

SILICA/PHOSPHATE CHROMIUM-CONTAINING
OLEFIN POLYMERIZATION CATALYSTS AND
CATALYST COMPOSITIONS AND PROCESSES
FOR THE PREPARATION AND USE THEREOF

5 This invention relates to supported chromium catalysts and catalyst compositions for olefin polymerization, and processes for the preparation and use thereof.

 Supported chromium oxide catalysts can be used to prepare olefin polymers in a hydrocarbon solution to give a product
10 having excellent characteristics from many standpoints. Silica 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 to as a particle-
15 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
20 with lower molecular 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
25 the slurry or particle-form process. It is known to extend the range of melt flow capability of a given catalyst through the use of hydrogen. However, it has not heretofore been commercially feasible to produce a complete spectrum of polymers so far as melt flow is concerned in a slurry system with a single chromium
30 catalyst system. Also it is frequently desired to have a polymer with greater shear response than is normally obtained in the slurry or particle-form process.

 While it has long been known to use metal phosphates as supports for chromium oxide-containing olefin polymerization
35 catalysts, such supports have never achieved commercial success.

Thus chromium oxide catalysts are generally supported on silica-containing bases similar to those used decades ago when the chromium catalyzed polymerization of olefin polymers first became commercial.

5 In a principal aspect the present invention provides an olefin polymerization catalyst composition comprising chromium oxide supported on a mixed support comprising both silica and a metal phosphate, particularly aluminium phosphate, and an organometallic cocatalyst, especially an organoboron compound.

10 Particular advantages of such catalyst compositions according to the invention include one or more of the following:

the ability to provide olefin polymers having both high melt flow and high shear response;

suitability for use in slurry polymerization systems;

15 the ability to provide polymers suitable for blow molding, film and other applications requiring good melt strength;

the ability to provide olefin polymers having unexpectedly high flexural modules;

20 the ability to provide a broad spectrum of polymers so far as melt flow is concerned;

a catalyst composition having unusual sensitivity to molecular weight control agents such as hydrogen; and

the ability to produce polymers having unusually broad molecular weight distribution.

25 In accordance with subsidiary aspects of this invention methods are provided for the preparation of chromium oxide containing mixed silica/metal phosphate supports for use as olefin polymerization catalysts and as olefin catalyst compositions comprising in addition an organometallic cocatalyst. In this
30 invention, boron is classified as a metal for convenience.

The silica/metal phosphate supports used in the catalysts and catalyst compositions of this invention can be made in four separate ways.

First, the two can be coprecipitated as is known in the art, for instance as shown in Kirby, U.S. 3,342,750 (September 19, 1967), the disclosure of which is hereby incorporated by reference. In accordance with this technique, a silicate
 5 is combined with a source of aluminum ions and a source of phosphate ions and neutralized to form a cogel. The silicate is preferably a tetrahydrocarbyl orthosilicate, such as ethyl silicate, although sodium silicate can also be used. The aluminum component is preferably aluminum nitrate although aluminum chloride or other
 10 aluminum salts can be used. The source of phosphate ions is preferably orthophosphoric acid although dihydrogen ammonium phosphate, and hydrogen diammonium phosphate, for instance, can also be used. This reaction is generally carried out in an aqueous medium although a polar organic solvent can be used. It is frequently preferred
 15 that a small amount of a boron compound such as boric acid be introduced into the reaction mixture to be coprecipitated with the aluminum phosphate and silica. Other suitable boron compounds include borates such as ammonium borate. By coprecipitated as it relates to the boron compound, it is meant that the silica/
 20 aluminum phosphate is formed into a hydrogel in the presence of the boron compound. It is not known to what extent the boron compound becomes incorporated into the hydrogel structure. The amount of boron compound present when the silica/aluminum phosphate cogel is formed can vary widely but it is generally used in an
 25 amount so as to give 0.5 to 15 mole percent boron based on the moles of phosphorus.

While any agent which neutralizes acid can be used, a base such as concentrated ammonium hydroxide, ammonia gas, or ammonia dissolved in alcohol or other nonaqueous solvents is preferred.
 30 Also ammonium carbonate, ethylene oxide and propylene oxide can be used.

The neutralization can be carried out either by adding the acid phase (metal salt/phosphate source combination) to the base phase or vice versa. One suitable practice is to drip or
 35 spray or otherwise slowly add the acid phase into the base phase. It is preferred that the gellation occur at a pH of at least 5,

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preferably as least 6. Generally the pH when the gellation occurs will be in the range of 5 to 10, more generally 6 to 7. However, in this embodiment as in embodiment three described hereinbelow, gellation can occur after any partial neutralization at which point the composition is acidic.

Gellation occurs spontaneously at a pH of about 4, which is achieved by combining about 72 percent of the neutralizing agent, and it has been found that this is undesirable. Therefore, neutralization is preferably achieved by either: (1) combining slowly with stirring about 72 percent of the amount of neutralizing agent needed for complete neutralization and thereafter quickly adding the rest so as to go quickly through the 4-5 pH range and achieve gellation at a pH of 5 or greater, preferably at least 6, generally 6 to 10, or (2) combining 60 to 70 percent of the neutralizing agent needed for complete neutralization and aging until gellation occurs which will generally be 1 minute to 48 hours, more generally 5 minutes to 10 hours, more generally 10 minutes to 3 hours; thus, gellation occurs at a pH below 4, generally about 2.

It may be desirable in some instances to coprecipitate other materials such as titania with the silica/phosphate cogel or have other materials present during the gellation. Also, the chromium compound such as chromium nitrate can be introduced with the reactants.

It is preferred to remove water by azeotropic distillation or by washing with a volatile, water miscible, low surface tension organic liquid. If water is not employed as a solvent, any small amount of water carried over from water of hydration or from the base used in neutralization can be removed by conventional spray drying, tray drying or oven drying, thus avoiding the necessity for azeotropic distillation. However, even in these situations, if it is desired to water wash the hydrogel, then azeotropic distillation or washing with a volatile oxygen-containing water-miscible solvent is desirable. After water removal to convert the hydrogel to a xerogel, the xerogel is activated by calcination in an oxygen-containing ambient.

In accordance with the second method of making the silica/ phosphate support, a silica hydrogel or xerogel is impregnated with aluminum orthophosphate. This can be carried out by combining the source of aluminum ions and phosphate ions with a slurry of silica hydrogel or xerogel and then evaporating the solvent by conventional techniques such as oven drying or more preferably by spray drying. To a substantial extent it is believed the aluminum phosphate forms within the pores of the silica. Alternatively, the source of aluminum and phosphate ions can be adsorbed into the dry silica. This is largely a physical impregnation and entrapment of the phosphorus component in the pores of the silica. When a silica xerogel is used, instead of evaporating to dryness, the evaporation can stop when the liquid in excess of the pore volume is gone but some liquid remains in the pores, or an amount of liquid equal to or less than the pore volume can be added initially and the gel formed by adding a neutralizing agent. Even when the precipitate is formed by evaporation to dryness, a neutralizing agent can subsequently be added but it is not essential. When the liquid is not evaporated to dryness and the phosphate gel is formed in the pores of silica xerogel by neutralization, the impregnated silica can sometimes be directly activated but preferably the material is dried at a slightly elevated temperature before being activated. No azeotrope drying is required, simple oven drying, for instance, being satisfactory, although azeotrope drying could be used if desired.

As to the scope of the aluminum and phosphorus components, the base when used, and the solvent, is the same as that set out hereinabove with regard to the first embodiment. One difference in scope between these two embodiments is that in this embodiment ammonium borate or boric acid can be substituted for part or all of the aluminum salt in the technique where the solvent is evaporated so as to form what is believed to be boron phosphate onto the silica on evaporating the solvent. If a base is used to form the phosphate, a boron compound can be present as in the first embodiment.

In accordance with the third embodiment of forming the silica/phosphate support, aluminum orthophosphate is precipitated

in the presence of a silica hydrogel or xerogel. This results in forming the silica as a dispersed phase in an aluminum phosphate matrix as opposed to having the aluminum phosphate impregnated into the pores of the silica. In accordance with this method,

5 a source of aluminum and phosphate ions are combined with a silica hydrogel or xerogel and the aluminum phosphate formed by combining with a neutralizing agent. The scope of the ingredients is the same as in the first embodiment hereinabove except monobasic ammonium phosphate is the preferred source of phosphate ions.

10 As with the first embodiment, a boron compound can be present during the precipitation of the aluminum phosphate. Also, the same pH considerations of the first embodiment apply. Finally, as with the first embodiment, the free water is preferably removed by azeotropic distillation or washing with a water miscible organic

15 liquid to convert the hydrogel to a xerogel preparatory to activating. The dried support is then ready for activation. In the case of a xerogel, the phosphate ingredients must be greater than one pore volume as it is the same as the second embodiment.

In accordance with the fourth embodiment for making the

20 mixed silica/metal phosphate support, a silica xerogel and an aluminum phosphate xerogel are simply physically mixed. The scope of the ingredients for making the separate silica and aluminum phosphate are the same as those used in embodiment 1 for making the cogel. More broadly, any known method of making silica suitable

25 for use as a base in olefin polymerization catalysts and any known methods of making aluminum orthophosphate having relatively high surface area can be used for producing the silica and aluminum orthophosphate, respectively. In addition, the aluminum orthophosphate can be made by forming a melt of an easily melted

30 aluminum salt such as hydrated aluminum nitrate, adding a source of phosphate ions of the same scope as that utilized in embodiment 1 to the melt, and neutralizing with a base having the same scope as that set out for embodiment 1. The resulting silica and aluminum orthophosphate xerogels can simply be ground together or blended

35 in a conventional dry blender or mixed in a slurry with a nonreactive diluent such as a hydrocarbon. In making the phosphate, the same pH considerations of the first embodiment apply.

(17)

The two most preferred methods of achieving this mixture are as follows. First, the silica and aluminum orthophosphate in powder form are simply charged to the activator together with the fluidization normally employed during the activation serving to effect the mixing. Alternatively, the silica and aluminum phosphate may be separately activated and the ultimate chromium-on-silica and chromium-on-aluminum phosphate catalysts added separately to the reactor, (or mixed after activation but prior to introduction) thus allowing precise control of the amounts of each utilized.

The aluminum and phosphorus components of the aluminum orthophosphate are selected so as to give an atom ratio of phosphorus to aluminum within the range of 0.2:1 to 1:1, preferably 0.6:1 to 0.9:1.

Further with respect to the relative proportions in all embodiments, except embodiment 2, the silica and metal orthophosphate will generally be used in molar ratios of 10:1 to 1:20 moles of silica per mole of phosphate (or gram atom of phosphorus), more commonly, 2:1 to 1:2 moles of silica per mole of phosphate (or gram atom of phosphorus).

In embodiment 2 where the silica is impregnated with the metal orthophosphate, from about 1 to 50 mole percent metal phosphate based on the moles of silica is used, more preferably 5-25 mole percent.

Because the different supports, particularly when employed in conjunction with a boron-containing cocatalyst, have different effects on the structure of the ultimate polymer, adjustment of the ratio of silica to metal phosphate in the support can be utilized to effect quality control of the ultimate product.

The chromium can be coprecipitated as noted hereinabove. Alternatively, a water soluble chromium compound such as chromium nitrate, chromium acetate, or CrO_3 can be added to the hydrogel. Alternatively, a chromium compound preferably dissolved in an anhydrous solvent such as a hydrocarbon can be used to impregnate the xerogel. Suitable chromium compounds for such anhydrous impregnation include tertiary-butyl chromate. The chromium compounds are used in amounts sufficient to give 0.001 to 10, preferably 0.1 to 5, more preferably about 1 weight percent chromium based on the weight of the xerogel base after activation is completed.

The term xerogel is used to refer to the gel resulting from the removal of free water from the hydrogel.

The activation of the xerogel can be carried out at temperatures known in the art although the phosphate base can be activated at slightly lower temperatures, for instance temperatures of 150-800°, preferably 300-800°, more preferably 400-600°C are particularly suitable for the phosphate component, as compared with the 450-1000°C temperature generally employed for silica bases. Thus broadly any temperature from 150-1000°C can be used. In the embodiment where the xerogels are physically mixed after the supports are separately activated, each can be activated at the optimum temperature for that particular support. In the other embodiments, either the preferred activation temperature for silica or the preferred activation temperature for phosphate can be utilized.

The activating ambient can be any oxidizing ambient but for convenience and economy an oxygen-containing ambient such as air is preferred. The chromium is at least predominantly in the hexavalent state after activation. If an excess of chromium over what is required is used, the excess may not be in the hexavalent state, if it remains on the catalyst at all. Times of 2 minutes to 48 hours, preferably 0.5 to 10 hours are suitable for the activation or calcination step. The chromium is thought to be reduced in the polymerization zone by the monomer, probably to plus two oxidation state. If desired, this reduction can be carried out before the catalyst is contacted with the monomer, for instance in the activator. Hexavalent chromium can be added to the activated base or bases from an anhydrous solution but generally the chromium is introduced prior to activation and hence is converted to the hexavalent state from whatever valence it may have had initially, be that 0 or a higher valence, although as noted hereinabove one of the preferred chromium components for addition prior to activation is CrO_3 which is already in the hexavalent state. Thus, the chromium is in, or is convertible to the hexavalent state when introduced into the reactor. If hexavalent chromium is added to the support after activation, which is less preferred, and if done must be done anhydrously, then the activation ambient does not have to be oxygen-containing but can be any dry ambient including reducing ambients such as CO , inert ambients such as nitrogen or even a vacuum. However, if this is done, a second activation using the oxidizing ambient is required to burn off organic matter.

The cocatalyst, when used, is an organometal compound, preferably a trihydrocarbylborane, more preferably trialkylborane, the alkyl groups preferably having 1 to 12, more preferably 2 to 5, carbon atoms per group. Triethylborane, tripropylborane, and tri-n-butylborane are especially preferred. Tri-n-butylborane is most preferred because it is believed to give greater MI (Melt Index) increase than the others tested. Other boron compounds such as boron alkoxides, for instance $\text{B}(\text{C}_2\text{H}_5)_2\text{OC}_2\text{H}_5$, alkyl haloboron compounds, for instance BCl_2H_5 , aryl borons such as triphenylborane and metal aryl borate (MBR_4) can also be used. Conventional organoaluminum cocatalysts such as triethylaluminum are sometimes desirable either alone or in combination with the organoboron compound.

The cocatalyst when used is utilized in an amount so as to give an atom ratio of metal such as boron to chromium within the range of

0.5:1 to 10:1, preferably 2:1 to 5:1. Based on the solvent or diluent employed during polymerization if any, the amount of metal compound cocatalyst is generally within the range of 0.5 to 20, preferably 2 to 10 parts by weight per million parts by weight of the solvent, these amounts being based on the total reactor contents in instances where no solvent or diluent is utilized. The cocatalyst can either be premixed with the catalyst or added as a separate stream to the polymerization zone, the latter being preferred. Since the boron-containing cocatalyst has a particularly dramatic effect on the metal phosphate base, in the embodiment where the silica based catalyst and the phosphate based catalyst are added separately, the cocatalyst may be premixed with the phosphate base catalyst component if desired

The catalysts of this invention can be further treated in the same manner as chromium on conventional silica catalysts are sometimes given special treatments, such as being fluorided or being reduced and reoxidized as disclosed in McDaniel et al, U.S. 4,151,122 (April 24, 1979), the disclosure of which is hereby incorporated by reference.

The catalysts and catalyst compositions of this invention are useful for the polymerization of mono-1-olefins containing 2 to 8 carbon atoms per molecule. The invention is of particular applicability in producing ethylene homopolymers and copolymers from mixtures of ethylene and 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 96 to 99.7 weight percent polymerized ethylene units and 0.3 to 4 weight percent comonomer. Propylene, 1-butene, 1-pentene, 1-hexene, and 1-octene are especially preferred comonomers.

The polymers can be prepared using the catalysts and catalyst compositions 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. One conventional method is to suspend the catalyst

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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 including the production of 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.

Using such slurry polymerization systems, a complete spectrum of polymers so far as melt flow is concerned, can be obtained utilizing a single catalyst or catalyst composition. Everything from blow molding grade resins which may require a melt index of as little as 0.1 or less to paper coating and injection molding grade resins which may require a melt flow of 20 or greater can be produced from a single catalyst system simply by the use of a molecular weight control agent, such as hydrogen. While hydrogen is known as a molecular weight control agent, the catalysts of this invention display an extraordinary sensitivity to hydrogen so that by controlling the amount of hydrogen utilized, polymers having a very high molecular weight as indicated by low melt flow, though polymers having a very low molecular weight as indicated by high melt flow can be obtained. This can further be fine tuned by varying the ratio of silica support to phosphate support in the catalyst component. Further control of melt flow can be obtained by the small amount of leeway in temperature control and by the known effect of higher catalyst activation temperature causing the melt flow of the resulting polymer to be higher. However, yet a further advantage of this invention is that a single activation temperature for the catalyst and a single polymerization temperature can be utilized and still obtain a broad spectrum of polymers utilizing a single catalyst.

With slurry polymerization of ethylene and predominantly ethylene copolymer systems, the feasible temperature range is generally about 200-230°F (93-110°C) and the commercial systems are generally run as close to the maximum as possible, i.e. 225°F $\pm$ 5°F (107°C $\pm$ 3°C) in order to get the highest possible melt index. The catalyst of this invention allows running at the low end of the possible temperature 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.

Catalysts of this invention have the further advantage of the metal phosphate component not having any measurable induction time between initial contact with the monomer and the initiation of polymerization.

5 When hydrogen is used in the prior art, it is generally used at partial pressures up to 120 psia (0.83 MPa), preferably within the range of 20 to 70 psia (0.14 to 0.48 MPa). Similar amounts are used in accordance with this invention, although because of the high sensitivity to hydrogen, it is possible to use slightly smaller amounts.

10 The tendency of the metal phosphate component of the catalysts of this invention to produce higher melt flow polymers when hydrogen is utilized corresponds to the tendency of other catalyst systems to produce higher melt flow polymers when hydrogen is utilized, the difference being that the metal phosphate component of the catalyst of this invention is
15 extraordinarily sensitive to the effects of hydrogen. In other areas, the metal phosphate component of the catalyst of this invention acts in a manner different from the prior art catalysts. For instance, boron cocatalysts sometimes are used in the prior art in spite of the fact that they tend to have an adverse effect on melt flow, i.e., cause the melt
20 flow to drop. However, the boron cocatalysts of this invention substantially increase the melt flow capability of the metal phosphate component of the catalyst. Thus, by varying the amount of metal phosphate component which increases melt flow and the amount of silica component which decreases melt flow when used in conjunction with the
25 boron cocatalysts, a novel method of broadening the molecular weight distribution is provided. Also, the use of hydrogen broadens the molecular weight distribution because, while it reduces the molecular weight with both silica and phosphorus bases, the effect is minor with the silica component and dramatic with the phosphate.

30 It is known in the art that the presence of a comonomer in ethylene polymerization may increase the melt flow of the resulting polymer. However, the metal phosphate component of the catalyst of this invention causes this effect to be unexpectedly magnified, with only small amounts of comonomer giving larger increases in melt flow of the
35 resulting polymer. Thus, this allows the use of comonomer addition as a method of controlling melt flow. If the object is to produce a polymer which is essentially a homopolymer, 0.001 to 0.3, preferably 0.01 to 0.1 mole percent comonomer based on the moles of ethylene in the feed can be

utilized. If the object is to produce a copolymer, 0.5 to 20 mole percent or more can be used, although enough to give 0.4 to 3 weight percent incorporation is preferred.

Another area in which the prior art olefin polymers always represent a compromise in properties is with regard to shear response. For certain applications, a high shear response as evidenced by the ratio of high load melt index to melt index, is desirable. This has heretofore been associated with broad molecular weight distribution as determined by size exclusion chromatography, for instance. Unexpectedly, the polymers produced by the catalysts of this invention exhibit a high shear response as evidenced by high HLMI/MI ratios indicating relatively broad molecular weight distribution. Molecular weight distribution or heterogeneity index (HI) as indicated by M_w/M_n where M_w refers to weight average molecular weight and M_n refers to number average molecular weight is determined by size exclusion chromatography. In this regard, it must be kept in mind that HLMI/MI ratios are meaningful only if compared on a comparable melt index basis. The references herein to melt index (MI) refer to ASTM D1238-65T, Condition E, and to high load melt index (HLMI) refer to ASTM D1238-65T, Condition F, the difference being 21,600 gram weight in the high load test and 2,160 gram weight in the regular melt index test, the temperature being 190°C in each instance when the tests are utilized for predominantly ethylene polymers and copolymers.

Example I

This is an example of a silica/metal phosphate support made by the cogel method. A 50/50 mole percent $\text{SiO}_2/\text{AlPO}_4$ cogel having 10 percent solids was made by simultaneously adding the following ingredients.

- (1) 187.5 grams $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in water.
- (2) 34.6 mL orthophosphoric acid.
- (3) 104 grams $\text{Si}(\text{OEt})_4$ (111.3 mL).
- (4) 18 grams water.
- (5) 20 mL isopropyl alcohol.

The above ingredients were chosen so as to give 61 grams aluminum orthophosphate and 30 grams of SiO_2 , i.e., one-half mole each. Thereafter approximately 200 mL of concentrated ammonium hydroxide were added which produced a thick gel at a pH of about 6-7 which then turned soupy at a pH of about 9 (the ideal pH of 6-7 was slightly overrun). It was filtered to make a cake.

One-half of the hydrogel was dried in an oven to form the basis for runs 1 and 2, the other half was azeotrope dried using isoamyl alcohol to form the basis for runs 3, 4, and 5. Each finished, calcined catalyst contained 1 percent chromium from chromium acetate in alcohol which was added to the xerogel. Each catalyst was activated in air at 700°C after addition of the chromium acetate and tested for polymerization at 205°C. The results are shown hereinbelow in Table I.

Table I

Run No.	Drying Method	% Cr +6(1)	PV (2)	SA (2)	Cat. Wt., gm.	Polymer Yield, gm.	Reactor Additive	Prod. (3)	MI	HLMI/MI	gm/mL Density	HI (4) (Mw/Mn)	Run Time (Min.)
1	Oven	0.94	0.19	117	.2620	~ 0	None	Dead	-	-	-	-	-
2	Oven	0.94	0.19	117	.4570	~ 0	1 ppm TEB	Dead	-	-	-	-	-
3	Azeop.	0.87	1.14	363	.0795	296	None	3720	HLMI=2.4	0.9600	16.0	16.0	50
4	Azeop.	0.87	1.14	363	.0540	288	8 ppm TEB	5330	0.31	172	0.9684	17.9	90
5	Azeop.	0.87	1.14	363	.0625	250	50 psi H ₂	4000	1.24	112	0.9688	12.0	90
							8 ppm TEB						

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(1) By titration to the ferroin end point with divalent iron.

(2) PV = pore volume, SA = surface area in m²/g; determined by N₂ absorption by B.E.T. method.

(3) Productivity, grams polymer per gram catalyst (g/g).

(4) HI is heterogeneity index.

The properties in this and subsequent examples were determined as follows:

Melt Index (MI) ASTM 1238-65, Condition E.

High Load Melt Index (HLMI) ASTM D 1238-65T, Condition F.

5 Density, grams per cc, ASTM D 1505-68.

M_w/M_n from size exclusion chromatography.

The above table shows that the azeotrope dried catalyst was very active even without a cocatalyst. While the oven dried half was dead, this is probably due to the low porosity due to the sequence of
10 washing and oven drying and is not representative of all oven dried preparations which, when used with a boron-containing cocatalyst, give good results as shown by Example 1A hereinafter. As can be seen, the catalysts of this invention produce a broad molecular weight distribution polymer and give hydrogen sensitivity intermediate between
15 that of chromium oxide supported on pure SiO_2 and pure AlPO_4 .

The details of the polymerization for the above and the following examples is as follows. Each run was conducted in a clean, dry, air-free, stirred stainless steel reactor of about 2 L capacity. About 600 g of isobutane was used in each run as diluent with a catalyst
20 charge ranging from about 0.03 to 0.8 gram. The reactor and its contents were heated to the desired operating temperature, ethylene pressure added to give about 565 psia (3.9 MPa), and the run was started immediately. Ethylene pressure was maintained during the run by supplying additional ethylene as required from a pressurized reservoir.
25 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 set out in terms of grams polymer per gram of catalyst for the run time employed.

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Example 1A

This is another example of a silica/metal phosphate support made by the cogel method. In this preparation, 94 g of aluminum nitrate, specifically $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, plus 23 g of $\text{H}_2\text{NH}_4\text{PO}_4$ plus 2.4 g of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were mixed with a solution of: 13 mL isopropanol plus 5 mL
35 H_2O plus 5 drops H_3PO_4 plus 23 mL ethyl silicate plus 1 drop H_2SO_4 to make a clear solution. Then 55 mL of concentrated ammonium hydroxide were added to effect gellation.

The gel was dried in a vacuum oven, washed two times with water and filtered, then washed two times with isopropanol and filtered after which it was again dried in a vacuum oven. It was activated at 500°C in air for 5 hours to give 1 weight percent chromium based on the dry support.

Polymerization was carried out at 205°F (96°C) with 4 ppm by weight triethylboron based on the weight of the reactor contents.

The results were as follows:

Table IA

Run No.	Productivity, g/g	Run Time, Min.	MI	HLMI/MI	Density	ESCR ⁽¹⁾
6	1930	60	0.12	240	0.9681	110

(1) Environmental Stress Crack Resistance.

ASTM D1693-70, Condition A (50°C).

Example II

This example illustrates production of this silica metal phosphate base by means of impregnating silica with aluminum phosphate or boron phosphate. The silica used in this example was a commercial grade of silica containing 1 weight percent chromium calculated on a dry basis of support plus chromium compound formed by spray drying a silica hydrogel having about 0.1 weight percent alumina containing an aqueous solution of chromium acetate. Essentially identical catalysts can be formed by impregnating 952 grade silica commercially available from Davison Chemical Company with an aqueous solution of chromium acetate and drying at about 200-400°F (129-204°C) in air. The polymerization runs were carried out as in Example I with the results shown hereinbelow in Table II.

Table II

AlPO₄ or BPO₄ Impregnated Onto Silica

Run No.	Atom Mole Ratio % Al P/Al	Preparation	Act. Temp.	Reactor (12) Additive	Run Temp.	Min. Run Time	g/g Prod.	MI (13)	HLMI MI	HLMI g/mL Den.	HI (14)	Nv	Mn	ESCR
6	5	1.0 Acid (2)	500C	TEB	215°F (98°C)	30	1580	0	0.55	-	.9623	33.2	515	15.5
8	5	1.0 Acid (2)		TEB + H ₂	215°F (98°C)	90	1780	0.17	10.9	641	.9652	25.1	276	11.0 82
9	5	1.0 Basic (NH ₄ OH Vapor) (3)	500C	TEB	215°F (98°C)	90	1126	0	0.86	-	.9648	43.2	570	13.2
10	5	1.0 Basic (NH ₄ OH Vapor) (3)		TEB + H ₂	215°F (98°C)	45	2185	0.02	4.5	227	.9623	-	-	-
11	5	1.0 Basic (NH ₄ OH Vapor) (3)		TEB + H ₂	215°F (98°C)	70	2740	0.04	9.4	235	-	-	-	-
12	5 (1)	1.0 (1) Acid (4)	500C	TEB	215°F (98°C)	50	1625	0	7.6	-	.9663	21.6	259	12.0
13	5 (1)	1.0 (1) Acid (4)		TEB	215°F (98°C)	90	1695	0.26		188	.9658	15.7	196	12.5 23
14	5 (1)	1.0 (1) Acid (4)		TEB + H ₂	215°F (98°C)	90	850	1.9		99	.9700	12.7	119	9.4
15	0	Control Catalyst (5)	500C	TEB	215°F (98°C)	90	2220	0	0.15	-	.9598	27.6	445	16.1
16	0	Control Catalyst (5)		H ₂ + TEB	215°F (98°C)	90	705	0	1.8	-	.9611	17.6	236	13.4
17	2.5	0.8 Acid (6)	500C	TEB + H ₂	215°F (98°C)	80	3615	0	2.0					
18	5	0.8 Acid (7)	500C	TEB + H ₂	215°F (98°C)	45	2820	0	4.8					
19	10	0.8 Acid (8)	500C	TEB + H ₂	215°F (98°C)	80	3760	0	1.6					
20	15	0.8 Acid (9)	500C	TEB + H ₂	215°F (98°C)	80	3070	0	2.7					
21	25	0.8 Acid (10)	500C	TEB + H ₂	215°F (98°C)	80	2145	0	2.4					
22	15	0.8 Dry Mix Acid Melt (11)	500C	TEB	215°F (98°C)	40	3320	0	4.9					
23	15	0.8 Dry Mix Acid Melt (11)		TEB	215°F (98°C)	80	4155	0	13.0					
24	15	0.8 Dry Mix Acid Melt (11)		TEB + H ₂	215°F (98°C)	80	3460	0.25	56.0	224	.9664			57

(1) Boron instead of phosphorus.

(2) 20 Grams of the silica (1/3 mole) were slurried in water to which was added 1.2 mL H₃PO₄ + 6.15 grams Al(NO₃)₃·9H₂O. The solvent was boiled off on a hot plate and resulting xerogel activated in air at 500°C.

(3) 20 Grams of the silica (1/3 mole) were slurried in water to which was added 1.2 mL H₃PO₄ + 6.15 grams Al(NO₃)₃·9H₂O. Nitrogen was bubbled through ammonium hydroxide to the slurry at 200°C to form the gel which was then dried and activated at 500°C.

- (4) 20 Grams of the silica (1/3 mole) were slurried in water and to this slurry was added 0.51 grams boric acid + 1.2 mL H_3PO_4 . The solvent was boiled off on a hot plate and the resulting xerogel activated in air at 500°C.
- (5) The chromium containing silica used in the above runs with no treatment.
- (6) 94 Grams of $Al(NO_3)_3$ and 14 mL of H_3PO_4 were diluted in water to 300 mL.. 10 Grams (1/6 mole) of the silica was slurried in water to which was added 5 mL of the above solution of $Al(NO_3)_3$ and H_3PO_4 . The water was then evaporated off and resulting gel was activated at 500°C in air.
- (7) Same procedure as in footnote (6) except 10 mL of the solution were used.
- (8) Same procedure as in footnote (6) except 20 mL of the solution were used.
- (9) Same procedure as in footnote (6) except 30 mL of the solution were used.
- (10) Same procedure as in footnote (6) except 50 mL of the solution were used.
- (11) The following ingredients were mixed together and heated to melt: 94 grams $Al(NO_3)_3 \cdot 9H_2O$; 23 grams ammonium dihydrogen phosphate; 2.4 grams $Cr(NO_3)_3 \cdot 9H_2O$ and 20 mL water. The final volume was 100 mL. 20 Grams of the silica described hereinabove was added to 20 mL of the above solution with much shaking and stirring. The pore volume of the silica was 1.67 cc per gram. Thus the silica should hold greater than 20 mL of solution and still be dry. After the solution was added to the silica and shaken, 10 mL of concentrated ammonium hydroxide (a stoichiometric amount) was added and it was shaken again. Since it was still dry to the touch, it was activated at 500°C without further drying.
- (12) TEB in runs 6-14 was 8 ppm by weight based on the weight of diluent. In runs 15-24 it was 4 ppm. Hydrogen pressure when used was 50 psi (0.34 MPa).
- (13) MI, HLMI, Density, HI and ESCR determined as in prior examples.
- (14) HI is the heterogeneity index, i.e. M_w/M_n .

A comparison of control run 14 with the other runs utilizing only TEB (i.e., no H_2) show higher melt index in every instance for the invention run which have the silica impregnated with aluminum phosphate or boron phosphate. Similarly, a comparison of control run 15 with all of the other runs shows that with hydrogen a higher melt index is obtained with the aluminum phosphate or boron phosphate impregnated silica than is obtained with the pure silica. These runs also show unusually broad molecular weight distribution as evidenced by high HI and in the few runs tested especially good environmental stress crack resistance especially when it is noted that the density is increased over the nominal 0.960 expected for an ethylene homopolymer.

Example IIA

This example shows further examples of impregnation of a silica catalyst with $AlPO_4$ or BPO_4 . The $AlPO_4$ catalysts were made by impregnating a silica of the type described in Example II with an aqueous

solution of $\text{Al}(\text{NO}_3)_3 + \text{H}_3\text{PO}_4$ to equal 5 mole percent aluminum phosphate. The BPO_4 base was prepared by impregnating the silica with a solution of boric acid and orthophosphoric acid to equal 5 mole percent BPO_4 . In each instance, the impregnated silica was dried and activated in air at 500°C and tested for polymerization of ethylene at 205°F (96°C), 565 psia (3.99 MPa) and about 2 parts per million triethylborane based on reactor contents. The results are set out hereinbelow in Table IIA. This table shows that the impregnation with either aluminum phosphate or boron phosphate even though a gel may not be formed under these conditions greatly increases the melt flow sensitivity to hydrogen and produces broad molecular weight distribution polymers.

Table IIA

Run No.	Additive	H_2	Wt. Cat., g	Wt. Polymer, g	Prod., g/g	MI	HLMI/MI
15	25 None	0	0.1440	320	2220	0.15 HLMI	
	26 AlPO_4	0	0.2070	327	1580	0.55 HLMI	
	27 BPO_4	0	0.2260	367	1625	7.6 HLMI	
	28 None	50	0.1735	122	705	1.8 HLMI	
	29 AlPO_4	50	0.0905	161	1780	0.17 MI	641
20	30 BPO_4	50	0.1955	331	1695	0.26 MI	188

Example III

In this example, 94 grams of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ plus 23 grams ammonium dihydrogen phosphate plus 7.1 grams $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 100 ml H_2O plus 65 grams of Davison 952 silica hydrogel (30% solids) was stirred well and heated for 15 minutes at 30°C. Then 50 ml concentrated ammonium hydroxide was added to make a gel. The gel was washed in water once and twice in acetone and then dried in a vacuum oven at 60°C. Thereafter it was activated at 600°C in air for 3 hours. The resulting catalyst was used in ethylene polymerization at 205°F with 5 ppm TEB and 50 psia hydrogen with a 60 minute run time. The productivity was 5650, the melt index 5.84 and the HLMI/MI ratio was 85. This is an example of a 40/60 silica/aluminum phosphate combination formed by forming the phosphate in the presence of the silica hydrogel and demonstrates good productivity, high melt index and high shear response.

Example IIIA

In this example, 94 grams of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ plus 23 grams ammonium dihydrogen phosphate plus 7.1 grams $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 100 ml H_2O

and 15 grams of Cabosil (Registered Trade Mark) Grade S17, which is a flame hydrolyzed nonporous silica with a surface area of 400 square meters per gram was stirred well and heated 15 minutes at 30°C. Thereafter 50 ml concentrated ammonium hydroxide was added to
5 make a gel. The resulting gel/silica mixture was washed in water and twice in acetone. Then it was dried in a vacuum oven at 60°C and activated at 600°C in air for three hours. In an ethylene polymerization run at 205°F with 5 ppm TEB and 50 psia hydrogen, run for 60 minutes, the productivity was 5450, the melt index 6.68 and
10 the HLMI/MI ratio was 80.

Example IV

This example shows physical mixing of a silica based chromium catalyst and an aluminum phosphate based chromium catalyst. The silica based chromium catalyst was the silica described hereinabove
15 in Example II, activated at 760°C. The aluminum phosphate catalyst was prepared by the melt method.

The phosphorus to aluminum atom ratio of the aluminum phosphate was 0.8. The chromium acetate was included in the phosphate preparation so as to cogel a sufficient amount of the chromium
20 compound to give 1 weight percent chromium based on the weight of the final dried xerogel. Silica-based catalyst (0.0198 gram) and 0.0562 gram of the aluminum phosphate-based catalysts were separately added to the reactor along with 8 parts per million triethylborane and 50 psi (0.34 MPa) hydrogen. The reaction was
25 run for 30 minutes and yielded 249 grams of polymer which corresponds to a productivity of 3,280 g polymer per g catalyst or a productivity in grams polymer per gram catalyst per hour of 6560 assuming a linear response over the 60 minutes. The melt index was 2.6 and the HLMI/MI ratio was 86 which is very high.

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Example V

This example shows the different effects of TEB as cocatalyst with a chromium oxide catalyst on silica compared with catalysts of the invention having a silica/phosphate support. All of the catalysts had one weight percent chromium based on the weight of
35 the dry base.

Table V

	Run No.	Reactor Additive ppm, TEB	Support	Prod. g/g	Density g/mL	Melt Index	Polymerization Time, min.	Remarks
5	1	0	Silica	3330	0.962	0.58	70	Prior art
	2(a)	2.5	Silica	3450	0.955	0.15	37	Prior art
	3(a)	3.8	Silica	3890	0.952	0.21	45	Prior art
	4(b)	0	Silica/ phosphate	3720	0.960	HLMI=2.4	50	Invention
10	5(c)	8	Silica/ phosphate	5330	0.968	0.31	90	Invention

(a) The TEB for runs 2-4 is calculated based on 600 g isobutane diluent and 0.03 g catalyst weight.

(b) Same as run 3, Table I.

15 (c) Same as run 4, Table I.

It can be seen in Table V with the prior art chromium oxide on silica catalyst (runs 1-3) that not only the melt index of the product decreases as TEB is added but that also the density of the product decreases. Apparently, some of the ethylene is converted into higher 1-olefins such as 1-butene which is copolymerized with the ethylene thus lowering the density of the product. Thus, if an ethylene homopolymer is desired, then the presence of TEB must be avoided.

On the other hand, it can be seen that in invention runs 4 and 5 that TEB increases the melt index of the product, increases the density of the product, and substantially increase the amount of polymer produced.

While this invention has been described in detail for the purpose of illustration, it is not to be construed as limited thereby but is intended to cover all changes and modifications within the spirit and scope thereof.

CLAIMS

1. A catalyst composition for the polymerization of olefins comprising:
as a first component, chromium oxide supported on a mixed
5 silica/metal phosphate support; and
as a second component an organometallic cocatalyst.
2. A catalyst composition according to claim 1, wherein said support comprises a mixed silica/metal phosphate xerogel obtained by coprecipitating silica and aluminum phosphate and drying the
10 resultant gel.
3. A catalyst composition according to claim 1, wherein said support comprises a silica xerogel impregnated with aluminum phosphate.
4. A catalyst composition according to claim 1, wherein said
15 support comprises a silica xerogel impregnated with boron phosphate.
5. A catalyst composition according to claim 1, wherein said support comprises an admixture of a silica xerogel and an aluminum phosphate xerogel.
6. A catalyst composition according to any one of claims 1-
20 3 and 5, wherein the support comprises silica and an aluminum phosphate having a P:Al atomic ratio of from 0.6:1 to 0.9:1.
7. A catalyst composition according to any one of the preceding claims wherein the cocatalyst is a trialkylborane.



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8. A catalyst composition according to claim 7, wherein the cocatalyst is triethyl, tripropyl or tri-n-butylborane.
9. A catalyst composition according to claim 7 or 8, wherein the B:Cr atomic ratio is from 2:1 to 5:1.
- 5 10. A catalyst composition according to any one of the preceding claims, wherein the amount of chromium is from 0.1 to 5% by weight based on the weight of the support.
11. A method of preparing a chromium oxide-containing olefin polymerization catalyst, which comprises:
- 10 a) forming a silica hydrogel or xerogel;
- b) impregnating the silica hydrogel or xerogel with a liquid medium comprising a source of aluminum ions and a source of phosphate ions;
- 15 c) evaporating the liquid medium or adding a neutralising agent to deposit aluminum phosphate in the pores of the silica gel;
- d) incorporating a chromium compound into the gel, before, after or during the deposition of the aluminum phosphate; and
- 20 e) activating the chromium-containing silica/aluminum phosphate support material by heating in an oxidising atmosphere at a temperature of from 150 - 1000°C.
12. A method according to claim 11, wherein said silica is impregnated with said phosphate by forming a slurry of silica
- 25 hydrogel in an aqueous solution of aluminum nitrate and ortho-phosphoric acid, and evaporating off the aqueous solvent.



13. A method according to claim 11, wherein said silica is impregnated with said phosphate by impregnating a silica xerogel with a liquid medium containing aluminum nitrate and orthophosphoric acid, the volume of said liquid being less than the pore volume of the silica xerogel and either evaporating the liquid to deposit aluminum phosphate in the xerogel, or neutralising the impregnating liquid and then drying the impregnated gel.

14. A method of preparing a chromium oxide-containing olefin polymerization catalyst composition which comprises:

- a) forming a silica hydrogel or xerogel;
- b) impregnating the silica hydrogel or xerogel with a liquid medium comprising a source of boron ions and a source of phosphate ions;
- c) depositing boron phosphate in said hydrogel or xerogel by evaporating the liquid medium;
- d) incorporating a chromium-containing compound into the silica gel, before, during or after deposition of the boron phosphate;
- e) activating the chromium and boron phosphate silica gel by heating in an oxidising atmosphere at a temperature of 150 - 1000°C; and
- f) admixing the activated product of step (e) with an organometallic cocatalyst.

15. A method according to claim 14, wherein the silica is impregnated with said phosphate by forming a slurry of silica hydrogel in a liquid medium containing boric acid and a source of phosphate ions, and evaporating the liquid medium.



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16. A method of making chromium oxide-containing olefin polymerization catalyst, which comprises:

- 5 a) precipitating an aluminum phosphate hydrogel in the presence of a previously formed silica hydrogel or xerogel;
- b) removing water to convert the resulting aluminum phosphate hydrogel/silica mixture to a xerogel;
- 10 c) introducing a chromium-containing compound before, after or during the precipitation of the aluminum phosphate hydrogel; and
- d) activating the catalyst by heating in an oxidising atmosphere to a temperature of from 150 to 1000°C.

17. A method according to claim 16, wherein said aluminum phosphate hydrogel is formed by adding a aluminum nitrate and
15 phosphoric acid to a silica xerogel and thereafter adding ammonium hydroxide.

18. A method of forming chromium oxide-containing olefin polymerization catalyst which comprises:

- 20 coprecipitating silica and aluminum phosphate to form a cogel;
- incorporating a chromium-containing compound into the cogel;
- drying the cogel; and
- activating the chromium-containing cogel by heating in an oxidising atmosphere.

25 19. A method according to claim 18, in which the cogel is formed by neutralising a mixture containing ethyl silicate, aluminum nitrate

and orthophosphoric acid with ammonia or ammonium hydroxide.

20. A method according to claim 18 or 19, wherein cogel is converted to a xerogel by azeotropic distillation with a water-miscible organic compound, or washing with a water-miscible organic compound.

5 21. A method according to claim 18, 19 or 20, wherein the cogel is precipitated in the presence of a boron compound.

22. A method according to claim 21, wherein the boron compound is boric acid.

23. A method according to claim 21 or 22, wherein the boron
10 compound is sufficient to provide in the cogel 0.5 to 15 mole percent of boron based on the moles of phosphorus.

24. A method of forming a chromium oxide-containing olefin polymerization catalyst which comprises:

- 15 a) mixing a silica xerogel and an aluminum phosphate xerogel;
b) incorporating a chromium-containing compound into the mixed xerogels either by addition to each of the xerogels prior to admixture, or by addition to the admixture; and
c) activating the chromium-containing xerogel mixture by heating in an oxidising atmosphere at a temperature of
20 150 - 1000°C.

25. A method according to claim 24, modified in that the two xerogels are impregnated with the chromium-containing compound and activated prior to mixing.

26. A method according to any one of claims 11-25, wherein the



chromium-containing compound is incorporated into the support in an amount of from 0.1 to 5 percent by weight based on the weight of the support.

27. A method according to any one of claims 11-13 and 16-26,
5 wherein following activation, the catalyst is combined with an organometallic cocatalyst.

28. A method according to claim 14,15 or 27, wherein the cocatalyst is an organoborane.

29. A method according to claim 28, wherein the cocatalyst is
10 a trialkylborane.

30. A method according to claim 29, wherein the cocatalyst is tri-n-butyl borane.

31. A method according to claim 28,29 or 30, wherein the cocatalyst provides a B:Cr atomic ratio of from 2:1 to 5:1.

15 32. An olefin polymerization catalyst or catalyst composition, when prepared by a method claimed in any one of claims 11-26.

33. An olefin polymerization catalyst composition as claimed in claim 1, when prepared by a method claimed in any one of claims 14,15 or 27-31.

20 34. An olefin polymerization process which comprises polymerizing one or more 1-olefins in the presence of a chromium oxide-containing catalyst or catalyst composition as claimed in claim 32.



35. An olefin polymerization process which comprises polymerizing one or more 1-olefins in the presence of a chromium oxide-containing catalyst composition as claimed in any one of claims 1 - 10 or 33.
- 5 36. A process according to claim 35, wherein the cocatalyst is fed to the polymerization reactor as a separate stream, thereby to form the catalyst system in situ.
37. A process according to any one of claims 34-36, wherein the polymerization is effected in an inert liquid diluent containing
10 the catalyst component (1) in suspension.
38. A process according to any one of claims 34-37, wherein the monomer is or comprises one or more mono-1-olefins of 2-8 carbon atoms.
39. A process according to claim 38, wherein the monomer is
15 predominantly ethylene and the polymerization is effected at a temperature of from $205^{\circ}\text{F} \pm 5^{\circ}\text{F}$ ($96^{\circ}\text{C} \pm 3^{\circ}\text{C}$).
40. A process according to claim 38 or 39, wherein the monomer comprises ethylene and from 0.01 to 0.1 mole percent of propylene, 1-butene, 1-pentane, 1-hexene or 1-octene.
- 20 41. A process according to any one of claims 34-40, wherein there is used a catalyst system as claimed in claim 5, or as prepared by a method claimed in claim 24 or 25, wherein the chromium-containing silica xerogel and the chromium-containing aluminum phosphate xerogel are added separately to the reactor
25 to form the catalyst mixture in situ.