600061

FORM 1

REGULATION 9

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

APPLICATION FOR A STANDARD PATENT

We, RHONE-POULENC CHIMIE, of 25, quai Paul Doumer - 92408, Courbevoie, France, hereby apply for the grant of a Standard Patent for an invention entitled:-

"CERIC OXIDE CATALYST AND METHOD OF MANUFACTURE"

which is described in the accompanying Complete Specification.

Details of basic application:-

Number: 86/17805

Country: France

Date: 19th December, 1986

PATENT OFFICE 5 AUSTRALIA FIVE DOLLARS

PATENT OFFICE 20 AUSTRALIA TWENTY DOLLARS

Our address for service is:

SHELSTON WATERS
55 Clarence Street
SYDNEY, N.S.W. 2000.

DATED this 18th day of December, 1987
RHONE-POULENC CHIMIE

by W J Lloyd

Fellow Institute of Patent Attorneys of Australia
of SHELSTON WATERS

LODGED AT SUB-OFFICE
18 DEC 1987
Sydney

To: The Commissioner of Patents
WODEN A.C.T. 2606

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18 DEC 1987
Sydney

APPLICATION ACCEPTED AND AMENDMENTS
ALLOWED 17-5-90

CONVENTION APPLICATION BY A COMPANY

FORM 8 – REGULATION 12 (2)

R 3602

AUSTRALIA
PATENTS ACT 1952

DECLARATION IN SUPPORT OF A CONVENTION APPLICATION FOR A PATENT

(a) Here Insert (in full) Name of Company.

In support of the Convention Application made by (a) RHONE-POULENC CHIMIE

(b) Here Insert Title of Invention.

(hereinafter referred to as "Applicant") for a patent for an invention entitled:
(b) "CERIC OXIDE CATALYST AND METHOD OF MANUFACTURE"

(c) and (d) Here Insert Full Name and Address of Company Official authorised to make declaration.

I, (c) Marie-Claude DUTRUC-ROSSET
of (d) 25, Quai Paul Doumer, 92408 Courbevoie Cedex,
France

do solemnly and sincerely declare as follows:

1. I am authorised by Applicant to make this declaration on its behalf.

(e) Here insert Basic Country followed by date of Basic Application.

(f) Here insert Full Name(s) of Applicant(s) in Basic Country.

2. The basic Application~~(s)~~ as defined by section 141 of the Act was / ~~were~~ made

in (e) FRANCE on the 19th day of December, 19 86
by (f) RHONE-POULENC CHIMIE DE BASE
in on the day of 19
by
in on the day of 19
by
in on the day of 19
by

(g) Here insert (in full) Name and Address of actual Inventor or Inventors.

3. (g) CLAIRE DAVID, of 14 BIS, rue Friant - 75014 - PARIS France; CLAUDE MAGNIER, of 3, rue des Chaufourniers - 75019 - PARIS, France and BERTRAND LATOURRETTE, of 2, allee des Erables - WATTWILLER - 68700 - CERNAY ~~is~~/are the actual Inventor(s) of the invention and the facts upon which Applicant is entitled to make the Application are as follows:

See reverse side of this form for guidance in completing this part.

Applicant is the Assignee of the said Rhone-Poulenc Chimie de Base who is the assignee of the said inventors.

4. The basic Application(s) referred to in paragraph 2 of this Declaration was/were the first Application(s) made in a Convention country in respect of the invention, the subject of the Application.

DECLARED at COURBEVOIE CEDEX, FRANCE
this 5th day of November, 19 87

(h) Personal Signature of Declarant (c) (no seal, witness or legalisation).

(h) Marie-Claude DUTRUC-ROSSET
(Signature of Declarant)

(12) PATENT ABRIDGMENT (11) Document No. AU-B-82803/87
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CERIC OXIDE CATALYST AND METHOD OF MANUFACTURE

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(56) Prior Art Documents
AU 571650 38949/85 C01F
AU 571929 38950/85 C01F
AU 70605/87 C01F

(57) Claim

1. A ceric oxide with a specific surface of at least 100 m^2/g, after calcination at between 350 and 450^o C, and having a porous volume of at least 0.30 cm^3/g and pores with an average diameter greater than 50 Å.

14. A method for producing a ceric oxide, comprising preparing a true cerium hydroxide by the reaction of a cerium salt and a strong base in the presence of carboxylate ions, or by the reaction of a cerium carboxylate and a strong base, separating a precipitate of true cerium hydroxide thus produced, and washing and calcining said precipitate.

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COMMONWEALTH OF AUSTRALIA

FORM 10

PATENTS ACT 1952

COMPLETE SPECIFICATION

FOR OFFICE USE:

		Class	Int.Class
Application Number:			
Lodged:			

Complete Specification Lodged:
Accepted:
Published:

This document contains the amendments made under Section 49 and is correct for printing.

Priority:

Related Art:

Name of Applicant: RHONE-POULENC CHIMIE

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Address for Service: SHELSTON WATERS, 55 Clarence Street, Sydney

Complete Specification for the Invention entitled:

"CERIC OXIDE CATALYST AND METHOD OF MANUFACTURE"

The following statement is a full description of this invention, including the best method of performing it known to me/us:-

CERIC OXIDE CATALYST AND METHOD OF MANUFACTURE

This invention relates to a ceric oxide with new morphological characteristics. The process for producing it is also described.

When specific surfaces are mentioned in the description of the invention which follows, we mean the B.E.T. specific surface, determined in accordance with the BRUNAUER - EMMETT - TELLER method, as described in the "Journal of American Society 1938, 60, 309".

Ceric oxide on its own or mixed with other metallic oxides is used as a catalyst for synthesis, in particular that of methanol (Report Seances Acad. Sci. Ser. 2. 292 (12), 883-5 (1981)) or in the treatment of residual gasses (Japanese patent application no. 76/62 616).

In order to obtain a good catalytic reaction it is desirable to use a ceric oxide possessing the greatest possible specific surface.

A ceric oxide was proposed in FR-A 2 559 754 which had a specific surface of at least 85± 5 m^2/g obtained after calcination at between 350 and 450°C. This particular oxide is prepared by hydrolising an aqueous solution of ceric nitrate in a nitric acid medium, separating the precipitate obtained, washing it and drying it, then calcining at between 300 and 600°C. The ceric oxide obtained has a high specific surface but low porosity, the micropores having an average porous volume of approximately 0.02 cm^3/g.

Also previously know (FR-A 2 559 755) is ceric oxide with a specific surface of at least 85 ± 5 m^2/g after calcination at between 350 and 500°C and preferably between 150 and 180 m^2/g after calcination at between 400 and 450°C. This oxide is obtained by a process which consists in precipitating a basic ceric sulphate by the reaction of an aqueous solution of ceric nitrate and an aqueous solution containing suphate ions, separating the precipitate obtained, washing and eventually drying it, then calcining it at a temperature varying between 300 and 500^{o}C. Ceric oxide prepared in this way has a high specific surface and a distributed porosity from 10 to 200 Å and a porous volume of approximately 0.15 cm^{3}/g. It also contains a quantity of residual sulphate ions and can therefore only be used selectively in the area of catalysis.

Compared to the products described in this literature, the applicant has produced a ceric oxide having a large specific surface and possessing new characteristics of porosity and displaying good heat stability.

This invention, according to one aspect, provides a ceric oxide with a specific surface of a least 100 m^{2}/g after calcination at between 350 and 450^{o}C., characterised by the fact that the ceric oxide displays a porous volume of at least 0.3 cm^{3}/g and pores with a average diameter greater than 50 Å.

In this application, the specific surfaces given are measured on a product which has been calcined for at least 2 hours at a given temperature.

The porous volume and dimensions of the pores are determined, like the specific surface, by the B.E.T. method.

A primary characteristic of the ceric oxide of this invention is that it has a high specific surface.

The preferred ceric oxide of the invention has a specific surface of 100 to 160 m^{2}/g after calcination at between 400 and 450^{o}C.

Another characteristic of the ceric oxide of this invention is that it has a relatively stable specific surface within a range of temperatures from 400 to 600^{o}C.

Thus, the preferred ceric oxide still displays a specific surface of 80 to 130 m^{2}/g after calcination at 600^{o}C. Preferably still, the ceric oxide has a specific surface greater than 100 m^{2}/g for preference between 100 and 130 m^{2}/g after calcination at 600^{o}C.

Another characteristic of the ceric oxide of the invention is that it has a high porosity.

The porous volume of the ceric oxide of this invention may vary between 0.3 and 0.45 cm^3/g.

The size of the pores is staggered between 20 and 1000 Å. Their average diameter (d_{50}) varies between 50 and 200 Å.

The average diameter is defined as the diameter whereby all the pores with a smaller diameter than this make up 50% of the total porous volume (p_v).

Examination by electronic scanning microscopy shows that the ceric oxide is made up of very fine grains, from 1 µm to 5 µm with large agglomerates of 20 to 50 µm present.

Examination using electronic microscopy by transmission shows acicular shaped crystals.

The size of the needles vary between 100 and 1000 Å and are more frequently close to 500 Å.

Figure 1 shows a photograph taken with an electronic microscope by transmission (enlargement G = 220 000) and shows the morphology of the ceric oxide in the form of needles : this oxide has been calcined at 600°C.

Analysis by X-ray diffraction shows that the ceric oxide of the invention has a crystalline phase of the CeO_2 type, with a mesh parameter which varies from 5.42 to 5.44 Å. and a rate of crystallisation between 50 and 80%. In the crystallised area, the size of the crystallites of the ceric oxide obtained after calcination at 400°C, varies between 40 and 100Å.

This invention produces a ceric oxide containing a residual amount of an alkaline cation which corresponds to the base used in the preparation of the ceric oxide of the invention. The residual content of the alkaline cation is usually at most 0.2 % expressed as a weight % of metallic cation in relation to the ceric oxide.

The process for obtaining the ceric oxide of the invention includes preparing true cerium hydroxide by the reaction of a cerium salt and a base with a concentration of carboxylate ions, or by the reaction of a cerium carboxylate and a strong base, separating the precipitate obtained, washing it and calcining it.

By true cerium hydroxide we mean Ce $(OH)_3$ cerous hydroxide or Ce $(OH)_4$ ceric hydroxide which may also be expressed as CeO_2, 2 H_2O.

In the first stage of the process, true cerium hydroxide is prepared.

A first variation of the process of the invention consists in forming a precipitate by reacting a cerium salt and a base in the presence of carboxylate ions which can be supplied in an acid form or in the form of an alkaline metal or ammonium salt.

To simplify the explanation ; by carboxylic acid, we denote all sources of carboxylate ions, whether they be in an acid form or a salified form.

The cerium salt and carboxylic acid are mixed and then reacted with a base.

The cerium salt used in accordance with the process of the invention can be any cerium salt in a cerous or ceric state, soluble under the conditions of the invention.

A mixture of cerium salts in a cerous or ceric state may also be used.

Examples of the cerium salts which may be used are cerous nitrate, cerous chloride in solid form or as an aqueous solution.

Also may be used, an aqueous solution of ceri-ammoniacal nitrate or ceric nitrate.

Again, also may be used a solution of ceric nitrate obtained by the action of nitric acid on hydrated ceric oxide obtained in the usual manner by the reaction of a solution of a cerous salt, for example, cerous carbonate and a solution of ammonium hyroxide in the presence of hydrogen peroxide.

The ceric nitrate solution obtained in accordance with the electrolytic oxidation of a cerous nitrate solution and which is described in FR-A 2 570 087 is an excellent raw material.

The cerium salt solution is chosen so that it contains no impurities which could appear in the final product. It would be useful to use a cerium salt solution with a degree of purity greater than 99%.

The degree of concentration of the cerium salt solution is not a critical factor, according to the invention it can vary widely: a concentration between 0.1 and 3 moles per litre is preferable.

The carboxylate ions may be drawn from all soluble carboxylic acids soluble under the conditions of the invention, notably aliphatic carboxylic acids. For preference, linear or branched chain aliphatic carboxylic acids with 1 to 10 carbon atoms are used.

Suitable carboxylic acids are formic acid, acetic acid, propionic acid, benzoic acid. Acetic acid is used for preference.

The proportion of carboxylic acid used in relation to the cerium salt is not critical. The molar ratio between the acid used and the cerium salt expressed in CeO_2 may vary between 1 and 10 and is preferably between 2 and 5.

In accordance with the process of this invention, the mixture of the aqueous solution of cerium salt and the carboxylic acid is reacted with a base.

According to the invention, the base employed is the aqueous solution of a strong base such, for example, as soda or potassium. For preference an aqueous solution of soda is used.

The normality of the basic solution used is not a critical factor of the invention and may vary widely, for example between 0.1 and 11 N, but it is preferable to use solutions in which the concentration varies between 2 and 10 N.

The ratio between the base and the cerium salt is such that the molar ratio OH/Ce expressed in CeO_2, is greater than or equal to 3.0 and less or equal to 10 : OH represents the number of OH moles supplied by the base and Ce represents the number of moles of Ce^{111} and/or Ce^{IV} present in the reaction medium. The defined limits are not critical but are preferred for reasons of economy.

The final concentration of the cerium reaction medium expressed in CeO_2 is preferably between 0.2 and 1 mole/litre but better still around 0.5 mole/litre.

The mixing of the various reagents used in quantities stated is done at a temperature which can be between the ambient temperature and the boiling point of the reactive mixture; for preference between $80^{o}C$ and the boiling point of the reactive mixture.

The duration of the reaction is not critical. It can be from 1 to 8 hours but preferably between 2 and 5 hours.

The reagents referred to may be mixed in a number of ways. For example, the aqueous solution of cerium salt and the carboxylic acid may be added simultaneously to the basic solution while stirring, or the base can be added continously or all at once to the mixture or vice versa.

Another variation of this invention is to precipitate a true cerium hydroxide by reacting a cerium III to IV carboxylate with a base.

As far as cerium carboxylates are concerned, all those soluble under the conditions of the invention may be used and more particularly those derived from a carboxylic acid of the aliphatic, cycloaliphatic, aromatic acids or mixtures of these. For preference, linear or branched chain aliphatic carboxylic acids with between 2 and 18 carbon atoms are used.

For examples of cerium III carboxylates we would mention acetate, 2-ethyl hexanoate, neodecanoate, cerous stearate.

The cerium carboxylate usually being in solid form is preferably added to the aqueous base solution.

The proportion of reagents and the process remain identical to that previously given.

In a favoured variation of the invention, where cerium hydroxide is precipitated in a cerous state, whichever variation of the invention is used, it is preferable to oxidise it in a ceric state by adding, at the end of the precipitation, an oxidising agent compatible to this medium.

Among the oxidising agents which are suitable are solutions of perchlorate, chlorate, hypochlorite, sodium persulphate, potassium or ammonium, hydrogen peroxide or air, oxygen or ozone. The cerium may also be oxidised electrochemically. Hydrogen peroxide being used for preference.

The ratio of oxidising agent in relation to the cerous salt to be oxidised may vary considerably. It is usually greater than the stoichiometry and preferably corresponds to an excess between 10 and 40 %.

The reactive mixture is then kept at a temperature between 10 and 95° C, more precisely between 50 and 70° C for a period which may vary considerably, but preferably between 5 minutes and 5 hours.

The cerium hydroxide precipitate can be separated from the reactive medium by the usual methods for solid-liquid separation : filtration, decantation, centrifugation or drying.

This separation usually takes place at the ambient temperature.

The precipitate is then washed.

This washing is preferably done with water. For preference deionised or distilled water.

This washing may also be done with a solution of diluted acid, e.g. nitric acid with a pH between 3.0 and 5.5.

This particular washing can take the place of or follow washing in water or vice versa.

Should cerium carboxylate be used, the carboxylate of which corresponding to the cation of the base is insoluble in the cerium hydroxide, it may be useful to do the washing in an organic solvent which will dissolve the cerium carboxylate. Can be used, for example, a solvent such as alcohols, methanol, ethanol, n-propanol, isopropanol and the aldehydes or ketones, acetone for example.

One or several washes are carried out, usually 1 to 2.

A preferred method of washing consists in placing the separated precipitate in suspension in water at 100 to 300 g/l. for example.

After a washing of this kind, the precipitate is separated using the usual method, as previously stated.

The free water content of the separated precipitate is between 20 and 80 %, more often between 20 and 50 %.

The product obtained after separation and washing can then be dried in the air or under reduced pressure of about 10^{-2} at 100 mm of mercury (133.322 Pa and 13 332.2 Pa). The drying temperature can vary between the ambient temperature and 100° and the duration of the drying is not critical, it can be between 2 and 24 hours, but preferably 10 to 24 hours.

In the final stage of the process of this invention, the dried product is calcined at a temperature selected between $300^{\circ}C$ and $800^{\circ}C$, preferably between $350^{\circ}C$ and $600^{\circ}C$. It lasts about 30 minutes to 24 hours but preferably 4 to 8 hours.

The lower limit of the temperature range is not critical and may be lowered.

On the other hand, there is no point in raising the upper limit of the calcination temperature as a decrease in the specific surface of the ceric oxide obtained is noted.

The ceric oxides obtained by the method described in this invention can be used for may applications. Particularly as fillers, binding agents, washcoats, thickeners, dispersing agents, reinforcers, pigments, adsorbents and raw materials for manufacturing ceramics.

The ceric oxide produced by the invention has a high specific surface and is therefore well suited for use as a catalyst or catalytic support.

The examples which follow, illustrate the invention without in any way placing limitations upon it. In these examples, the percentages given are expressed by weight.

Example 1

The ceric hydroxide of this example was prepared in a reactor with a usable capacity of 500 cm^3, equipped with a double jacket in which thermoregulated water circulated at the desired temperature; and agitating means, together with a system for the introduction of the reagents.

1 000 cm^3 of an aqueous solution of 4.25 N soda is introduced.

For 20 minutes a mixture composed of 175 cm^3 of an aqueous solution of cerous nitrate at 2.85 moles/litre and 150 g of acetic acid at 17.5 N is added.

It is mixed at 20°C by agitating at 600 turns per minute.

The reactive temperature is raised to 90°C and this temperature maintained for 3 hours.

The reactive mixture, composed of an aqueous suspension of cerous hydroxide is left to cool to the ambient temperature.

38 cm^3 of hydrogen peroxide is then added at 110 volumes (9.8 moles/litre); this represented a stoichiometric excess of 50%.

The reactive mixture is maintained at 70°C for approximately 1 hour.

The ceric hydroxide precipitate is separated by filtration on a Buchner filter (no 3 porosity).

The recovered precipitate is washed twice by suspension of 100 g of precipitate for every litre of water and a third washing done also by placing the precipitate in suspension in a diluted solution of nitric acid at a pH of 3.

After filtering the precipitate recovered is dried in a drying oven at 100^{o}C for 24 hours.

89 g of a product are obtained which contain 92% CeO_2, establishing a reaction yield of 95%.

The dried product is placed in an alumina boat and calcined in a muffled furnace for 6 hours at 400^{o}C.

The morphology of the ceric oxide obtained is represented by the figure 1 (G= 220 000).

Analyses by X-ray diffraction shows crystallites with a size of 45 Å.

BET porosimetric analyses shows :

- a specific surface in the order of 145 m^2/g.
- a volume of pores with a diameter below 1 000Å of 0.42 cm^3/g ; the porosity appears to be primarily intergranular.
- a volume of pores with a diameter of less than 200 Å of 0.32 cm^3/g.
- sizes of pores graduated from 20 to 1 000 Å.
- pores with an average diameter of 190 Å.
- a residual soda ratio of 0.16 %.

Example 2

Example 1 is reproduced except that the calcination temperature is 600^{o}C instead of 400^{o}C.

The ceric oxide which results has a specific surface of 95 m^2/g and a size of crystallites of 55 Å.

Example 3

In apparatus like that described in example 1, 1 000 cm^3 of a 4.36 N aqueous solution of soda is introduced at 20^{o}C.

227 cm^3 of a ceric nitrate aqueous solution at 2.2 moles/litre and 150 g of 17.5 N concentrated acetic acid are added while stirring for a period of 20 minutes.

The reactive temperature is raised to 90°C and this temperature maintained for 3 hours.

The reactive mixture made up of an aqueous suspension of ceric hydroxide is left to cool to the ambient temperature.

The precipitate is separated by filtration through a Buchner funnel (no 3 porosity).

The recovered precipitate is washed twice in water, placing 100 g of precipitate in suspension in every litre of water, it is washed a third time in an aqueous solution of diluted nitric acid with a pH = 4.5.

After filtering, the solid material recovered is dried for 24 hours at 100°C and then calcined for 6 hours at 400°C.

This produces ceric oxide with a specific surface of 130 m^2/g and pores with an approximate average diameter of 180 Å containing 0.15 % of residual soda.

<u>Example 4</u>

Ceric oxide is prepared as in example 3 but the 150 g of concentrated acetic acid is replaced by 115 g of concentrated formic acid.

BET analyses of the ceric oxide obtained shows :

- a specific surface of 125 m^2/g,
- a ratio of residual soda of 0.12 %.

<u>Example 5</u>

Example 4 is repeated with a slight modification in that the calcination is done at 600°C instead of 400°C.

The ceric oxide obtained has a specific surface of 91 m^2/g.

<u>Example 6</u>

Ceric oxide is prepared as in example 3 but the 150g of concentrated acetic acid are replaced with 185.2 g of concentrated formic acid.

BET analysis of the ceric oxide obtained shows :

- a specific surface of 128 m^2/gm

- a porous volume of approximately 0.39 cm^3/g,
- an average diameter of the pores of 170 Å,
- a ratio of residual soda of 1.12 %.

Example 7

Example 6 is followed but differs in that the calcination is at 600°C instead of 400° C.

Ceric oxide is obtained with a specific surface of 99 m^2/g.

Example 8

Ceric oxide is prepared in accordance with the method described in example 1 but using a mixture of 179 cm^3 of an aqueous solution of cerous nitrate at 2.85 moles/litre and 305.3 g of benzoic acid.

After calcining at 400°C, ceric oxide is obtained with a specific surface of 107 m^2/g.

Example 9

In this example, cerium hydroxide is precipitated by reacting a base with cerous acetate.

The cerous acetate is prepared beforehand by adding small fractions of 236 g of ammonium acetate at 2.85 moles/litre to 350 cm^3 of an aqueous solution of cerous nitrate at 1 mole/litre : this mixing is done at the ambient temperature and is agitated for 20 minutes. A precipitate is recovered (at a ratio of 81 %) by filtering through a Buchner funnel.

The precipitate is then dried in a drying oven at 100°C for 20 hours.

In the same equipment as that described in example 1 is placed at 20°C, 1 250 cm^3 of an aqueous solution of soda 5 N and over a period of 15 minutes, 397 g of cerous acetate in solid form is added.

The mixing is done at 20°C, stiring at 600 turns a minute.

The reactive temperature is raised to 80° C and maintained for 4 hours.

The reactive mixture which is an aqueous suspension of cerous hydroxide is left to cool at the ambient temperature.

95.4 cm^3 of hydrogen peroxide is added to 110 volumes (9.8 moles/litre) which represents an excess, in relation to the stoichiometry of 50 %.

The reactive mixture is kept at 70° C for approximately 1 hour.

The ceric hydroxide precipitate is separated by filtration with a Buchner funnel (porosity no 3.)

The precipitate recovered is washed twice in water by placing a 100 g of the precipitate in suspension in each litre of water and it is washed a third time by suspension of the precipitate in a diluted solution of nitric acid with a pH- 5.

Once filtered the solid recovered is dried in a drying oven at 100° C for 24 hours.

The dried product is placed in an alumina boat and calcined in a muffle furnace for 6 hours at 400°C.

243 g of a product is obtained containing approximately 88.6 % of CeO_2 giving a reaction ratio of 100 %.

BET porosimetric analysis shows :

- a specific surface of 148 m^2/g,
- a volume of pores with a diameter of less than 1 000 Å of 0.39 cm^3/g,
- a volume of pores of less than 200 Å equal to 0.27cm^3/g,
- a size of pores from 20 to 1 000 Å ; the porosity appears to be both intergranular and intragranular.
- an average diameter of the pores of 80 Å.

Example 10

Example 9 is repeated except for the calcination temperature which is 600° C instead of 400 °C.

Ceric oxide is obtained with a specific surface of 117 m^2/g.

Example 11

In the example which follows, the cerous hydroxide is precipitated by reacting with a base of cerous stearate.

The reaction takes place as in example 9 but the following are used : 49.4 g cerous stearate and an aqueous solution of 1 000 cm^3 of 0.5 N soda.

The reactive mixture is kept at 80°C for 4 hours, the mixture of cerium hydroxide and sodium stearate is then left to cool.

This mixture solidifies during cooling and is treated with 1 000 cm^3 of ethanol.

The mixture is brought to boiling point dissolving the sodium stearate which can then be separated from the precipitate of ceric hydroxide by filtering through a Buchner funnel.

The precipitate recovered is washed in water, dried and calcined at 400° C for 6 hours.

Ceric oxide is obtained which has a specific surface of 140 m^2/g and pores with an average diameter of approximately 75 Å.

Example 12

Example 11 is repeated with a slight variation in that the calcining is done at 600° C instead of 400° C.

Ceric oxide is obtained with a specific surface of 110 m^2/g.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

1. A ceric oxide with a specific surface of at least 100 m^2/g, after calcination at between 350 and 450° C, and having a porous volume of at least 0.30 cm^3/g and pores with an average diameter greater than 50 Å.

2. A ceric oxide according to claim 1, having a specific surface of 100 to 160 m^2/g after calcination at a temperature between 400 and 450° C.

3. A Ceric oxide according to claim 1, having a specific surface of 140 to 160 m^2/g after calcination at a temperature between 400 and 450° C.

4. A Ceric oxide according to any one of claims 1 to 3, having a specific surface which is relatively stable within a range of temperatures from 400 to 600° C.

5. A Ceric oxide according to any one of claims 1 to 4, having a specific surface of 80 to 130 m^2/g after calcination at 600° C.

6. A Ceric oxide according to any one of claims 1 to 5, having a specific surface greater than 100 m^2/g after calcination at 600°C.

7. A Ceric oxide according to any one of claims 1 to 6, having a specific surface of 100 to 130 m^2/g after calcination at 600° C.

8. A Ceric oxide according to any one of claims 1 to 7, having a porous volume varying between 0.3 and 0.45 cm^3/g.

9. A Ceric oxide according to any one of claims 1 to 8, having pores with a pore diameter between 20 and 1000 Å.

10. A Ceric oxide according to claim 9, having pores with an average diameter between 50 and 200 Å.

11. A Ceric oxide according to any one of claims 1 to 10, having crystals of an acicular form.

12. A Ceric oxide according to claim 11, in the form of needles of a size which varies between 100 and 1000 Å.

13. A Ceric oxide according to any one of claims 1 to 12, having a residual content of alkaline cation representing at most 0.2 % of the weight of the ceric oxide.

14. A method for producing a ceric oxide, comprising preparing a true cerium hydroxide by the reaction of a cerium salt and a strong base in the presence of carboxylate ions, or by the reaction of a cerium carboxylate and a strong base, separating a precipitate of true cerium hydroxide thus produced, and washing and calcining said precipitate.

15. A method according to claim 14, wherein the true cerium hydroxide is prepared by reacting a cerium salt and a base in the presence of carboxylate ions supplied in the form of an acid or of an alkaline or ammonium metal salt.

16. A method according to claim 14 or claim 15, wherein the cerium salt is a cerium salt in a cerous or ceric state or a mixture of these soluble under the conditions of the reaction.

17. A method according to claim 16, wherein the cerous salt is cerous nitrate or cerous chloride either in solid form or in the form of an aqueous solution and the ceric salt being an aqueous solution of ceri-ammoniacal nitrate or ceric nitrate.

18. A method according to claim 17, wherein the cerium IV salt aqueous solution is a solution supplied by the electrochemical oxidation of a solution of cerous nitrate or a solution obtained by the action of nitric acid on a hydrated ceric oxide.

19. A method according to any one of claims 14 to 18, wherein the concentration of the cerium salt solution expressed in cerium is between 0.1 and 3 moles per litre.

20. A method according to any one of claims 15 to 19, wherein the carboxylic acid is an aliphatic, cycloaliphatic, or aromatic carboxylic acid or a mixture thereof.

21. A method according to claim 20, wherein the carboxylic acid is an aliphatic, linear or branched chain carboxylic acid with 1 to 10 carbon atoms.

22. A method according to claim 21, wherein the carboxylic acid is formic acid, acetic acid, propionic acid or benzoic acid.

23. A method according to any one of claims 15 to 22, wherein the molar ratio between the carboxylic acid and the cerium salt expressed in CeO_2 varies between 1 and 10.

24. A method according to claim 23, wherein the molar ratio is between 2 and 5.

25. A method according to any one of claims 15 to 24, wherein an aqueous solution of the cerium salt and the carboxylic acid may be added simultaneously to the basic solution while stirring, or the base can be added continuously or all at once to the mixture, or vice versa.

26. A method according to claim 14, wherein the true cerium hydroxide is prepared by reacting a cerium III or IV carboxylate with a strong base.

27. A method according to claim 26, wherein the cerium carboxylate is derived from a carboxylic acid selected from aliphatic, cycloaliphatic, aromatic carboxylic acids or a mixture thereof.

28. A method according to claim 27 wherein the cerium carboxylate is derived from a linear or branched chain carboxylic acid having between 2 and 18 carbon atoms.

29. A method according to one of claims 27 and 28, wherein the cerium III carboxylate is cerium acetate, 2-ethyl hexanoate, neo-decanoate, or cerous stearate.

30. A method according to one of the claims 26 and 29, characterised by the fact that the cerium carboxylate is added to an aqueous solution of the base.

31. A method according to any one of claims 14 to 30, wherein the base is soda or potassium.

32. A method according to any one of claims 14 to 31, wherein the ratio between the base and cerium salt is such that the molar ratio OH/Ce expressed in $Ce0_2$ is 3.0 or more or 10 or less.

33. A method according to claim 32, wherein the final concentration of cerium of the reaction medium expressed in $Ce0_2$ is between 0.2 and 1 mole/litre.

34. A method according to any one of claims 14 to 33, wherein the temperature of the reaction is between ambient temperature and the boiling point of the reactive mixture.

35. A method according to claim 34, wherein the reaction temperature is between 80° C and the boiling point of the reactive mixture.

36. A method according to any one of claims 14 to 35, wherein an oxidising agent compatible with the reaction medium is added to oxidise the precipitate in the cerous (III) state to the ceric (IV) state.

37. A method according to claim 36, wherein the oxidising agent is hydrogen peroxide.

38. A method according to claim 36 or claim 37, wherein the reactive mixture is kept at between 10 and 95° C.

39. A method according to claim 38, wherein the temperature of the reactive mixture is maintained between 50 and 70° C.

40. A method according to any one of claims 14 to 39, wherein the separated precipitate is washed in water using a solution of a diluted acid with a pH between 3.0 and 5.5 or an organic solvent which dissolves the carboxylate which corresponds to the cation of the base.

41. A method according to claim 40, wherein the solvent is methanol, ethanol, n-propanol, isopropanol, or acetone.

42. A method according to any one of claims 14 to 41, wherein the separated precipitate is dried in air or under reduced pressure at a temperature between the ambient temperature and 100°C prior to the calcining step.

43. A method according to claim 42, wherein the dried product is calcined at a temperature between 300 and 800°C.

44. A method according to claim 43, wherein the calcination temperature is between 350 and 600° C.

45. A method according to claim 43 or claim 44, wherein the calcination is carried out for 30 minutes up to 24 hours.

46. A method according to claim 45, wherein the calcination is carried out for 4 to 8 hours.

47. A method of producing a ceric oxide substantially as hereinbefore described with reference to any one or more of Examples 1 to 12.

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FIGURE 1