

PATENT SPECIFICATION

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(54) OLEFIN POLYMERIZATION CATALYST

(71) We, NATIONAL PETRO CHEMICALS CORPORATION, a corporation organised and existing under the laws of the State of Delaware, United States of America, of 99 Park Avenue, City and State of New York, 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:-

The use of chromium compounds in the polymerization of olefins is well known. U.S. Patents 2,825,721 and 2,951,816 teach the use of CrO₃ supported on an inorganic material such as silica, alumina or combinations of silica and alumina and activated by heating at elevated temperatures to polymerize olefins. When these catalyst systems are used in various polymerization processes such as the well-known particle-form process, the resins produced, while useful in many applications, are unsatisfactory for others because of a deficiency in certain properties such as melt index.

Attempts to improve deficient properties of polyolefins produced using supported, heat-activated chromium oxide catalysts have been made by adding various metal and non-metal compounds to the supported chromium oxide prior to activation by heating. For example, in U.S. Patent 3,622,522 it is suggested that an alkoxide of gallium or tin be added to supported chromium oxide prior to heat activation. U.S. Patent 3,715,321 suggests adding a compound of a Group II-A or Group III-B metal to supported chromium oxide prior to heat treatment whereas U.S. Patent 3,780,011 discloses adding alkyl esters of titanium, vanadium or boron and U.S. Patent 3,484,428 discloses adding alkyl boron compounds.

In columns 5 and 6 and Table I of U.S. Patent 3,622,522 the addition of aluminum isopropoxide to supported chromium oxide prior to heat activation is shown for purposes of comparison with the addition of alkoxide of gallium or tin. The patentee concluded that the addition of the aluminum compound gave substantially the same or an increased HLMI/MI ratio of polymers produced as compared to the chromium oxide catalyst with no metal alkoxide added, whereas the addition of gallium or tin alkoxides produced polymers having a lower HLMI/MI ratio.

None of the above-mentioned patents disclose adding to the heat-activated supported catalyst a metal or non-metal reducing agent.

It is also known to utilize other chromium compounds as catalysts for the polymerization of olefins. Such compounds include various silyl chromate and polyalicyclic chromate esters as described, for example, in U.S. Patents 3,324,095; 3,324,101; 3,642,749; and 3,704,287. The use of phosphorus-containing chromate esters in olefin polymerization catalysts has also been disclosed in the aforesaid U.S. Patent 3,704,287; and in U.S. Patent 3,474,080 and British Patent No. 1490141.

Use of the above chromium compound catalysts in Ziegler-type coordination catalyst systems has also been proposed. As is well known in the art, such catalysts frequently additionally comprise organometallic reducing agents such as, for example, trialkyl aluminum compounds. Ziegler-type catalyst systems incorporating supported chromium

compound catalysts and organometallic reducing agents, particularly organoaluminum compounds, are disclosed, for example, in U.S. Patents 3,324,101; 3,642,749; 3,704,287; 3,806,500; and in the aforesaid British Patent No. 1490141.

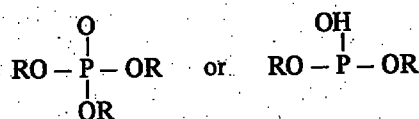
It has been discovered in accordance herewith that olefin polymers having improved properties (e.g. melt index), may be obtained by utilization of an olefin polymerization catalyst prepared by depositing a chromium-containing compound and an aluminum-containing compound on a solid inorganic support material having surface hydroxyl groups, said chromium-containing compound and said aluminum-containing compound being capable of reacting with said surface hydroxyl groups, heating said support material having the chromium-containing compound and the aluminum containing compound deposited thereon in a non-reducing atmosphere at a temperature above 300°C up to the decomposition temperature of the support material, and admitting into the presence of the heat-treated, supported chromium-containing compound and aluminum-containing compound a metallic or non-metallic reducing agent other than hydrogen and the said aluminum-containing compound. Polymers produced using a catalyst according to the present invention may have improved flow properties and shear response.

The reducing agent used according to the invention is preferably a boron-containing compound.

It is believed that the chromium-containing compounds and the aluminum-containing compounds may react with the surface hydroxyl groups on the inorganic support material during the course of preparation of the catalyst of the present invention. However, the precise mechanism involved is not known and applicants do not wish to be restricted to the mechanism postulated above.

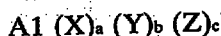
The inorganic support materials useful in the present invention include those normally employed in supported chromium catalysts used in olefin polymerizations such as those discussed in U.S. Patent 2,825,721. Typically, these support materials are inorganic oxides of silica, alumina, silica-alumina mixtures, thoria, zirconia and comparable oxides which are porous, have a medium surface area, and have surface hydroxyl groups. Preferred support materials are silica gels, especially silica xerogels or xerogels containing silica as the major constituent. Especially preferred are the silica xerogels described in U.S. Patent 3,652,214 which silica xerogels have a surface area in the range of 200 to 500 m²/g and a pore volume greater than 2.0 cc/g, a major portion of the pore volume being provided by pores having diameters in the range of 300 to 600 Å.

The chromium-containing compounds useful in the present invention comprise any chromium-containing compound capable of reacting with the surface hydroxyl groups of the inorganic support. Examples of such compounds include chromium trioxide, chromate esters such as those disclosed in U.S. Patent 3,642,749 or 3,704,287, and organophosphoryl chromium compounds such as those disclosed in applicants British Patent Specification No. 1490141 which comprise the reaction product of chromium trioxide with an organophosphorus compound having the formula:



wherein R is alkyl, aralkyl, aryl, cycloalkyl or hydrogen, but at least one R is other than hydrogen. The preferred organophosphorus compounds are trialkyl phosphates such as triethyl phosphate.

Aluminum-containing compounds useful in the present invention are characterized as any aluminum-containing compound capable of reacting with the surface hydroxyl groups of the inorganic support material. Preferred aluminum-containing compounds may be represented by the formula:



wherein X is R, Y is OR, and Z is H or a halogen; a is 0-3, b is 0-3, c is 0-3, and a + b + c equals 3; and R is an alkyl or aryl group having from one to eight carbon atoms.

Examples of such aluminum-containing compounds include aluminum alkoxides such as aluminum sec-butoxide, aluminum ethoxide, aluminum isopropoxide; alkyl aluminum alkoxides such as ethyl aluminum ethoxide, methyl aluminum propoxide, diethyl aluminum ethoxide, diisobutyl aluminum ethoxide, alkyl aluminum compounds such as triethyl aluminum, triisobutyl aluminum; alkyl or aryl aluminum halides such as diethyl aluminum chloride; aryl aluminum compounds such as triphenyl aluminum; aryloxy aluminum compounds such as aluminum phenoxide; and mixed aryl, alkyl and aryloxy, alkyl aluminum compounds.

The catalysts of the present invention may be prepared by depositing the chromium-

containing compound and the aluminum-containing compound on the solid inorganic support in any suitable manner such as by vapor coating or by impregnating the support with solutions of the chromium-containing compound and the aluminum-containing compound in a suitable inert solvent which is normally an anhydrous organic solvent. Such organic solvents include aliphatic, cycloalkyl, and alkylaryl hydrocarbons and their halogenated derivatives. A preferred organic solvent is dichloromethane. The chromium-containing compound may be applied to the support first or the aluminum-containing compound may be applied first or the chromium- and aluminum-containing compounds may be applied together. In applicants' usual method of catalyst preparation, the support is impregnated first with the chromium-containing compound and then the aluminum-containing compound.

When an organophosphoryl chromium compound of the type disclosed in the aforesaid British Patent No. 1490141 is utilized in the practice of the present invention, it is preferred to employ the particular catalyst preparation techniques described in that specification, to which attention is directed for full detail. In such instance the organoaluminum compound may be applied to the catalyst support under conditions similar to those utilized for deposition of the organophosphoryl chromium compound.

The most effective catalysts have been found to be those containing the chromium-containing compound in an amount such that the amount of Cr by weight based on the weight of the support is from 0.25 to 2.5%, preferably from 0.5 to 1.25%, although amounts outside of these ranges still yield operable catalysts. The aluminum-containing compound should be added in sufficient amounts to provide from 0.1 to 10% of aluminum by weight based on the weight of the support, preferably from 0.5 to 5.5%, although other amounts outside of these ranges can be used to prepare operable catalysts.

After the chromium-containing compound and the aluminum-containing compound have been deposited on the inorganic support, the support is heated in a non-reducing atmosphere, preferably in an oxygen-containing atmosphere, at a temperature above 300°C up to the decomposition temperature of the support. Typically, the supported compositions are heated at a temperature of from 500 to 1000°C. The heating time may vary, for example, depending on the temperatures used, from ½ hour or less to 50 hours or more. Normally the heating is carried out over a period of 2 to 12 hours. The non-reducing atmosphere which is preferably air or other oxygen-containing gas should be dry and preferably should be dehumidified down to a few parts per million (ppm) of water to obtain maximum catalyst activity. Typically, air used in the procedure described in this application is dried to less than 2-3 ppm of water.

The heat-treated supported chromium- and aluminum-containing are used in combination with metallic and/or non-metallic reducing agents for the polymerization of olefins. Examples of metallic reducing agents include trialkyl aluminums, such as triethyl aluminum or triisobutyl aluminum, alkyl aluminum halides, alkyl aluminum alkoxides, dialkyl zincs, dialkyl magnesiums, and metal borohydrides including those of the alkali metals, especially sodium, lithium and potassium, and of magnesium, beryllium and aluminum. The non-metallic reducing agents include boron alkyls such as triethyl borane, triisobutyl borane, and trimethyl borane and hydrides of boron such as diborane, pentaborane, hexaborane and decaborane.

The heat-treated, supported chromium containing compound and aluminum-containing compound may be combined with the metallic or non-metallic reducing agent prior to being fed to an olefin polymerization reactor or these two components may be fed separately to an olefin polymerization reactor.

In proportioning the amount of metallic or non-metallic reducing agent to the amount of chromium-containing compound used in the catalyst of the present invention, fairly wide latitude is available; but some guidelines have been established consistent with good yield, favorable polymer properties and economic use of materials. For example, in the use of metallic and/or non-metallic reducing agents with an amount of chromium-containing compound sufficient to yield about 1% Cr by weight of the support the parameters set forth below are representative. The atomic ratios are based upon a calculation of the metal in the metallic reducing agent and/or the non-metal in the non-metallic reducing agent versus the chromium content present in the chromium-containing compound on the support.

For example, based upon a catalyst composition containing about 1% by weight of Cr based upon the weight of the support, the preferred amount of an organometallic reducing agent for use therewith, e.g., triisobutyl aluminum (TIBAL), is about 11.4% by weight and equivalent to an Al/Cr atomic ratio of about 3/1. The preferred range of atomic ratios of Al to Cr is from about 0.5/1 to about 8/1, or from about 1.9% to about 30% by weight TIBAL. The overall commercially practicable limits of TIBAL in terms of the Al/Cr atomic ratio are from about 0.1/1 to 20/1, and in terms of weight are from about 0.4% to about 75% by weight.

Another example of an organometallic reducing agent for use in the catalyst compositions of the present invention is triethyl aluminum. Again based upon a catalyst composition containing about 1% by weight of Cr based upon the weight of the support, the preferred amount of triethyl aluminum (TEA) is about 6.6% by weight based upon the weight of the support giving an Al/Cr atomic ratio of about 3/1. The preferred range of atomic ratios of Al to Cr is from about 0.5/1 to about 8/1, or from about 1.1% to about 18% by weight of TEA. The overall commercially practicable limits of TEA, in terms of an Al/Cr ratio, are from about 0.1/1 to 20/1, and in terms of weight are from about 0.22% to about 44% by weight.

Triethyl boron (TEB) may be taken as the preferred example for the proportions of non-metallic reducing agent for use in the catalyst compositions of the present invention. Again based upon a catalyst composition containing about 1% by weight of Cr based upon the weight of the support, the preferred amount of TEB is about 5% by weight based upon the weight of the support giving a B/Cr atomic ratio of about 2.7/1. The preferred range of atomic ratios of B to Cr is from about 0.1/1 to 10/1, or from about 0.19 to about 19% TEB. The overall practicable limits, in terms of a B/Cr ratio, are from about 0.01/1 to about 20/1, and in terms of weight, are from about 0.02% to about 38% by weight based upon the weight of the support.

As indicated above, the catalyst compositions of this invention are amenable to use with conventional polymerization processes for olefins, in particular 1-olefins having 2-8 carbon atoms, and are suitable for polymerization effected under temperature and pressure conditions generally employed in the art, e.g., temperatures of from about 40°C to about 200°C and preferably from 70° to 110°C, and pressures of from 200 to 1000 psig and preferably from 300 to 800 psig, as are used in slurry or particle form polymerizations.

A series of olefin polymerizations, the results of which are reported in Tables I to VI below, were carried out to demonstrate the ability of the catalysts of the present invention to produce polymers having enhanced physical properties such as increased melt indices. The polymerizations were carried out in a stirred autoclave using isobutane as a diluent. The supported chromium-containing compound and aluminum-containing compound where used and the reducing agent where used are added along with the isobutane solvent to a stirred one gallon autoclave. The contents of the stirred autoclave are then heated to the polymerization temperature, i.e., 88 to 108°C. Hydrogen, if used, is added and then ethylene is added to give 10 mol % in the liquid phase at which time the total pressure will be from 425 to 455 psig. Polymerization begins almost immediately as noted by the ethylene coming from the ethylene demand supply system to the reactor. After approximately one hour of polymerization, the reaction is terminated by dropping the reactor contents into a pressure let-down system. The melt index (M.I.) and the high load melt index (HLMI) of the polymers prepared were determined using ASTM D-1238-65T (conditions E and F respectively).

The catalysts used in the polymerizations run of Tables I - VI below were prepared in accordance with the following Catalyst Preparation Procedure.

CATALYST PREPARATION PROCEDURE

A. Silica gel having a pore volume of about 2.5 cc/g prepared in accordance with the disclosure in USP 3,652,215 is added to a 2000 ml, three-neck round bottom flask equipped with a stirrer, nitrogen inlet and Y-tube with water condenser. A nitrogen atmosphere is maintained during the coating operation. Dichloromethane is then added to the flask containing the silica gel and stirring is commenced to ensure uniform wetting of the gel. A dichloromethane solution of the reaction product of CrO_3 and triethyl phosphate prepared as described in British Patent No. 1490141 is then added to the flask in sufficient quantity to provide a dry coated catalyst containing about 1% by weight of Cr. The supernatant liquid is removed by filtration and the coated gel is dried in a rotary evaporator at 60°C and with 29 inches of Hg vacuum.

B. Dichloromethane is added to a similar flask as used in step A and while maintaining a nitrogen atmosphere stirring is commenced. To the flask is added the supported chromium composition prepared in step A above. A solution of dichloromethane and aluminum secbutoxide is prepared in a pressure equalizing dropping funnel and the funnel attached to the stirred flask. The aluminum sec-butoxide solution is gradually added to the flask at the rate of 10 grams of solution per minute. After the addition of the solution is complete the slurry in the flask is stirred for about 1 hour. The supernatant liquid is removed by filtration and the coated gel is dried in a rotary evaporator at temperatures up to about 60°C and 29 inches Hg vacuum. The amount of aluminum compound added depends on the % aluminum desired for the production of olefin polymers having specific properties necessary for certain end use applications.

C. To heat activate the catalyst composition prepared in step B, the supported catalyst is

placed in a cylindrical container and fluidized with dry air at 0.20 feet per second superficial linear velocity while being heated to a temperature of 900°C and held at this temperature for six hours. The activated supported catalyst is recovered as a powder.

In Table I a series of polymerizations were carried out to illustrate the results from using increased amounts of the aluminum compound in the preparation of the catalyst. The catalysts were prepared as in the Catalyst Preparation Procedure above. Except as noted, polymerizations were carried out at 93.5°C and hydrogen (30psi) and triethyl borane (2.7B/Cr atomic ratio) were added to the polymerization reactor.

TABLE I

Al% wt./SiO ₂ (1)	Productivity (gms) Polymer/gm cat./hr.)	MI	HLMI
None	558	low	7.0
.1	1328	0.04	9.1
.2	717	0.05	11.4
1.0	780	0.36	67.5
2.4	926	1.10	116.5
3.7	886	2.68	340
5.5(2)	616	4.90	390

(1) gms Al per 100 gms SiO₂ support

(2) Polymerization temperature 99°C
B/Cr atomic ratio 2.9

In Table II below a series of polymerizations were carried out to demonstrate the dramatic response of the catalysts of the present invention to increasing hydrogen concentrations. The catalysts were prepared in accordance with the Catalyst Preparation Procedure above. For comparison purposes polymerizations using a catalyst prepared without the aluminum compound of step B were included. The polymerizations were carried out at about 99°C and triethyl borane (2.9 B/Cr atomic ratio) was added to the polymerization reactor.

TABLE II

Hydrogen (psi)	Al%Wt./SiO ₂	Productivity (gmPE(gm cat./hr.)	MI	HLMI
None	3.7	1198	1.5	127.2
None	None	1158	0.07	9.0
30	3.7	1032	5.52	419
30	None	1194	0.12	14.5
75	3.7	910	18	High
75	None	684	0.37	32.0
120	3.7	613	22.6	High
120	None	482	0.69	52.4

In Table III below a series of polymerizations were carried out to demonstrate the improved hydrogen response of the catalysts of the present invention as indicated by the increase in melt index compared to catalysts without the aluminum and/or triethyl borane (TEB) present. The catalysts were prepared as in the Catalyst Preparation Procedure above, except that the aluminum compound of step B was omitted where indicated. The polymerizations were carried out at about 99°C and hydrogen was added to the reactor at a pressure of 120 psi except as otherwise indicated.

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TABLE III

	B/Cr (Atomic Ratio)	Al% Wt./SiO ₂	H ₂ (psi)	Productivity (gmPE/gm cat./hr.)	MI	HLMI	
5							
	0	None	0	622	0.26	27.8	
	2.9	None	0	1158	0.07	9.0	
	0	3.7	0	1032	0.71	53.6	10
	0	3.7	0	1048	1.70	118.8	
10	2.9	3.7	0	190	0.58	43.9	
	0	None	30	1399	0.75	58.2	
	0	3.7	30	636	0.24	26.0	
	1.45	None	120	736	10.0	High	15
	1.45	3.7	120	482	0.69	52.4	
15	2.9	None	120	613	22.6	High	
	2.9	3.7	120	483	0.50	49.5	
	5.8	None	120	4.22	40.3	High	20
	5.8	3.7	120				

In Table IV below polymerizations were carried out to illustrate the effect of increasing polymerization reaction temperature on the melt index of polymers produced using the catalysts of the present invention. The catalysts were prepared in accordance with the Catalyst Preparation Procedure above. For comparison purposes polymerizations using a catalyst prepared without the aluminum compound of step B were included. Hydrogen, at a pressure of 120 psi and triethyl borane (2.9B/Cr atomic ratio) were added to the reactor.

TABLE IV

	Al%Wt./SiO ₂	Polymerization Temperature (°C)	Productivity (gmPolymer/gm cat./hr)	MI	HLMI	
30						
	3.7	88	561	1.75	183	
	None		544	low	5.2	
35	3.7	93.5	784	6.2	(1)	
	None		879	0.10	12.4	40
	3.7	99	613	22.6	(1)	
40	None		482	0.69	52.4	
	3.7	101.5	437	189.0	(1)	
	None		434	0.58	59.8	45

(1) Too high to measure accurately

In Table V a series of polymerizations were carried out to illustrate the suitability of using aluminum-containing compounds other than aluminum sec-butoxide in the catalysts of the present invention. The catalysts were prepared in accordance with the Catalyst Preparation Procedure above using the aluminum-containing compound specified in the table in step B. The polymerizations were carried out at about 99°C and hydrogen at a pressure of 120 psi and triethyl borane (2.9 B/Cr atomic ratio) were added to the reactor.

TABLE V

Productivity
(gm Polymer/gm
cat./hr)

Al Compound	Al% Wt./SiO ₂	Productivity (gm Polymer/gm cat./hr)	MI	HLMI
None	None	482	.69	52.4
Aluminium	3.7	613	22.6	High
Sec-butoxide				
Diisobutyl Aluminum	3.7	801	20.8	1052
Ethoxide				
Diethyl Aluminum	3.7	669	16.8	1093
Ethoxide				
Aluminum Phenoxide	3.7	540	4.3	417
Triisobutyl	2.1	744	24.2	1980
Aluminum				

In Table VI, polymerizations were carried out to demonstrate the use of other supports and other chromium-containing compounds in the catalysts of the present invention. In Runs 1 and 2 a catalyst was prepared in accordance with the Catalyst Preparation Procedure of step A using MS 952 silica gel, a product of W. R. Grace & Co., which has a pore volume of about 1.6 cc/g as the support material. In Runs 3 and 4 a similar catalyst using MS 952 silica gel was used with the aluminum compound of step B added. The catalysts used in Runs 1-4 were heat activated as in step C at a temperature of 840° instead of 900°C. In Runs 5 and 6 a catalyst prepared by depositing CrO₃ on a silica gel having a pore volume of about 2.5 cc/g and heat activating at a temperature of about 900°C for six hours was used. Runs 7 and 8 used the same CrO₃ catalyst as Runs 5 and 6 with the aluminum compound being added as in Step B of the Catalyst Preparation Procedure. The chromium content of the catalysts in Runs 5-8 is about 0.69%. The polymerization of Runs 1-8 were carried out at 99°C using triethyl borane (2.9 B/Cr atomic ratio) with or without hydrogen as indicated in Table VI.

TABLE VI

Run No.	Al% Wt./SiO ₂	Productivity (gm Polymer/gm cat./hr)	H ₂ (p.s.i.)	MI	HLMI
1	None	660	None	0.05	9.6
2	None	669	30	.125	17.9
3	3.7	701	None	0.62	85.6
4	3.7	639	30	3.3	497
5	None	1097	None	0.15	18.1
6	None	832	30	0.86	62
7	3.7	704	None	19.6	1823
8	3.7	683	30	114.2	High

WHAT WE CLAIM IS:-

1. An olefin polymerisation catalyst comprising (1) a solid inorganic support material having surface hydroxyl groups and having deposited thereon (a) a chromium-containing compound capable of reacting with said surface hydroxyl groups, and (b) an aluminum-containing compound capable of reacting with said surface hydroxyl groups, the supported chromium-containing compound and aluminum-containing compound having been heated in a non-reducing atmosphere at a temperature above 300°C up to the decomposition temperature of the support material, and the thus heat-treated supported chromium- and aluminum-containing compounds being in the presence of (2) a metallic or non-metallic reducing agent other than hydrogen of said aluminum-containing compound.

2. A catalyst according to claim 1 wherein the support material comprises silica gel.

3. A catalyst according to claim 2 wherein the inorganic support material is a silica gel having a surface area of 200 to 500 m²/g and a pore volume above 2.0 cc/g, a major portion of the pore volume being provided by pores having diameters of 300 to 600 Å.

4. A catalyst according to any of claims 1 to 3 wherein said chromium-containing compound is the reaction product of chromium trioxide and a phosphorus compound having the formula:



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TABLE V

	Al Compound	Al% Wt./SiO ₂	Productivity (gm Polymer/gm cat./hr)	MI	HLM I	
5	None	None	482			5
	Aluminium	3:7	613	.69	52.4	
	Sec-butoxide			22.6	High	
10	Diisobutyl Aluminium	3.7	801	20.8	1052	10
	Ethoxide					
	Diethyl Aluminium	3.7	669	16.8	1093	
	Ethoxide					
15	Aluminium Phenoxide	3.7	540	4.3	417	15
	Triisobutyl	2.1	744	24.2	1980	
	Aluminium					

In Table VI, polymerizations were carried out to demonstrate the use of other supports and other chromium-containing compounds in the catalysts of the present invention. In Runs 1 and 2 a catalyst was prepared in accordance with the Catalyst Preparation Procedure of step A using MS 952 silica gel, a product of W. R. Grace & Co., which has a pore volume of about 1.6 cc/g as the support material. In Runs 3 and 4 a similar catalyst using MS 952 silica gel was used with the aluminum compound of step B added. The catalysts used in Runs 1-4 were heat activated as in step C at a temperature of 840° instead of 900°C. In Runs 5 and 6 a catalyst prepared by depositing CrO₃ on a silica gel having a pore volume of about 2.5 cc/g and heat activating at a temperature of about 900°C for six hours was used. Runs 7 and 8 used the same CrO₃ catalyst as Runs 5 and 6 with the aluminum compound being added as in Step B of the Catalyst Preparation Procedure. The chromium content of the catalysts in Runs 5-8 is about 0.69%. The polymerization of Runs 1-8 were carried out at 99°C using triethyl borane (2.9 B/Cr atomic ratio) with or without hydrogen as indicated in Table VI.

TABLE VI

Run No.	Al% Wt./SiO ₂	Productivity (gm Polymer/gm cat./hr)	H ₂ (p.s.i.)	MI	HLM I	
1	None	660				35
2	None	669	None	0.05	9.6	
3	3.7	701	30	.125	17.9	
4	3.7	639	None	0.62	85.6	40
5	None	1097	30	3.3	497	
6	None	832	None	0.15	18.1	
7	3.7	704	30	0.86	62	
8	3.7	683	None	19.6	1823	45
			30	114.2	High	

WHAT WE CLAIM IS:-

1. An olefin polymerisation catalyst comprising (1) a solid inorganic support material having surface hydroxyl groups and having deposited thereon (a) a chromium-containing compound capable of reacting with said surface hydroxyl groups, and (b) an aluminum-containing compound capable of reacting with said surface hydroxyl groups, the supported chromium-containing compound and aluminum-containing compound having been heated in a non-reducing atmosphere at a temperature above 300°C up to the decomposition temperature of the support material, and the thus heat-treated supported chromium- and aluminum-containing compounds being in the presence of (2) a metallic or non-metallic reducing agent other than hydrogen of said aluminum-containing compound.
2. A catalyst according to claim 1 wherein the support material comprises silica gel.
3. A catalyst according to claim 2 wherein the inorganic support material is a silica gel having a surface area of 200 to 500 m²/g and a pore volume above 2.0 cc/g, a major portion of the pore volume being provided by pores having diameters of 300 to 600 Å.
4. A catalyst according to any of claims 1 to 3 wherein said chromium-containing compound is the reaction product of chromium trioxide and a phosphorus compound having the formula:

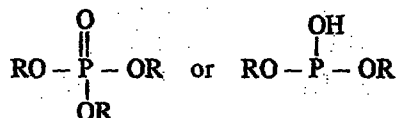
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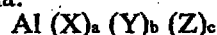


wherein R is alkyl, aralkyl, aryl, cycloalkyl or hydrogen, but at least one R is other than hydrogen.

5. A catalyst according to claim 4 wherein the chromium-containing compound is the reaction product of chromium trioxide and triethyl phosphate.

6. A catalyst according to any of claims 1 to 3 wherein the chromium-containing compound is chromium trioxide.

7. A catalyst according to any of claims 1 to 6 wherein the aluminum-containing compound is represented by the formula:



wherein X is R, Y is OR and Z is H or a halogen; a is 0-3, b is 0-3, c is 0-3, and a + b + c = 3; and R is an alkyl or aryl group having from one to eight carbon atoms.

8. A catalyst according to claim 7 wherein the aluminum-containing compound is an aluminum alkoxide.

9. A catalyst according to claim 8 wherein the aluminum-containing compound is aluminum sec-butoxide.

10. A catalyst according to claim 7 wherein the aluminum compound is an aluminum alkyl.

11. A catalyst according to claim 10 wherein the aluminum compound is triethyl aluminum or triisobutyl aluminum.

12. A catalyst according to any of claims 1 to 11 wherein the chromium-containing compound is present in an amount sufficient to provide 0.25 to 2.5% by weight of Cr based upon the weight of the support and the aluminum-containing compound is present in an amount sufficient to provide 0.10 to 10% by weight of Al based upon the weight of the support.

13. A catalyst according to any of claims 1 to 12 wherein the supported chromium-containing compound and aluminum containing compound has been heated at a temperature of from 300 to 1000°C for a period of 1/2 to 50 hours.

14. A catalyst according to claim 13 wherein the supported chromium-containing compound and aluminum-containing compound has been heated at a temperature of from 500 to 1000°C for a period of 2 to 12 hours.

15. A catalyst according to any of claims 1 to 14 wherein the reducing agent is a boron-containing compound.

16. A catalyst according to claim 15 wherein the boron-containing compound is a trialkyl borane.

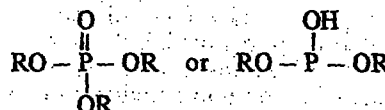
17. A catalyst according to claim 16 wherein the trialkyl borane is triethyl borane.

18. A process for the preparation of an olefin polymerization catalyst which comprises (i) depositing a chromium-containing compound and an aluminum-containing compound on a solid inorganic support material having surface hydroxyl groups, said chromium-containing compound and said aluminum-containing compound being capable of reacting with said surface hydroxyl groups, (ii) heating said support material having the chromium-containing compound and the aluminum-containing compound deposited thereon in a non-reducing atmosphere at a temperature above 300°C up to the decomposition temperature of the support material, and (iii) admitting into the presence of the heat-treated, supported chromium-containing compound and aluminum containing compound a metallic or non-metallic reducing agent other than hydrogen and the said aluminum-containing compound.

19. A process according to claim 18 wherein the support material comprises silica gel.

20. A process according to claim 19 wherein the inorganic support material is a silica gel having a surface area of 200 to 500 m²/g and a pore volume above 2.0 cc/g, a major portion of the pore volume being provided by pores having diameters of 300 to 600 Å.

21. A process according to any of claims 18 to 20 wherein said chromium-containing compound is the reaction product of chromium trioxide and a phosphorus compound having the formula:





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wherein R is alkyl, aralkyl, aryl, cycloalkyl or hydrogen, but at least one R is other than hydrogen.

22. A process according to claim 21 wherein the chromium-containing compound is the reaction product of chromium trioxide and triethyl phosphate.

23. A process according to any of claims 18 to 20 wherein the chromium-containing compound is chromium trioxide.

24. A process according to any of claims 18 to 23 wherein the aluminum-containing compound is represented by the formula:



wherein X is R, Y is OR and Z is H or a halogen; a is 0-3, b is 0-3, c is 0-3, and $a + b + c = 3$; and R is an alkyl or aryl group having from one to eight carbon atoms.

25. A process according to claim 24 wherein the aluminum-containing compound is an aluminum-alkoxide.

26. A process according to claim 25 wherein the aluminum-containing compound is aluminum sec-butoxide.

27. A process according to claim 24 wherein the aluminum compound is an aluminum alkyl.

28. A process according to claim 27 wherein the aluminum compound is triethyl aluminum or triisobutyl aluminum.

29. A process according to any of claims 18 to 28 wherein the chromium-containing compound is present in an amount sufficient to provide 0.25 to 2.5% by weight of Cr based upon the weight of the support and the aluminum-containing compound is present in an amount sufficient to provide 0.10 to 10% by weight of Al based upon the weight of the support.

30. A process according to any of claims 18 to 29 wherein the supported chromium-containing compound and aluminum containing compound is heated at a temperature of from 300 to 1000°C for a period of ½ to 50 hours.

31. A process according to claim 30 wherein the supported chromium-containing compound and aluminum-containing compound is heated at a temperature of from 500 to 1000°C for a period of 2 to 12 hours.

32. A process according to any of claims 18 to 31 wherein the reducing agent is a boron-containing compound.

33. A process according to claim 32 wherein the boron-containing compound is a trialkyl borane.

34. A process according to claim 33 wherein the trialkyl borane is triethyl borane.

35. A process according to any of claims 18 to 34 wherein the aluminum-containing compound is dissolved in an inert organic solvent and then deposited on the support material.

36. A catalyst obtained by a process according to any of claims 18 to 35.

37. A process for the polymerization of an olefin which comprises contacting the olefin with a catalyst according to any of claims 1 to 17 and 36 under polymerization conditions.

38. A process according to claim 37 wherein the polymerization is carried out in the presence of hydrogen.

39. An olefin polymerization catalyst which comprises a heat-treated supported chromium-containing compound and aluminum-containing compound in the presence of a reducing agent other than hydrogen or said aluminum-containing compound and which is substantially as hereinbefore described with reference to any one of the runs of any one of Tables I to VI.

40. A process for the preparation of an olefin polymerization catalyst which comprises a heat-treated supported chromium-containing compound and aluminum-containing compound in the presence of a reducing agent other than hydrogen or said aluminum-containing compound, the process being substantially as hereinbefore described with reference to any one of the runs of any one of Tables I to VI.

41. A catalytic olefin polymerization process using a catalyst which comprises a heat-treated supported chromium-containing compound and aluminum-containing compound in the presence of a reducing agent other than hydrogen or said aluminum-containing compound, the process being substantially as hereinbefore described with reference to any one of the runs of any one of Tables I to VI.

42. A polyolefin obtained by a process according to claim 37, 38 or 41.

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