temperature.
However, in the slurry process, this technique is inherently limited since
any efforts to increase the melt flow to any appreciable extent by
increasing temperature would cause the polymer to go into solution and
thus destroy the slurry or particle-form process. Also, it is frequently
20 desired to have a polymer with a broader molecular weight distribution
than is normally obtained in the slurry or particle-form process.

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In accordance with this invention an olefin polymerisation catalyst is provided which inherently produces high molecular weight polymer and which is especially sensitive to molecular weight control agents so that a single catalyst can produce a complete spectrum of polymers so far as melt flow is concerned; the catalyst is also particularly suitable for use in slurry polymerization systems; and

Broadly speaking, the catalyst of this invention comprises:

a) a hexavalent chromium-containing compound, or a chromium-containing compound in which the chromium is convertible to the hexavalent state upon activation of the catalyst, supported on an activated support material comprising phosphated alumina or phosphated aluminum phosphate, said aluminum phosphate, prior to phosphating, having a low phosphorus to aluminum atomic ratio, i.e. in the range 0.02:1 to 0.6:1, and generally less than 0.4:1; and

b) an organoaluminum or organoboron compound as cocatalyst.

In the first embodiment of this invention, the support of the catalyst of this invention is a phosphated alumina-containing material. The alumina can be phosphated either by adding the phosphating agent to the alumina hydrogel or adding the phosphating agent to the alumina xerogel. In the second embodiment of this invention, an aluminum phosphate having a low phosphorus to aluminum ratio is treated in the same manner with the phosphating agent to impart additional phosphate to the surface.

While low phosphorus aluminum phosphate can be conveniently thought of as a mixture of aluminum phosphate and alumina, it is in fact not a mixture but rather a gel having a network wherein trivalent PO_4 groups are replaced with trivalent AlO_3 groups. Obviously, at the very low ratios, it is predominantly alumina.

With either alumina or low phosphorus aluminum phosphate, it may be desirable to form the hydrogel in the presence of 1 to 30 mole percent of a boron compound such as boric acid, based on the moles of alumina or aluminum phosphate. The alumina can also contain minor amounts of other ingredients which do not adversely affect the quality of the final catalyst but is generally essentially pure alumina. Similarly, the _____

low phosphorus aluminum phosphate can contain other ingredients which do not adversely affect the quality of the final catalyst, but is generally essentially low phosphorus aluminum phosphate.

It has been found from work with aluminum phosphate that the best polymer properties, such as high melt index, high density, good environmental stress crack resistance (ESCR) are obtained using a high P/Al ratio, i.e., about 0.8. However, surface area and pore volume are optimum at a lower P/Al ratio, i.e., about 0.4 because of sintering at the higher ratios. This invention makes it possible to have the good physical stability of a low P/Al ratio support since the bulk of the support is either pure alumina or low P/Al ratio aluminum phosphate and still have the good catalytic effect of the high ratio because of the high content of phosphorus on the surface.

In the case of phosphating a hydrogel, it is preferred that after phosphating, the water be removed to convert the hydrogel to a xerogel by means of azeotropic distillation or washing with a water miscible liquid. Any water miscible liquid effective in aiding in removing water can be utilized. Generally, such liquids are relatively volatile, oxygen-containing organic compounds having relatively low surface tension. Exemplary classes of such compounds are alcohols, ketones, and esters. Particularly suitable are alcohols, such as isoamyl alcohol, and esters, such as ethyl acetate. Where xerogel is phosphated, it is preferred that it be converted to the xerogel from the hydrogel in the same manner particularly if it is a low phosphorus aluminum phosphate.

Whether the starting material is alumina or a low phosphorus aluminum phosphate, the invention takes advantage of the fact that some properties, such as surface area, are favored by high alumina content whereas others, such as melt index potential, are favored by high phosphate content. By imparting a phosphate layer on the surface of alumina or low phosphorus aluminum phosphate, it is possible to take advantage of both trends.

The alumina can be made as is well known in the art, for instance by reacting sodium aluminate, which is basic, with aluminum sulfate, which is acidic, by neutralizing an aluminum salt with a base such as ammonia or ammonium hydroxide, or by flame hydrolysis.

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The low phosphorus aluminum phosphate can also be made by methods well known in the art as disclosed in Hill et al, U. S. 4,219,444, the disclosure of which is hereby incorporated by reference whereby an aluminum salt is combined with a source of phosphate ions (insufficient to give a high phosphorus ratio) and neutralized with a base, or by combining an aluminum alkoxide with phosphoric acid (insufficient to give a high phosphorus ratio) which gives a xerogel directly, as disclosed in Pine, U. S. 3,904,550, the disclosure of which is hereby incorporated by reference.

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Preferably, the low phosphorus aluminum phosphate is made by utilizing an aluminum salt which will melt, with the source of the phosphate ions being combined with the melt and then neutralized to give the hydrogel. Generally those salts with a sufficiently low melting point are hydrated. Orthophosphoric acid and monoammonium dihydrogen phosphate are preferred sources of phosphate ions. $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ is a particularly preferred aluminum salt. In a variation of this, a very concentrated syrup of a soluble aluminum salt in 20 weight percent or less added water can be used in place of the melt. Thus broadly, the aluminum salt and source of orthophosphate ions are combined in a concentrated mass and neutralized. The neutralization can occur by using enough base to force formation of the gel in which case the gel should occur of a high pH generally above 5, preferably 6 to 7 or above (by quickly adding the last one-third of the neutralizing agent, for instance). Alternatively, only 60 to 70 percent of the base needed to neutralize can be used and the concentrated mass allowed to stand until gellation occurs spontaneously at low pH after about 1 minute to 48 hours.

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The phosphating agent can be any source of phosphate ions, preferably orthophosphoric acid. Alternatively, an orthophosphate such as monoammonium dihydrogen phosphate or diammonium hydrogen phosphate or even a metal phosphate can be used. Alternatively, a phosphorus compound which can be vaporized such as POCl_3 (phosphoryl chloride) or PCl_3 (phosphorus trichloride) can be used, when treating a xerogel. However, when an alumina xerogel is phosphated, the treatment is preferably carried out by forming a slurry of the support and the source of phosphate ions such as orthophosphoric acid in a diluent such as water.

The phosphating agent may be incorporated in an organic water miscible liquid used to treat either a hydrogel or a xerogel. If the starting material is a hydrogel, then the organic liquid/phosphating agent composition effects both the conversion of the hydrogel to a xerogel and the phosphating. More specifically if a hydrogel is used, the hydrogel may be washed with water, then with an organic liquid such as isoamyl alcohol containing the phosphating agent such as phosphoric acid, then filtered and the solvent allowed to evaporate.

The phosphating agent is preferably used in an amount to react with the alumina or low phosphorus aluminum phosphate surface to give a P/Al atom ratio of the reaction product on the surface of 0.2:1 to 2:1, preferably 0.6:1 to 0.9:1. In practice, however, it is possible to use as much phosphating agent as desired with the excess simply being washed off after the phosphating treatment is complete. The phosphating treatment is generally carried out at a temperature of 15°C to 500°C, preferably room temperature to the boiling point of the solvent if a phosphate solution is used or about 200°C if a vapor is used and a time of 1 minute to 2 hours, preferably 2 minutes to 30 minutes.

The phosphorus component is added in an amount to give 0.1 to 20, preferably 1 to 10 mole percent of the phosphorus compound incorporated based on the total moles of alumina or low phosphorus aluminum phosphate. Most preferably about 1 to 5 atom percent is incorporated which would be about 1 to 5 atoms of phosphorus per atom of chromium particularly when the preferred 1 weight percent chromium based on the weight of the silica-containing support is used. Generally, the ratio of atoms of phosphorus per atom of chromium will be in the range of 0.1 to 20, preferably 1 to 10. Based on surface area, the phosphorus compound from the phosphating agent is preferably present in an amount sufficient to give about 0.005 to 1, preferably about 0.01 to 0.5 mg P/m² of alumina or low phosphorus aluminum phosphate surface as measured by BET nitrogen sorption.

The chromium compound can be any compound in or convertible to the hexavalent state and can be introduced anytime prior to activation. The catalyst contains chromium in an amount generally within the range of about 0.001 to 10, preferably 0.1 to 5, more preferably about 1 weight percent based on the weight of the dried phosphated support. The chromium

compound can be incorporated as known in the art. For instance, a hydrocarbon solution of a material such as tertiary butyl chromate can be used to impregnate the xerogel or an aqueous solution of a chromium compound such as CrO_3 (chromium trioxide), chromium acetate or chromium nitrate can be added to the hydrogel before drying, or chromium can be coprecipitated along with the alumina or low phosphorus aluminum phosphate. In general, it is preferred to phosphate the alumina before adding the chromium component. Most preferably, the phosphated base is heated prior to addition of the chromium. Thus, in this preferred embodiment, the base is heated twice, once after the phosphorus is added, then the chromium is added and it is heated again to activate the catalyst for polymerization.

The activation of the chromium-containing catalyst can be carried out at a lower temperature than is generally required for activating silica based chromium catalysts. Temperatures of 150-800°C, preferably 300-800°C, more preferably 300-600°C are suitable. The activating ambient can be any oxidizing ambient but for reasons of convenience is generally air. Times of 1 minute to 48 hours, preferably 0.5 to 10 hours are suitable. Similar times and temperatures can be used for heating the phosphated base if such is done prior to adding chromium. In this prior heating step, the ambient can be either the same as in the subsequent activation or it can be an inert ambient such as nitrogen or a reducing ambient such as carbon monoxide. If the phosphating agent contains halide such as POCl_3 , a steam treatment before activation may be helpful to remove halide.

The catalysts of this invention also comprise an organoaluminum or organoboron compound as a cocatalyst. Suitable cocatalysts include aluminum and boron alkyls. The most preferred boron compounds are trihydrocarbyl boron compounds, particularly tri-n-butylborane, tripropylborane, and triethylborane (TEB). Other suitable boron compounds include trialkyl boron compounds broadly, particularly those having alkyl groups of 1 to 12 carbon atoms, preferably 2 to 5 carbon atoms, triaryl boron compounds such as triphenylborane, boron alkoxides such as $\text{B}(\text{C}_2\text{H}_5)_2\text{OC}_2\text{H}_5$ and halogenated alkyl boron compounds such as $\text{BC}_2\text{H}_5\text{Cl}_2$. Suitable aluminum alkyls include R_3Al , R_2AlX and RAlX_2 compounds where R is a 1 to 12 carbon atom

hydrocarbyl radical and X is a halogen, preferably chlorine. Triethylaluminum and diethylaluminum chloride are particularly suitable.

The cocatalyst is used in an amount within the range of about 0.5 to 25, preferably 2 to 10 parts per million based on the solvent or diluent in systems employing a solvent or diluent and based on total reactor contents in systems not employing a solvent or diluent. Based on the chromium in the catalyst, they are used in an amount so as to give from 0.1 to 3, preferably 0.3 to 2 times as much boron by weight as chromium by weight. Based on atoms of boron per atom of chromium, the amount of cocatalyst used will give about 0.5 to about 14, preferably about 1.5 to about 10 atoms of boron per atom of chromium. The boron cocatalysts give higher density polymer than aluminum cocatalysts or catalyst system with no cocatalyst.

The cocatalyst can be either premixed with the catalyst or introduced into the reactor as a separate stream, the latter being the preferred procedure.

Of course, the final catalyst can be used with, or contain, other ingredients which do not adversely affect its performance, as for example other cocatalysts, antistatic aids in the polymerization zone and other conventional ingredients.

The catalyst of this invention can be used to polymerize at least one mono-1-olefin containing 2 to 8 carbon atoms per molecule, preferably ethylene, propylene, 1-butene, 1-pentene, 1-hexene and 1-octene. The invention is of particular applicability in producing ethylene homopolymers and copolymers from mixtures of ethylene and 0.5 to 20 mole percent one or more comonomers selected from 1-olefins containing 3 to 8 carbon atoms per molecule. Exemplary comonomers include aliphatic 1-olefins, such as propylene, 1-butene, 1-pentene, 1-hexene, 1-octene and other higher olefins and conjugated or non-conjugated diolefins such as 1,3-butadiene, isoprene, piperylene, 2,3-dimethyl-1,3-butadiene, 1,4-pentadiene, 1,7-hexadiene, and other such diolefins and mixtures thereof. Ethylene copolymers preferably constitute at least about 90, preferably 97 to 99.6 weight percent polymerized ethylene units. Propylene, 1-butene, 1-pentene, 1-hexene and 1-octene are especially preferred comonomers for use with ethylene. Alternatively, 0.001 to 0.3 mole percent of the same comonomer can be used with ethylene to give an essentially ethylene homopolymer having a higher melt flow.

The polymers can be prepared from the catalyst of this invention by solution polymerization, slurry polymerization, and gas phase polymerization techniques using conventional equipment and contacting processes. Contacting of the monomer or monomers with the catalyst can be effected by any manner known in the art of solid catalysts. One convenient method is to suspend the catalyst in the organic medium and to agitate the mixture to maintain the catalyst in suspension throughout the polymerization process. Other known contacting methods such as fluidized bed, gravitating bed, and fixed bed can also be employed. The catalyst of this invention can be used to produce ethylene polymers in a particle form process as disclosed in U. S. 3,624,063 which issued November 30, 1971 to Witt, the disclosure of which is hereby incorporated by reference.

The catalyst of this invention is particularly suitable for use in slurry polymerizations. The slurry process is generally carried out in an inert diluent (medium) such as a paraffin, cycloparaffin or aromatic hydrocarbon. For predominantly ethylene polymers, a temperature of about 66-110°C is employed. Pressures in the particle form process can vary from about 110 to about 700 psia (0.76-4.8 MPa) or higher. The catalyst is kept in suspension and is contacted with the monomer or monomers at sufficient pressure to maintain the medium and at least a portion of the monomer or monomers in the liquid phase. The medium and temperature are thus selected such that the polymer is produced as solid particles and is recovered in that form. Generally in slurry polymerization of ethylene homopolymer and predominantly ethylene copolymer systems, the feasible temperature range is 200-230°F (93-110°C), and the commercial systems are run as close to the maximum as possible, i.e., 225°F $\pm$ 5°F (107°C $\pm$ 3°C) in order to obtain the highest possible melt index without the polymer going into solution. The catalyst of this invention allows running at the low end of this range, i.e., 205°F $\pm$ 5°F (96°C $\pm$ 3°C) in systems normally employing 225°F (107°C). The lower temperature gives a relatively higher monomer partial pressure, thus giving higher activity.

Catalyst concentrations can be such that the catalyst content ranges from 0.001 to about 1 weight percent based on the weight of the reactor contents.

When hydrogen is used in the prior art, it is generally used at pressures up to 120 psia (0.8 MPa), preferably within the range of 20 to

70 psia (0.14 to 0.48 MPa). Similar amounts can be used in accordance with this invention although smaller amounts are sometimes preferred because of the sensitivity of this catalyst system to the effects of hydrogen.

5 The presence of comonomer has a tendency to increase melt flow more than would be expected. Hence the use of only a small amount of comonomer, say 0.001 to 0.3, preferably 0.01 to 0.1 mole percent in the feed can be used to give a polymer which is essentially a homopolymer but which has increased melt flow.

10 Each run in all of the following examples was conducted in a clean, dry, air-free, stirred, stainless steel reactor of about a 2 L capacity. About 600 g of isobutane was used in each run as diluent with a catalyst charge ranging from about 0.03 to about 0.8 g. The reactor and its contents were heated to the desired operating temperature, ethylene
15 was pressured in to give about 565 psia (3.9 MPa), and the run was started immediately as the catalysts, unlike the corresponding chromium oxide-silica catalysts, do not have an induction period. Ethylene pressure was maintained during the run by supplying additional ethylene as required from a reservoir.

20 Each run was terminated by stopping the ethylene flow and venting the gaseous reactor contents to a flare line for disposal. The polymer was recovered, dried and weighed to determine catalyst productivity which is expressed in terms of grams polyethylene per gram catalyst. TEB stands for triethylborane.

25 Example I

In this example, a phosphated alumina catalyst was prepared as follows. One hundred grams of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was combined with 500 mL water. To this was added 60 mL concentrated ammonium hydroxide to give a pH of 8 where hydrated alumina precipitate formed. Then 15 mL of H_3PO_4 in
30 100 mL water was added as the phosphating agent. The pH was then below 4. Thereafter 5 mL concentrated ammonium hydroxide was added to return the pH to neutrality. The precipitate was filtered, azeotrope dried with isoamyl alcohol and impregnated with sufficient chromium acetate in methanol to give 1 weight percent chromium based on the weight of the final activated
35 alumina. This is run 2 in the following table.

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The control run 1 was made in an essentially identical manner except no phosphoric acid was used. The results were as follows:

Run No.	Catalyst	Productivity ⁽¹⁾	Run Time,	MI ⁽²⁾	HLMI ⁽³⁾	HLMI/MI	Cocatalyst
			min.				
1	Al ₂ O ₃ ⁽⁴⁾	1340	60	0	0	-	8 ppm TEB
2	Al ₂ O ₃ /PO ₄ ⁽⁵⁾	2425	60	0.81	172.	213	8 ppm TEB

(1) Grams of polymer per gram of catalyst for the entire run time which was 60 minutes.

(2) Melt index as determined by ASTM D1238-65T, Condition E.

(3) High load melt index ASTM D1238-65T, Condition F.

(4) Activated in air at 700°C.

(5) Activated in air at 500°C.

The control was activated at 700°C compared with 500°C for the invention run. Had the control been activated at 500°C in the same manner as the invention run, it would have not produced as good of results as it did. Indeed, it would have barely been operable. This further demonstrates the advantage of the invention. That is a remarkable improvement in both productivity and melt index was obtained even though a less favorable activation temperature was used.

Example IA

This example, like Example I demonstrates phosphating the hydrogel in an aqueous medium. In this example, 79.8 grams of aluminum sulfate, Al₂(SO₄)₃·16H₂O was combined with 2.38 g chromic nitrate, Cr(NO₃)₃·9H₂O in water to give a final volume of 125 mL. This solution was dripped into an excess of concentrated ammonium hydroxide containing some ammonium carbonate. Afterward the ammonium hydroxide was drained off and the gel was rinsed in water several times. Finally, it was washed in about 1 liter of warm water to which was added 13.8 mL of phosphoric acid. The gel was filtered, washed twice in isopropyl alcohol, dried and activated at 600°C in air for 5 hours. In an ethylene polymerization run with 4 ppm TEB cocatalyst, a productivity of 3510 g/g was obtained in 44 minutes. The MI was not run.

Example II

In this example, 8 g of flame treated alumina (sold under the tradename DeGussa) was slurried in 200 mL isopropyl alcohol and 6 mL orthophosphoric acid was added. The slurry was warmed to about 40°C and held 15 minutes. It was then washed in isopropyl alcohol, dried and calcined in air at 500°C for 3 hours. Dicumene chromium was added in an amount sufficient to provide 1 weight percent chromium based on the dry catalyst and it was calcined again at 500°C in air to convert at least a portion of the chromium to the hexavalent state. Productivity was 2060 in 60 minutes with 8 ppm TEB. Melt index was 0.02 and the HLMI/MI ratio was 672.

This example shows that the phosphate treatment can be carried out on a xerogel.

Example III

Two runs were made using a low phosphorus gel. The procedure used to make the low phosphorus gel was as follows. Hydrated aluminum nitrate (1/4 mole) was heated to melt and combined with 7.2 grams of ammonium dihydrogen phosphate. A very small amount of water was added to give 100 mL and it was then neutralized with 54 mL concentrated ammonium hydroxide to form the gel. The gel was washed with 4 liters of warm water. The gel was then divided into two parts, each having a phosphorus to aluminum ratio of 0.2. The first part (control) was washed with 4 liters of isopropanol, dried, and impregnated with tertiary butyl chromate in an amount sufficient to give 1 weight percent chromium based on the weight of the dry gel and calcined at 700°C. It was run with 8 ppm TEB and gave 3270 g/g productivity in 60 minutes. The melt index was 0.0 and the HLMI was 0.77.

In the second (invention) run, the same hydrogel was used except in the last step the washing with isopropyl alcohol was done using alcohol containing enough phosphoric acid to convert the phosphorus to aluminum ratio to 0.8 (10 mL) overall, i.e. not just on the surface. But the recovered phosphoric acid in alcohol solution remained acidic indicating that not all of it reacted and therefore only the surface was upgraded. It was dried, impregnated with tertiary butyl chromate and calcined as before and used with 8 ppm TEB. The productivity was 3505 g/g in 35 minutes (just over half the time for the control), the HLMI was 136, the melt index was 0.92, and the HLMI/MI ratio was 148.

This example shows that a low phosphorus aluminum phosphate can be phosphated as well as alumina. The HLMI increased from 0.77 to 136, i.e., over a 17,000 percent increase, and activity was also greatly improved.

CLAIMS

1. A chromium-containing olefin polymerisation catalyst comprising:

5 a) a hexavalent chromium-containing compound, or a chromium-containing compound in which the chromium is convertible to the hexavalent state upon activation of the catalyst, supported on an activated support material, wherein the support material comprises phosphated alumina or phosphated aluminum phosphate, said aluminum phosphate, prior to phosphating, having a phosphorus to aluminum atomic ratio in the range 0.02:1 to 0.6:1, and

10 b) an organoaluminum or organoboron compound as cocatalyst.

2. A catalyst according to claim 1, wherein the support has an atomic ratio of P:Al at the surface of the support of from 0.2:1 to 2:1.

15 3. A catalyst according to claim 2, wherein the said surface atomic ratio is from 0.6:1 to 0.9:1.

4. A catalyst according to any one of claims 1 - 3, wherein the phosphorus concentration at the surface of the support material is in the range 0.005 to 1 mg. per sq. m. of support surface as measured by BET nitrogen sorption.

20 5. A catalyst according to claim 4, wherein said phosphorus concentration is from 0.01 to 0.5 mg/m².

6. A catalyst according to any one of claims 1 - 5, wherein the support additionally contains boron.

25 7. A catalyst according to any one of claims 1 - 6, which contains 0.001 to 10% chromium based on the dry weight of the support.

8. A catalyst according to claim 7, which contains 0.1 to 5% chromium based on the dry weight of the support.



9. A catalyst according to any one of claims 1 - 8, wherein the cocatalyst is an aluminum or boron alkyl.
10. A method of making an olefin polymerisation catalyst as claimed in any one of claims 1 - 9, which comprises treating an alumina gel with a phosphating agent, incorporating into the alumina gel, before or after phosphating, a hexavalent-chromium containing compound, or a chromium compound in which the chromium is convertible to the hexavalent state upon calcination, activating the phosphated and chromium-containing gel by heating in an oxidising atmosphere, and combining the activated chromium-containing support with an organoaluminum or organoboron compound as cocatalyst.
11. A method according to claim 10, wherein the phosphating agent is orthophosphoric acid.
12. A method according to claim 10 or 11 which comprises forming an alumina hydrogel, converting the hydrogel to a xerogel, phosphating the xerogel and adding the chromium compound to the phosphated xerogel prior to said activation.
13. A method according to claim 10 or 11, which comprises forming an alumina hydrogel, phosphating the hydrogel, adding the chromium compound to the hydrogel, converting the phosphated, chromium-containing hydrogel to a xerogel, and activating the xerogel.
14. A method of making an olefin polymerisation catalyst as claimed in any one of claims 1 - 9, which comprises treating a phosphate aluminum phosphate gel having a P:AL atomic ratio in the range 0.02:1 to 0.6:1 with a phosphating agent, incorporating into the aluminum phosphate gel before or after phosphating a hexavalent chromium compound, or a chromium compound in which the chromium is convertible to the hexavalent state by calcination, activating the phosphated and chromium-containing gel by heating in an oxidising atmosphere, and combining the chromium-containing activated support with an organoaluminum or organoboron compound as cocatalyst.



15. A method according to claim 14, wherein the phosphating agent is orthophosphoric acid or monoammonium dihydrogen phosphate.

16. A method according to any one of claims 10 - 15, wherein the phosphating agent is used in an amount sufficient to provide in the final catalyst from 1 to 5 atom percent of phosphorus based on the total moles of the alumina or aluminum phosphate support.

17. A method according to any one of claims 10 - 17, wherein the phosphating agent is used in an amount sufficient to provide a concentration of phosphorus on the surface of the support in the range 0.01 to 5 mg/m².

18. A method according to any one of claims 10 - 16 wherein the chromium compound is added in an amount sufficient to provide in the final catalyst, from 0.1 to 5% by weight of chromium base on the weight of the support.

19. A method according to any one of claims 10 - 18, wherein the catalyst is activated by heating in air at a temperature of from 150 - 800°C for a period of 1 minute to 48 hours.

20. A method according to any one of claims 10 - 19, wherein the cocatalyst is an aluminum or boron alkyl.

21. A method according to claim 20, wherein the cocatalyst is a triethylborane, tripropylborane or tri-n-butyl borane.

22. An olefin polymerisation process which comprises polymerising one or more mono-1-olefins of 2 - 8 carbon atoms in the presence of a catalyst as defined in any one of claims 1 - 9 or as made by a method claimed in any one of claims 10 - 21.

23. A process according to claim 22, wherein the olefin is or comprises ethylene, propylene, 1-butene, 1-pentene, 1-hexene or 1-octene.

24. A process according to claim 22, wherein the monomer is ethylene or a mixture of ethylene and 0.5 to 20 mole % of one or



more C_3-C_8 mono-1-olefins as comonomer.

25. A process according to claim 24, wherein the monomer comprises a mixture of ethylene and 0.001 to 0.3 mole percent of comonomer.

26. A process according to claim 24 or 25, wherein the comonomer is propylene, 1-butene, 1-pentene, 1-hexene or 1-octene.

27. A process according to any one of claims 22 - 26, in which hydrogen is introduced into the reaction zone to increase the melt flow of the product polymer.

28. A process according to any one of claims 22 - 27, wherein the polymerisation is effected in an inert diluent which the octalyst is suspended.

29. A process according to any one of claims 22 - 28, wherein the catalyst is prepared in situ in the polymerisation reactor by bringing together therein the chromium-containing activated support component and the cocatalyst.

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