

Description

Background of the invention

5 This invention relates to the production of silica-titania cogels.

Since its commercialization in the 1950's, chromium oxide on silica has become the dominant catalyst system used throughout the world to produce high density polyethylene. Over the years various refinements have been made in these catalysts, one of the most significant being the discovery that the presence of titanium imparts many beneficial characteristics to the catalyst. It has further been discovered that the very
10 best results are generally obtained by coprecipitating an alkali metal silicate and a titanium compound to give a silica-titania cogel. While this represents an extraordinarily satisfactory product from the standpoint of catalyst properties, it is hard to make because of the necessity to wash out alkali metal ions and because of the necessity to use a volatile, water-miscible organic solvent to very carefully remove the water.

Another method for producing silica-titania cogels is shown in U.S. Patent 4,339,559. According to this
15 method, a silica ester is hydrolyzed using an acid catalyst in an organic solvent and water, a titanium alkoxide is then added to the at least partially hydrolyzed silica, excess water is then added to allow growth, a gelling agent is then added to neutralize the acid, and finally the gel is aged. The present invention is a process for producing silica-titania cogel using hydrolysis under alkaline conditions and is thereby distinct from the method disclosed in U.S. Patent 4,339,559.

Summary of the invention

It is an object of this invention to produce a silica-titania cogel which does not require a washing step to
25 remove alkali metal ions;

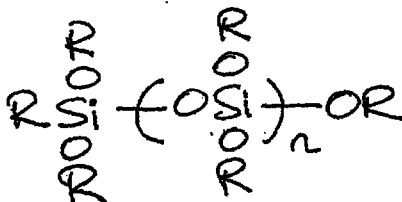
It is a further object of this invention to produce a silica-titania cogel which does not require the use of a water-miscible organic solvent to gently remove the water; it is yet a further object of this invention to provide an improved polymerization catalyst; and

it is still a further object of this invention to provide an improved polymerization process.

30 In accordance with this invention a process for preparing silica-titania cogel as defined in claim 1 is provided, in which a silicate ester is first only partially hydrolyzed with water. Thus, an organopolysilicate and/or a tetraorganosilicate are partially hydrolyzed in an organic solvent under alkaline conditions in a first hydrolysis step and thereafter a titanium tetraalkoxide is combined with the partially hydrolyzed product of the first step, followed by enough water in a second hydrolysis step to complete the hydrolysis, and finally
35 further base is added to effect gelation. The catalyst made by this process and the olefin polymerization using this catalyst constitute further embodiments of the invention and are defined in the claims.

Description of the Preferred Embodiments

40 The organopolysilicate and tetraorganosilicate utilized in forming the cogels of this invention can be represented by the formula below where R is an alkyl, aryl or alkaryl group containing from 1 to 8 carbon atoms, preferably from 2 to 4 carbon atoms and n is 0-8:



45 The scope of the R groups can be the same with the polysilicate (where n is 1-8) as with the tetraorganosilicate (where n is 0) but generally as a matter of convenience the preferred group for the tetraorganosilicate is n-propyl (tetra-n-propoxysilicate) and the preferred group for the polysilicate is ethyl (ethyl polysilicate). Other suitable organopolysilicates and tetraorganosilicates include for example tetraisobutoxysilane, tetra-n-phenoxyssilane, tetra-n-hexoxysilane, tetramethoxysilane, tetraethoxysilane,
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tetraisopropoxysilane, tetra(2-ethylhexoxy)silane, tetraphenoxysilane, hexaethoxydisiloxane, and methyltris-(tri-sec-butoxysiloxy)silane.

The preferred silicate esters are those where n is greater than 0 simply because for given weight there is a greater weight percentage of silicon in the polysilicate than in the tetraorganosilicate.

5 The organic solvent employed in the process of this invention can be any liquid which mutually dissolves or is at least sufficiently miscible with water, the silicate ester (tetraorganosilicate or polysilicate) and the resulting partially hydrolyzed silicate ester, that phase separation does not occur during the hydrolysis. Preferably, oxygen-containing, normally liquid organic materials are used although other materials can be used. It is most convenient to use a saturated aliphatic alcohol containing from 1 to 6 carbon
10 atoms, preferably 2 to 4 carbon atoms as the solvent, since an alcohol is formed from the silicate esters during their hydrolysis. Sometimes, particularly with the tetraorganoxysilicate esters, the alcohol solvent and silicon ester are chosen so that the ester on hydrolysis gives the same alcohol as is already present or at least has the same number of carbon atoms, although this is by no means an essential criteria. Exemplary solvents include acetone, methylethyl ketone, ethyl acetate, methanol, ethanol, 1-propanol, 2-propanol, 1-
15 butanol, 2-butanol, 2-methyl-1-propanol, 2-methyl-2-propanol, 1-pentanol, 2-pentanol, 3-methyl-1-butanol, 3-methyl-2-butanol, 3-pentanol, 2-methyl-2-butanol, 2,2-dimethyl-1-propanol, 2-methyl-1-butanol, 1-hexanol, and other liquid alcohols. Presently preferred compounds include ethanol and the 3- and 4-carbon alcohols because of their availability and solubility in water. The 3 and 4 carbon atom alcohols are preferred over ethanol because of their slightly lower volatility.

20 The titanium tetraalkoxide can be represented by the general formula $Ti(OR')_4$ wherein R' is a 1-6, preferably 2-4 carbon atom alkyl group. The most preferred compound is tetraisopropyl titanate.

The titanium ester can be added in an amount sufficient to give $\frac{1}{2}$ -20, preferably 1-5 wt. percent Ti in the final catalyst.

In the first hydrolysis step the amount of water employed ranges from 10-90 preferably 15-60 percent
25 of the stoichiometric amount required for complete hydrolysis. This water can simply come from the alkaline solution used to give alkaline conditions or water can be added separately instead of or in addition to that from the concentrated ammonium hydroxide or whatever aqueous base is being used.

After the partially hydrolyzed product of the first hydrolysis step is reacted with the titanium tetraalkoxide, water is added in the second hydrolysis step in an amount which brings the total added water within
30 the range of 1 to 10 preferably 1.5-5 times the stoichiometric amount needed to complete the hydrolysis.

The agent utilized to produce the alkaline conditions for the hydrolysis steps is preferably ammonia or concentrated ammonium hydroxide. Other suitable bases include normally gaseous or liquid primary, secondary or tertiary alkyl or cycloalkylamines which are at least partially stable in the organic solvent employed. Examples of the amines include methylamine, ethylamine, dodecylamine, octadecylamine, 2-
35 ethylhexylamine, cyclohexylamine, diisopropylamine, didodecylamine, trioctylamine, and the like. Also suitable are tetraalkylammonium hydroxides such as tetramethylammonium hydroxide. However, concentrated ammonium hydroxide is preferred because of its low cost. The same scope of alkaline agent can be used to precipitate the cogel from the resulting sol (silica colloid) after the hydrolysis is complete, again concentrated ammonium hydroxide being preferred.

40 After the formation of the cogel, it is preferably aged at room temperature to $100^\circ C$, preferably 50 to $100^\circ C$ for at least 10 minutes preferably 1 to 50 hours, more preferably 1 to 4 hours. If desired additional solvent can be added at this point in order to form a slurry. The aging can be done at any temperature from room temperature to reflux temperature for the solvent but preferably is at or about the reflux temperature.

The resulting cogel can be dried by conventional simple techniques such as oven drying, vacuum
45 drying, or tray drying to produce a xerogel. The drying temperature can be from room temperature to $400^\circ C$ but is preferably above the boiling point of the organic solvent. Because of the essentially anhydrous nature of the process the use of an azeotrope to remove water in a gentle manner so as to avoid collapse of the pores is totally unnecessary as are conventional washing steps to remove alkali metal ions since no alkali metal ions are present. Water is present when an excess of the stoichiometric amount is used in the
50 second hydrolysis step but this does not require the use of elaborate azeotrope drying for two reasons. First the amount of water present even if 10 times the amount needed for complete hydrolysis is used, is still a relatively small amount based on the solvent. Second, the critical factor in prior art techniques is removing water from the pores without collapse. Here the pores start out filled with alcohol rather than water since alcohol is the by-product of the hydrolysis reaction to produce the silica, i.e. $Si(OR)_4 + 2H_2O$ gives SiO_2
55 plus $4ROH$.

If the purpose is to produce a support for chromium olefin polymerization catalysts the chromium can be coprecipitated with the silica-titania cogel, thus producing a tergel of silica-titania-chromium. Alternatively the chromium compound can be added anhydrously to the resulting gel. Any chromium compound can be

utilized as is known in the art. For instance, the support can be activated and thereafter a zerovalent chromium compound utilized or a chromium compound such as chromium oxide, chromium acetate, chromium nitrate or tertiary-butyl chromate can be added and thereafter the chromium-containing composition activated. The activation is carried out in an oxygen-containing ambient such as air at a temperature of 300 to 900°C, preferably 500 to 700°C for a time of at least five minutes, preferably ten minutes to ten hours, more preferably 30 minutes to three hours.

The chromium compound is used in an amount sufficient to give 0.1 to 10, preferably 0.5 to 2, most preferably about 1, weight percent chromium based on the weight of dried silica, i.e. the xerogel, plus chromium compound.

The catalysts of this invention can be used to polymerize at least one mono-1-olefin 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 1 or more comonomers selected from 1-olefins or dienes containing 3 to 8 carbon atoms per molecule. Exemplary comonomers include aliphatic 1-olefins, such as propylene, 1-butene, 1-hexene, and the like and conjugated or nonconjugated diolefins, such as 1,3-butadiene, isoprene, piperylene, 2,3-dimethyl-1,3-butadiene, 1,4-pentadiene, 1,5-hexadiene, and the like and mixtures thereof. Ethylene copolymers preferably constitute about 90, preferably 95 to 99 mole percent polymerized ethylene units. Most preferred monomers are at least one of ethylene, propylene, 1-butene, and 1-hexene.

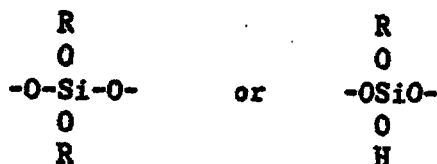
The polymers can be prepared from the activated catalysts of this invention by solution polymerization, slurry polymerization, and gas phase polymerization techniques using conventional equipment and contacting processes. However, the catalysts of this invention are particularly suitable in slurry polymerizations for the production of high melt index (MI) polymers. Particle form (slurry) polymerizations are carried out in an inert diluent such as a paraffinic, aromatic or cycloparaffinic hydrocarbon at a temperature where the resulting polymer is insoluble. For predominantly ethylene polymer, the particle form process is carried out at a temperature of about 66° to 110°C.

The catalysts of this invention can be used with conventional cocatalysts such as triethylaluminum, diethyl aluminum chloride, ethyl aluminum dichloride, triethylborane, and other known organometal cocatalysts preferably boron and aluminum alkyls, the alkyl groups generally being 1-4 carbon atoms, if desired. Also, hydrogen can be used to further increase the melt index if desired.

While the primary emphasis of this invention is on a simplified method of producing catalysts essentially identical to that produced with conventional techniques but without the necessity for removing alkali metal ions in water, the catalyst is not necessarily exactly identical to that produced by the conventional methods in that it is slightly more active and produces considerably higher melt flow polymer both of which are desirable characteristics.

Example 1-Invention Catalyst A

Invention catalyst A consists of silica-titania cogel impregnated with methanolic chromium nitrate solution sufficient to provide a composite, after calcining in air, containing a calculated amount of TiO₂ sufficient to give 1.5 weight percent titanium chromium oxide sufficient to give 1.0 weight percent chromium and the balance as silica. Invention catalyst A was prepared by admixing 100 mL of 1-propanol (1338 mmoles), 100 mL of Silbond® 40, a partly hydrolyzed tetraethoxysilane with a substantial portion thereof having an average of 4-5 silicon atoms per molecule and 40 weight percent SiO₂ content, available commercially from the Stauffer Chemical Co., Westport, Conn, and 5 mL of concentrated ammonium hydroxide (28 wt.% NH₃, about 75 mmoles NH₃ and 180 mmoles H₂O yielding a clear solution. Since 14.5 mL water are required to completely hydrolyze 100 mL Silbond 40®, this represents about 25 percent hydrolysis. However, the NH₄OH may also react to an unknown degree to make Si-NH₂ or other groups. After stirring 5 minutes, 5 mL (17.5 mmoles) of tetraisopropyl titanate [Ti(O-i-Pr)₄] was added to react with the siloxane chains resulting in a clear, rather viscous solution. By siloxane chains is meant the chains resulting from the partial hydrolysis of the organopolysilicate and/or tetraorganosilicate, such as:



The titanium ester is believed to react with hydroxyls on these chains, and thus become immobilized. After stirring the solution for 5 minutes, 20 mL (1111 mmoles) of deionized water was added and the resulting clear solution was stirred an additional 5 minutes. The fact that TiO_2 did not precipitate out indicates that the titanium ester had indeed reacted with the silica sol. Then 5 mL of concentrated ammonium hydroxide was added with stirring resulting in the formation of a clear colorless hard gel within about 2 minutes. This brings the total water added up to 27.2 mL or about 190 percent of that required for complete hydrolysis. The gel was allowed to sit undisturbed at ambient conditions over the weekend (about 65 hours), then it was aged for 2 hours at 80°C and dried overnight at 80° in a vacuum oven. The dry product was crushed and screened through a 0.40mm (35 mesh) screen and the screened material was impregnated with a methanolic solution of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, containing 0.01 g Cr/mL, sufficient to provide 1.0 weight percent Cr, based on the finished, activated (calcined) composite. After calcining for 3 hours in dry air at 850°C in a fluidized bed, the cooled product, flushed with nitrogen was stored for subsequent testing. Analysis disclosed the catalyst had a B.E.T. surface area of $404\text{ m}^2/\text{g}$ and a pore volume by alcohol adsorption of 2.19 mL/g .

Example 2 - Invention Catalyst B

Invention catalyst B consists of silica-titania cogel impregnated with alcoholic chromium nitrate solution sufficient to provide a composite, after calcining in dry air, containing a calculated 5.0 weight percent Ti as TiO_2 , 1.0 weight percent Cr as chromium oxide and the balance as silica. Invention catalyst B was prepared in a manner similar to that of invention catalyst A by admixing 100 mL of 1-propanol, 100 mL of Silbond 40 and 5 mL of concentrated ammonium hydroxide, that is to say enough water to effect about 25 percent hydrolysis. After stirring the resulting solution for 3 minutes, 12.4 mL (43.5 mmoles) of $\text{Ti}(\text{O}-i\text{-Pr})_4$ were added to react with the siloxane chains. After 3 minutes stirring, 30mL (1667 mmoles) of deionized H_2O was added and the resulting clear solution was stirred for 3 minutes. At that time a solution of 15mL of concentrated ammonium hydroxide equivalent to about 225 mmoles NH_3 and about 540 mmoles H_2O in 40 mL of 1-propanol was quickly added resulting in the formation of a clear, hard gel in about 30 seconds. Thus the total added water was about 44.4 ml or 300 percent of that required for hydrolysis. As before the gel was allowed to sit undisturbed over the weekend, then aged for 2 hours at 80°C and dried overnight at 80°C in a vacuum oven. After crushing and screening through a 0.40mm (35 mesh) screen, the resulting product was impregnated with sufficient of the methanolic solution of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as before to provide 1.0 weight percent Cr, based on the finished, activated composite. The composite was then activated as before. Analysis disclosed the catalyst to have a surface area of $356\text{ m}^2/\text{g}$ and a pore volume of 2.29 mL/g .

Example 3 - Invention Catalyst C

Invention catalyst C consists of a silica-titania-chromia tergel which after calcining in dry air, contains 3.6 weight percent Ti as TiO_2 , 1.0 weight percent Cr as chromium oxide and the balance as silica. Invention catalyst C was prepared in a manner similar to those of the previous Examples by admixing 100 mL of 1-propanol, 100 mL of Silbond® 40 and 5 mL of concentrated ammonium hydroxide. After stirring the resulting solution for about 3 minutes, 9.0 mL (31.6 mmoles) of $\text{Ti}(\text{O}-i\text{-Pr})_4$ were added to react with the siloxane chains resulting again in a clear solution. To the clear solution was added sufficient of methanolic chromium acetate solution containing 0.01 g Cr per mL to provide the desired 1.0 weight percent Cr resulting in a clear green solution. To the solution was added 20 mL of deionized water and then 5 mL of concentrated ammonium hydroxide. This brings the total water added up to about 190 percent that required for hydrolysis. Within 1 minute a hard, clear green gel formed. As before the gel was allowed to sit undisturbed over the weekend, then aged for 2 hours at 80°C and dried overnight in a vacuum oven at 80°C . The dry product was screened through a 0.40mm(35 mesh) screen and activated for 3 hours at 850°C in dry air as before. Analysis disclosed the catalyst had a surface area of $501\text{ m}^2/\text{g}$ and a pore volume of 2.02 mL/g .

Example 4 - Control Cogel Catalyst D

The control Catalyst D employed was a commercially obtained catalyst containing TiO_2 sufficient to give 2.5 weight percent Ti, chromium oxide sufficient to give 1.0 weight percent Cr and the balance as

silica. It can be prepared as disclosed in U.S. Patent 4,081,407 by contacting an aqueous solution of sodium silicate with an aqueous sulfuric acid solution containing titanyl sulfate to form a hydrogel. The hydrogel was aged, then repeatedly washed with water to reduce the sodium ion content to less than about 0.1 weight percent. The purified hydrogel is then impregnated with an aqueous solution of chromium(III) acetate sufficient to provide the desired quantity of Cr. Water is then removed from the mixture by azeotrope distillation with an alcohol such as 1-hexanol and the resulting product is activated in dry air as before to obtain the finished catalyst. Analysis disclosed the catalyst had a surface area of 430 m²/g and a pore volume of 2.25 mL/g.

Example 5 - Ethylene Polymerization

Ethylene polymerization runs were conducted in stirred, 2 liter, stainless steel reactor containing 1 liter of isobutane diluent containing 8 ppm triethylborane (TEB) adjuvant based on the weight of diluent. Charging order was catalyst, diluent and then sufficient ethylene supplied from a pressurized reservoir to maintain a reactor pressure of about 39.7 bar (565 psia) at the reactor temperature selected. Generally, a run was conducted for a time sufficient to produce approximately 3,000 g polymer per g catalyst. The recovered polymer in each run was dried, weighed and stabilized with a conventional antioxidant system, e.g. 2,6-di-*t*-butyl-4-methylphenol.

Productivity is expressed as that observed (OBS) in terms of g polymer per g solid catalyst per actual run time. It is also expressed as normalized (NORM) to a common run time of, e.g., 30 minutes for a better comparison in terms of g polymer per g solid catalyst per 30 minutes.

Melt index (MI) was determined in accordance with ASTM D1238, condition E.

High load melt index (HLMI) was determined in accordance with ASTM D1238, condition F.

HLMI/MI is thought to be related to polymer molecular weight distribution with the greater the value the broader the distribution.

The results are presented in Table I.

TABLE I

Ethylene Polymerization, No Hydrogen Present

36 Run No	Catalyst		Reactor Temp. °C	Polymer Yield g	Calculated Productivity		g/10 min.		HLMI MI	
	Wt% Ti	Wt mg			Obs. min. g/g/min	Norm. g/g/30 min.	MI	HLMI		
1	A	1.5	485	105	114	2350/60	1175	0.220	13.7	62
2	A	1.5	704	95	185	2630/28	2820	0.025	2.7	108
40 3	B	5.0	644	95	268	4160/31	4030	0.12	14.2	118
4	C	3.6	591	95	213	3600/39	2200	0.024	4.0	167
5	D	2.5	632	95	204	3230/33	2940	0.038	3.6	95

The data in Table I demonstrate that the invention catalysts A, B, C are active ethylene polymerization catalysts. At the same reactor temperature, 95°C, the productivity results indicate that the invention catalysts and the comparison catalyst have approximately similar activities and MI potential when compared at similar TI levels.

The polymerization results obtained indicate that cogel and tergel catalysts can be made by the two-stage hydrolysis process disclosed herein that are equivalent to similar catalysts made by prior art processes based on precipitation of alkali metal silicates with acids. The invention catalyst do not require the tedious, protracted washing needed by the prior art catalysts to reduce the alkali metal ion content and associated anions to a tolerable level.

Example 6

Invention catalyst E was prepared in the same manner as invention catalyst C of Example 3.

Comparison catalyst F was prepared in the same manner as comparison catalyst D of Example 4. The mercury intrusion profile of the interior pore volumes in each catalyst was determined by a standard mercury intrusion porosimetry method such as one described in ASTM D2873-70.

The results of the porosimetry tests are given in Table II in terms of mL/g at the specified pore size range in angstroms.

TABLE II

Interior Porosity Of Catalysts By Mercury Intrusion Porosimetry

Pore Size, nm	3 -9	9 -30	30 -60	60 -90	90 -200
Invention Catalyst E	0.248	0.41	0.31	0.21	0.40
Comparison Catalyst F	0.230	0.45	0.33	0.17	0.36

Pore Size, nm	200 - 400	400 - 10 00	1 ,000- 2 ,000	2 ,000- 10 ,000	Total
Invention Catalyst E	0.21	0.18	0.07	0.12	2.16
Comparison Catalyst F	0.19	0.14	0.07	0.15	2.09

The porosimetry data in Table II show that the invention catalyst made by the 2-step hydrolysis process and a comparison catalyst made by aqueous coprecipitation have nearly the same mercury intrusion profile. In fact, the data suggest that the invention catalyst may have slightly more volume inside the larger pores than does the comparison catalyst which is desirable in a 1-olefin polymerization catalyst.

Each catalyst was activated at 850° C and tested in ethylene polymerization at 105° C in isobutane containing 8 ppm TEB as described before. The results are given in Table III.

TABLE III

Ethylene Polymerization, 105°C, No Hydrogen

Run No	Catalyst		Polymer Yield g	Calculated Productivity		g/10 min.		HLMI MI
	No	Wt% Ti		Obs. g/g min	Norm. g/g/30 min.	MI	HLMI	
6	E	3.6	686	243	3542/20.7	5130	(a)	-
7	E	3.6	961	287	2986/77.5	1160	1.04	53.3
8	F	2.5	800	246	3071/34.2	2690	1.08	49.5

(a) A dash indicates not determined

The results in Table III demonstrate that the invention catalyst in run 7 and the comparison catalyst in run 8 have about the same melt index potential. This behavior is expected in view of the similar porosimetry results shown in Table II.

The run temperature of 105° C selected is near the fouling temperature because of the presence of TEB. This could account for relatively sluggish activity shown in run 7 with the invention catalyst wherein borderline fouling is believed to have occurred. That the sluggish activity is not due to the catalyst itself is seen by comparison with run 6 in which excellent activity is shown.

Example 7

A 1-step hydrolysis of a mixture of $\text{Si}(\text{OC}_2\text{H}_5)_4$ and $\text{Ti}(\text{O}-i\text{-Pr})_4$ in n-propanol was tried by adding sufficient water to precipitate titania and silica. However, the greater reactivity of the titanate precludes a cogel being formed. Instead, TiO_2 comes out first and later, the SiO_2 comes out separately.

Claims

1. A process for preparing a silica-titania gel characterized by
 - (a) partially hydrolyzing a silicate ester comprising at least one of an organopolysilicate and a tetraorganooxysilicate in an organic solvent under alkaline conditions using less than the stoichiometric amount of water required for complete hydrolysis;
 - (b) thereafter combining the partially hydrolyzed product of (a) with a titanium tetraalkoxide; thereafter
 - (c) adding water in an amount to complete the hydrolysis and produce a silica sol; and
 - (d) combining said silica sol with a base to form a silica-titania gel as well as, optionally,
 - (e) ageing the gel obtained in (d) and/or
 - (f) drying the gel to obtain a xerogel.
2. The process of claim 1 characterized in that in addition a chromium compound is introduced.
3. The process of claim 2 characterized in that said chromium compound is introduced prior to forming said gel so as to form a silica-titania-chromium target.
4. The process of any of claims 2 to 4 characterized in that said chromium compound is present in an amount to give 0.5 to 2 weight percent chromium based on the weight of the dried xerogel.
5. The process of any of the preceding claims characterized in that said organopolysilicate is ethyl polysilicate and said tetraorganooxysilicate is tetra-n-propoxysilane.
6. The process of any of the preceding claims characterized in that said organic solvent of (a) is rendered alkaline through the use of concentrated ammonium hydroxide.
7. The process of any of the preceding claims characterized in that said organic solvent is an alcohol; in particular wherein said alcohol is a 3 to 4 carbon atom alcohol; in particular wherein said alcohol is n-propanol.
8. The process of any of the preceding claims characterized in that said titanium tetraalkoxide is of the formula $Ti(OR')_4$ where R' is a 1 to 6 carbon atom alkyl group; in particular wherein said tetraalkoxide is tetraisopropyl titanate.
9. The process of any of the preceding claims characterized in that the total amount of water used is within the range of 1.5 to 5 times the stoichiometric amount needed for complete hydrolysis.
10. The process of any of the preceding claims characterized in that said base of (d) is ammonium hydroxide.
11. The process of any of the preceding claims characterized in that water is present in step (a) in an amount of 15-60 percent of the stoichiometric amount required for complete hydrolysis.
12. The chromium containing silica-titania cogel product obtained in any of claim 2 or claims referring back to claim 2.
13. A process for the polymerization of at least one mono-1-olefin having 2 to 8 carbon atoms per molecule employing the product of claim 12 as a catalyst.
14. A process of claim 13, wherein said olefin is selected from ethylene, propylene, 1-butene, 1-pentene, 1-hexene and 1-octene.
15. A process of claim 14, wherein said olefin comprises ethylene.
16. A process of claim 14 or 15, wherein said polymerization is carried out under slurry conditions.



Revendications

1. Procédé de préparation d'un gel silice-oxyde de titane, caractérisé en ce que :
 - (a) on hydrolyse partiellement un ester silicique comprenant au moins un polyorganosilicate et un tétraorganooxysilicate dans un solvant organique, en milieu alcalin, en utilisant une quantité d'eau inférieure à la quantité stoechiométrique nécessaire pour l'hydrolyse complète;
 - (b) on combine ensuite le produit partiellement hydrolysé de (a) avec un tétraalcoolate de titane; puis
 - (c) on ajoute de l'eau dans une quantité permettant d'achever l'hydrolyse et de préparer un sol de silice; et
 - (d) on combine ce sol de silice avec une base pour former un gel de silice-oxyde de titane, et le cas échéant,
 - (e) on fait vieillir le gel obtenu en (d) et/ou
 - (f) on sèche le gel pour obtenir un xérogel.
2. Procédé selon la revendication 1, caractérisé en ce qu'on introduit en outre un composé du chrome.
3. Procédé selon la revendication 2, caractérisé en ce que ce composé du chrome est introduit avant la formation de ce gel de manière à former un tégel silice-oxyde de titane-chrome.
4. Procédé selon l'une quelconque des revendications 2 à 4, caractérisé en ce que ce composé du chrome est présent dans une quantité donnant 0,5 à 2 % en poids de chrome par rapport au poids de xérogel séché.
5. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que ce polyorganosilicate est du polysilicate d'éthyle, et en ce que ce tétraorganooxysilicate est du tétra-n-propoxysilane.
6. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que ce solvant organique de (a) est alcalinisé au moyen d'hydroxyde d'ammonium concentré.
7. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que ce solvant organique est un alcool; en particulier dans lequel cet alcool est un alcool en C₃ à C₄, en particulier dans lequel cet alcool est le n-propanol.
8. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que tétraalcoolate de titane répond à la formule $Ti(OR')_4$ dans laquelle R' est un groupe alkyle en C₁ à C₆, en particulier dans lequel ce tétraalcoolate est le titanate de tétraisopropyle.
9. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que la quantité totale d'eau utilisée est dans l'intervalle de 1,5 à 5 fois la quantité stoechiométrique nécessaire pour une hydrolyse complète.
10. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que cette base de (d) est l'hydroxyde d'ammonium.
11. Procédé selon l'une quelconque des revendications précédentes, caractérisé en ce que l'eau est présente dans l'étape (a) dans une proportion qui est de 15 à 60 % de la quantité stoechiométrique nécessaire pour une hydrolyse complète.
12. Produit de co-gel silice-oxyde de titane contenant du chrome obtenu dans l'une quelconque des revendications 2 ou des revendications se référant à la revendication 2.
13. Procédé pour la polymérisation d'au moins une mono-l-oléfine en C₂ à C₈ en utilisant le produit de la revendication 12 comme catalyseur.
14. Procédé selon la revendication 13, dans lequel cette oléfine est choisie parmi l'éthylène, le propylène, le 1-butène, le 1-pentène, le 1-hexène et le 1-octène.



15. Procédé selon la revendication 14, dans lequel cette oléfine comprend de l'éthylène.

16. Procédé selon les revendications 14 ou 15, dans lequel cette polymérisation est effectuée en bouillie.

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Ansprüche

1. Verfahren zur Herstellung eines Siliciumdioxid-Titanoxid-Gels, gekennzeichnet durch
 - (a) partielles Hydrolysieren eines Silicatesters mit einem Gehalt an mindestens einem Organopolysilicat und einem Tetraorganooxysilicat in einem organischen Lösungsmittel unter alkalischen Bedingungen unter Verwendung einer Wassermenge, die im Verhältnis zu der für eine vollständige Hydrolyse erforderlichen Menge unterstöchiometrisch ist;
 - (b) anschliessendes Vereinigen des partiell hydrolysierten Produkts von (a) mit einem Titanetetraalkoxid; anschliessendes
 - (c) Zugabe von Wasser in einer Menge, die zur Vervollständigung der Hydrolyse und zur Bildung eines Siliciumdioxid-Sols ausreicht; und
 - (d) Vereinigen des Siliciumdioxid-Sols mit einer Base zur Bildung eines Siliciumdioxids-Titanoxids-Gels sowie gegebenenfalls
 - (e) Altern des in (d) erhaltenen Gels und/oder
 - (f) Trocknen des Gels unter Bildung eines Xerogels.
2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, dass zusätzlich eine Chromverbindung eingeführt wird.
3. Verfahren nach Anspruch 2, dadurch gekennzeichnet, dass die Chromverbindung vor der Bildung des Gels unter Bildung eines Siliciumdioxid-Titanoxid-Chrom-Tergels eingeführt wird.
4. Verfahren nach einem der Ansprüche 2 bis 4, dadurch gekennzeichnet, dass die Chromverbindung in einer solchen Menge vorliegt, dass sich 0,5 bis 2 Gew.-% Chrom, bezogen auf das Gewicht des getrockneten Xerogels, ergeben.
5. Verfahren nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, dass es sich beim Organopolysilicat um Ethylpolysilicat und beim Tetraorganooxysilicat um Tetra-n-propoxysilan handelt.
6. Verfahren nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, dass das organische Lösungsmittel von (a) durch Verwendung von konzentriertem Ammoniumhydroxid alkalisch gemacht wird.
7. Verfahren nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, dass es sich beim organischen Lösungsmittel um einen Alkohol handelt; wobei es sich insbesondere beim Alkohol um einen Alkohol mit 3 bis 4 Kohlenstoffatomen handelt; wobei es sich beim Alkohol insbesondere um n-Propanol handelt.
8. Verfahren nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, dass das Titanetetraalkoxid die Formel $Ti(OR')_4$ aufweist, wobei R' einen Alkylrest mit 1 bis 6 Kohlenstoffatomen bedeutet; wobei es sich beim Tetraalkoxid insbesondere um Tetraisopropyltitanat handelt.
9. Verfahren nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, dass die Gesamtmenge des verwendeten Wassers im Bereich des 1,5 - 5-fachen der zur vollständigen Hydrolyse erforderlichen stöchiometrischen Menge liegt.
10. Verfahren nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, dass es sich bei der Base von (d) um Ammoniumhydroxid handelt.
11. Verfahren nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, dass das Wasser in Stufe (a) in einer Menge von 15-60 % der stöchiometrischen Menge, die für eine vollständige Hydrolyse erforderlich ist, vorhanden ist.



12. Chrom enthaltendes Siliciumdioxid-Titanoxid-Cogel-Produkt, erhalten nach Anspruch 2 oder nach einem der auf Anspruch 2 zurückbezogenen Ansprüche.
- 5 13. Verfahren zur Polymerisation von mindestens einem Mono-1-olefin mit 2 bis 8 Kohlenstoffatomen pro Molekül unter Verwendung des Produkts nach Anspruch 12 als Katalysator.
14. Verfahren nach Anspruch 13, wobei das Olefin unter Ethylen, Propylen, 1-Buten, 1-Penten, 1-Hexen und 1-Octen ausgewählt ist.
- 10 15. Verfahren nach Anspruch 14, wobei das Olefin Ethylen umfasst.
16. Verfahren nach Anspruch 14 oder 15, wobei die Polymerisation unter Aufschlämmungsbedingungen durchgeführt wird.

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