FORM 1 608861

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:-

"METHOD OF PREPARATION OF CERIC OXIDE"

which is described in the accompanying Complete Specification.

Details of basic application:-

Number: 87/09122
Country: France
Date: 29th June, 1987

Our address for service is:

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

DATED this 29th Day of June, 1988
RHONE-POULENC CHIMIE

by W Lloyd
Fellow Institute of Patent Attorneys of Australia
of SHELSTON WATERS

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

File: 27E

Fee: $500.00

APPLICATION ACCEPTED AND AMENDMENTS
ALLOWED 25 · 1 · 91

REPRINT OF RECEIPT
5000655 29/06/88

CONVENTION APPLICATION BY A COMPANY

FORM 8 – REGULATION 12 (2)

AUSTRALIA
PATENTS ACT 1952

DECLARATION IN SUPPORT OF A CONVENTION APPLICATION FOR A PATENT

In support of the Convention Application made by

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

(a) RHONE-POULENC CHIMIE

(hereinafter referred to as "Applicant") for a patent for an invention entitled:

(b) Here insert Title of Invention.

(b) "METHOD OF PREPARATION OF CERIC OXIDE"

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

I, (c) MADELEINE-FRANCE FABRE

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 29th day of June, 19 87

by (f) RHONE-POULENC CHIMIE

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) JEAN-LUC LE LOARER, of 24 rue du General Guillaumat - 17000 - LA ROCHELLE, FRANCE

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 inventor.

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

this 16th day of SEPTEMBER, 19 88

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

(h) M-F Fabre

(Signature of Declarant)

Madeleine France FABRE

To THE COMMISSIONER OF PATENTS.

(12) PATENT ABRIDGMENT **(11)** Document No. **AU-B-18519/88**
(19) AUSTRALIAN PATENT OFFICE **(10)** Acceptance No. **608861**

(54) Title
METHOD OF PREPARATION OF CERIC OXIDE

International Patent Classification(s)
(51)⁴ C01F 017/00

(21) Application No. : 18519/88 (22) Application Date : 29.06.88

(30) Priority Data

(31) Number	(32) Date	(33) Country
87 09122	29.06.87	FR FRANCE

(43) Publication Date : 05.01.89

(44) Publication Date of Accepted Application : 18.04.91

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(56) Prior Art Documents
AU 604474 68910/87

(57) Claim

1. A method of preparing ceric oxide by calcination of a ceric hydroxide comprising the steps of solvothermally treating ceric hydroxide and then calcining the treated ceric hydroxide.

COMMONWEALTH OF AUSTRALIA 608861

FORM 10

PATENTS ACT 1952

COMPLETE SPECIFICATION

FOR OFFICE USE:

	Class	Int.Class
Application Number:		
Lodged:		

Complete Specification Lodged:
Accepted:
Published:

Priority:

Related Art:

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

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Complete Specification for the Invention entitled:

"METHOD OF PREPARATION OF CERIC OXIDE"

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

METHOD OF PREPARATION OF CERIC OXIDE

This invention is related to a method of preparation of ceric oxide. More precisely, the invention concerns a process to increase the specific surface of a ceric oxide and, according to a variant, to stabilize the specific surface at high temperature.

This invention provides a ceric oxide presenting an increased specific surface which is stabilized at high temperature.

In the following invention summary, the specific surface refers to the B.E.T. specific surface determined by nitrogen adsorption, according to the standard ASTM D 3663-78 established from the BRUNAUER-EMMETT-TELLER method described in the "Journal of American Society, 60, 309(1938)".

It is known that the ceric oxide can be used as a catalyst, or as a catalyst support. As an example, one can quote Paul MERIAUDEAU et al's work on the methanol synthesis based on CO + H2 on catalysts whose platinium is laid on ceric oxide (C.R. Acad. Sc. Paris t. 297 - Series II-471 - 1983).

It is also well known that catalyst efficiency is generally increased when the contact surface between the catalyst and the reagents is large. In order to do so, the catalyst must be maintained as divided as possible, i.e. that its solid particles must be as small and individualized as possible. Therefore, the main role of the support is to keep the catalyst particles or crystallites in the most possible divided state.

When using a catalyst support for a long time, the specific surface decreases, due to the coalescence of very thin micropores. During this coalescence, a part of the catalyst is included in the support mass and can no longer be in contact with the reagent.

Until now, most of the prepared ceric oxides shows a fast decreasing specific surface at operating temperatures above 500°C. By doing so, R.ALVERO et al. (J.Chem. Soc. Dalton Trans 1984, 87) have obtained from the ammonium cerinitrate a ceric oxide with a specific surface of 29 m^2/g after a 600°C calcination.

Furthermore, FR-A 2 559 754 describes a ceric oxide with a specific surface of at least 85 ± 5 m^2/g obtained after a 350 to 450°C calcination and, preferably, between 100 to 130 m^2/g after a 400 to 450°C calcination.The so-called oxide is prepared by hydrolysis on a ceric nitrate aqueous solution in a nitric acid medium followed by a separation of the obtained precipitate, washing with an organic solvent, possibly drying, and calcination.

The obtained ceric oxide shows an interesting specific surface when it is prepared under a range of calcination temperatures from 300 to 600°C. However, at a higher calcination temperature, a decrease of the specific surface is to be noted, this one being of 10 m^2/g after a 800°C calcination.

One may also quote FR-A 2 559 755 which refers to a ceric oxide with a specific surface of at least 85 ± 5 m^2/g after a 350 to 500°C calcination and, preferably between a 400-450°C calcination. This oxide is obtained by a process consisting in precipitating a basic ceric sulphate by making a ceric nitrate solution and an aqueous solution containing sulphate ions to react, then separating the obtained precipitate, washing it with an ammonium hydroxide solution, possibly drying it and calcinating it at a temperature between 300 and 500°C. The ceric oxide prepared this way presents a large specific surface but when it goes through an 800°C calcination, its specific surface decreases considerably and is of about 10 m^2/g.

One of the objectives of this invention is to provide a method which facilitates the increase of the specific surface of a ceric oxide obtained by calcination of a ceric hydroxide.

Another objective of the invention is to develop a method to improve the stability of the specific surface at high temperature.

In order to obtain the first objective, the present invention provides a method of preparing ceric oxide by calcination of a ceric hydroxide comprising the steps of solvothermally treating ceric hydroxide and then calcining the treated ceric hydroxide.

In a preferred embodiment, the method of the invention comprises the steps of:

- suspending the ceric hydroxide in a liquid medium,
- heating the ceric hydroxide suspension in a sealed area up to a temperature and a pressure respectively lower than the critical temperature and the pressure of the medium,
- cooling the reactive medium and bringing said medium back to atmospheric temperature,
- separating the treated ceric hydroxide, then
- calcining the treated ceric hydroxide.

The applicant has found that the fact of carrying out a thermal pre-treatment mentioned hereafter as "autoclaving" of the ceric hydroxide, before the calcination, facilitates an increase in the specific surface of the obtained ceric oxide.

Without limitating in any case the impact of the invention with the following theory, it is believed that the autoclaving treatment of the ceric hydroxide allows a recrystallization of the hydrate resulting in an increase of the crystallization rate and, consequently, in a decrease of the amorphous part, which discourages the aggregation of the crystallites during the calcination and therefore to increase the specific surface of the obtained ceric oxide.

It is to be noted that the calcination involves an increase of the crystallites size and that the autoclaving treatment enables the limitation of this increase, which results in a better stability of the specific surface.

Therefore, the present invention also provides a ceric hydroxide. Preferably, the ceric hydroxide is an hydrated ceric oxide.

CeO_2, $2H_2O$ or a ceric hydroxide which could contain residual quantities of binded or adsorbed anions.

Then the ceric hydroxide used in the invention method corresponds to the following formula :

$$Ce(OH)_{4-ay}\ (A)_y,\ nH_2O \qquad (I)$$

in which :

A	symbolizes a residual anion
a	is a whole number representing the anion charge
y	is a number between 0 and 2
n	is a number between 0 and about 20

The ceric hydroxide preferably used in the invention corresponds to the formula (I) in which "a" is a whole number smaller or equal to 1 or 2, and "y" is a number between 0 and 1,5.

Chlorides, sulphates, nitrates, acetates, formates, etc... and preferably nitrates and chlorides can be mentioned as residual anions A.

One should also note that it is also possible in the invention process to use a ceric hydroxide which might contain a ceric oxide phase. Therefore the cerium compounds described in European patent application 87 400 600.0 could be used but those are not preferred as they do not provide the maximum benefit of the present invention, because of the pre-existence of the ceric oxide phase, during the autoclaving treatment.

A quality raw material would be a ceric hydroxide corresponding to the formula (I) and prepared according to the method described hereafter which consists in making a cerium salt solution and a base to react, possibly in presence of an oxidizer, separating the obtained precipitate, possibly washing it and/or drying it.

The cerium salt solution used can be any cerium salt aqueous solution in a cerous state and/or ceric soluble in the conditions of preparation, namely a cerous chloride or cerium nitrate in a cerous or ceric state or a mixture of both.

The cerium salt solution is choosen in such a way that it does not contain any impurity that might be found in the calcined product. It might be favorable to use a cerium salt with a purity rate over 99 %.

The cerium salt concentration is not a critical factor, according to the invention and it may vary to a large extent ; a concentration between 0,2 and 4 moles per liter is preferred.

According to a preferred variant, the cerium is introduced into the reactive medium in a cerous state and is oxidized in a ceric state with an oxidizer.

Among the possible oxidizers, perchlorate, chlorate, hypochlorite, sodium persulphate, potassium, ammonium solutions, hydrogen peroxide or air, oxygen, ozone can be mentioned. Hydrogen peroxide is preferred.

The proportion of oxidizer with regard to the cerous salt to be oxidized may vary to a large extent. It is generally higher than stoichiometric and corresponds preferably to an excess of 10 to 40 %.

Another preferred variant of the invention consists in using a ceric nitrate aqueous solution. This one generally presents some initial acidity and may have a normality between 0,01 N and 5 N.The concentration of H ions is not critical. Between 0,1 N and 1 N would be advantageous.

As a raw material, one can use a ceric nitrate solution obtained by the action of nitric acid on a hydrated ceric oxide prepared in a classical way, for instance by the action of the nitric acid on the cerous carbonate and the addition of an ammonium hydroxide solution together with an oxidizer, preferably hydrogen peroxide.

The ceric nitrate solution obtained with the electrolytic oxidation of a cerous nitrate solution, which is described in French patent application FR A 2 570 087 (No. 84 13641) constitutes a first quality raw material.

The precipitation of the ceric hydroxide may be done by the reaction of the cerium salt solution and a basic solution.

The basic solution used may be an aqueous ammonium hydroxide solution or a sodium hydroxide or potassium hydroxide solutions. An ammonium hydroxide is preferably used. The normality of the basic solution used is not a critical factor according to the invention : it may vary to a large extent but will be more advantageous between 1 and 5 N, preferably 2 to 3 N.

The proportion between the basic solution and the cerium salt solution must be such as the number of basic equivalents be larger or equal to the number of cerium equivalents. It may be better to use an excess higher than 5 % of basic equivalents. The reactive medium pH may be set between 6 and about 10. It is at its best between 7,0 and 9,0. It is particularly advantageous to regulate the pH within these limits, ± 0,1 pH unit.

The reactive medium temperature must be preferably between 5 and 95°C, and more particularly between 40 and 70°C. The mixing duration in the reactive medium is not a critical factor in the invention and may vary to a large extent ; generally, durations between 15 minutes and 2 hours will be chosen.

A precipitate is obtained, which can be separated according to the traditional techniques of solid/liquid separation such as decanting, evaporation, filtration and/or centrifugation.

According to a favorite variant of the invention, it is desirable to wash the precipitate in order to eliminate the remaining adsorbed anions on the precipitate.

The washing is carried out preferably with water or with a basic solution having preferably a concentration between 1 and 5 N. An ammonium hydroxide solution is preferably used. One to several washings can be done and more often, from one to 3 washings.

The ceric hydroxide separated and possibly washed may be used directly in the invention process. It is also possible to dry it. Drying may be done with air or under reduced pressure, for instance, in the area of 1 to 100 mm of mercury (133,322 Pa to 13332,2 Pa). The drying temperature may vary between room temperature and 100°C and its duration is not critical and may vary between 2 and 48 hours.

The ceric hydroxide obtained with the above method is used preferably in the process of the present invention.

According to the invention process the ceric hydroxide is used in suspension in a liquid medium.

The liquid medium used may be any liquid not reacting with ceric hydroxide under the temperature and pressure conditions of the invention.

Among the possible liquids, one uses preferably water or a basic solution, namely an alkaline metal hydroxide or any solution with a decomposable base under the calcination conditions of the invention.

"Decomposable base" is to be understood as a compound presenting a pK_b lower than 7 and decomposable under the calcination conditions of the invention.

As an illustration, one can quote the ammonium hydroxide, urea, ammonium acetate, ammonium hydrogenocarbonate, ammonium carbonate, or a primary amine, secondary, tertiary, as for instance methylamine, ethylamine, propylamine, n-butylamine, sec-butylamine, n-pentylamine, amino-2 pentane, amino-2 methyl-2 butane, amino-1 methyl-3 butane, diamino-1,2 ethane, diamino-1,2 propane, diamino-1,3 propane, diamino-1,4 butane, diamino-1,5 pentane, diamino-1,6 hexane, dimethylamine, diethylamine, trimethylamine, triethylamine or a quaterly amine such as a tetraalkylammonium hydroxide with preferably alkyle radicals containing from 1 to 4 carbon atoms ; the tetramethylammonium hydroxide or the tetraethylammonium hydroxide are more particularly used.

A mixture of bases may also be used.

A preferred variant of the invention process consists in using a decomposable base solution because it has been unexpectedly found that carrying out the autoclaving operation in such a medium not only allows to increase the specific surface, but also to maintain a high specific surface and porous volume up to 900°C temperatures.

An ammonium hydroxide, a tetraalkylammonium hydroxide solutions or their mixtures are used preferably.

When the liquid medium is a basic solution, its concentration is not a critical factor according to the invention. It may vary to a large extent, for instance between 0,1 and 11 n, but it is preferable to use solutions whose concentration varies between 1 and 10 N.

In the liquid medium, the ceric hydroxide concentration expressed in CeO_2 may vary between 0,3 and 6 moles/litre, preferably between 2 and 3 moles/litre.

The autoclaving operation is carried out at a temperature between the back-flow temperature and the critical temperature of the reactive medium. A temperature between 100°C and 350°C is preferred and is even better between 150 and 350°C.

The temperature ascent is done at a non-critical speed. The reactive temperature is reached by heating between 30 minutes and 4 hours for instance.

The invention process may be carried out by troducing the ceric hydroxide in suspension into the liquid medium in a sealed area ; therefore the pressure only results from heating the reactive medium.

In the above mentioned temperature conditions and in an aqueous medium, it may be precised as an illustration that the pressure varies between 1(10^{5} Pa) and 165 Bars (165.10^{5} Pa), preferably between 5(5.10^{6} Pa) and 165 Bars (165.10^{5} Pa).

It is also possible to exert an outside pressure which is added to the heating one.

The duration of the autoclaving operation is not critical. It may vary between 30 minutes and 6 hours.

At the end of it, one allows to cool down through the system inertia and the system is brought back to the atmospheric pressure.

The product in suspension in the liquid medium is separated with the classical techniques of solid/liquid separation such as decanting, evaporation, filtration and/or centrifugation.

The obtained product may possibly be washed and/or dried in the previously described conditions.

As a last stage of the invention method, the obtained product is calcined at a temperature betwuen 300° C and 1000°C and, preferably selected between 350 and 800°C.

The calcination duration may vary to a large extent between 30 minutes and 10 hours, preferably between 2 and 6 hours.

When the invention process is carried out within the preferential conditions defined hereafter, it enables to obtain an oxide presenting new morphological characteristics.

The characteristic of the ceric oxide of the invention is a specific surface of at least 15 m^2/g after calcination at a temperature between 800 and 900°C.

The preferred ceric oxide of the invention shows a specific surface between 20 and 60 m^2/g after calcination at a temperature of 800°C.

According to the ceric hydroxide conditions of calcination, the ceric oxide shows a specific surface between 15 and 160 m^2/g after calcination at a temperature between 350 and 900°C.

Figure 1 represents a curve of the variation of the ceric oxide specific surface (expressed in m^2/g), according to the calcination temperature expressed in °C.

The ceric oxide of the invention shows a specific surface of at least 15 m^2/g after calcination at a temperature between 800° C and 900°C and a larger one after calcination at a lower temperature than the aforesaid range.

This is how it may present a specific surface varying between 70 and 160 m^2/g, and preferably between 100 and 160 m^2/g after calcination between 350 and 450 °C. However, at a higher temperature reaching up to 900°C at the time it is used, particularly in the catalysis area, it offers the characteristic of keeping a specific surface of at least 15 m^2/g, and preferably between 20 and 60 m^2/g at a 800°C temperature.

In the current application, the quoted specific surfaces are measured on a product calcined during at least two hours.

Another characteristic of the invention's ceric oxide is that it presents a porous volume higher than

0,1 cm^3/g at a temperature between 800 and 900 °C, and preferably higher than 0,15 cm3/g.

The porous volume corresponding to a pore diameter smaller than 60 nm (600 Å) is measured with the mercury porosimeter according to the ASTN D4284-83 standard, or according to the azote asdorption isotherm method, as per the above mentioned B.E.T. method.

As the specific surface, the porous volume is depending on the calcination temperature : it may vary between 0,35 and 0,15 cm^3/g at a temperature between 350 and 900 °C.

The preferred ceric oxide of the invention shows a porous volume between 0,15 and 0,25 cm^3/g after an 800 °C calcination.

The pore size of a ceric oxide calcined at 800°C varies between 3 nm (30 Å) and 60 nm (600 Å) : the pores' average diameter (d50) varies between 20 nm (200 Å) and 30 nm (300 Å), preferably around 25 nm (250 Å).

The average diameter is defined in such a way that all the pores smaller than this diameter represent 50 % of the total porous volume (Vp) of pores with a diameter smaller than 60 nm (600 Å).

A ceric oxide calcined at 350°C presents pores from 2 nm (20 Å) to 100 nm (1000 Å) : the average diameter being between 10 nm (100 Å) and 20 nm (200 Å) and preferably close to 15 nm (150 Å).

The X diffraction analysis shows that the ceric oxide of the invention presents a CeO_2 type of crystalline phase with a mesh parameter between 0,542 nm (5,42 Å) and 0,544 nm (5,44 Å).

As an indication, the crystallites size of a ceric oxide obtained after a 350°C calcination is between 4 nm (40 Å) and 6 nm (60 Å) and between 10 nm (100 Å) and 20 nm (200 Å) after an 800°C calcination.

With a specific surface of a least 15 m²/g at a measurement temperature between 800 and 900°C, the ceric oxide of the invention is characterized by the fact that it consists of :

- preparing a ceric hydroxide by making a cerium salt solution and a base to react, possibly with an oxidizer, the base proportion being such that the reactive environment pH is higher than 7 ; separating the precipitate, possibly washing it.

- placing the ceric hydroxide in suspension into water or in a decomposable base aqueous solution.

- heating it in a sealed area up to a temperature and a pressure respectively lower than the critical temperature and pressure of the medium.

- cooling down the reactive mixture and bringing it back to the atmospheric pressure.

- separating the ceric hydroxide treated this way.

- then calcinating it.

The reagents used in the ceric hydroxide preparation are the same as those previously defined.

As a ceric hydroxide used preferably, a ceric hydroxide corresponding to the formula (II) is used :

$$Ce(OH)_x(X)_y,nH_2O \qquad (II)$$

in which :

X represents a chloride or nitrate anion
y is lower than 0,5
x = 4-y
n varies between 0 and around 20

The preferred compound corresponds to the formula (II) in which "y" is between 0 and 0,1. Even more preferentially, "X" represents a nitrate anion.

The preferred compound corresponding to the formula (II) is prepared by making a chloride or cerous nitrate solution and an ammonium hydroxide solution to react, in presence of hydrogen peroxide, by separating the obtained precipitate and wash it at least once, preferably with water.

The added base proportion is such as the reactive pH be higher than 7 and preferably between 7,5 and 9,0.

The reactive medium temperature is chosen between 5 and 70°C, preferably between 40 and 70°C.

Then the ceric hydroxide is exposed to an autoclaving operation carried out according to the previously indicated conditions : the medium in which the ceric hydroxide is placed in suspension is from a decomposable base, preferably an ammonium hydroxide or a tetraalkylammonium hydroxide solutions.

The successive operations of separation, possible washing and calcination are identical to those previously mentioned.

The ceric oxide of the invention presents a large specific surface at a high temperature which makes it totally suitable in the catalysis area, as a catalyst or as a catalyst support.

It is particularly well adapted to be used as a catalyst support in the treatment reactions of the exhaust gas of internal combustion engines.

The following examples illustrate the invention without limitating it.

The examples 1 to 22 emphasize the impact of the autoclaving operation of the ceric hydroxide on the specific surface of the ceric oxide obtained by calcination of the ceric hydroxide treated according to the invention.

The tests A to H are given as a comparison : they do not involve an autoclaving treatment.

Example 1

Test A

1. Ceric hydroxide synthesis :

In a double jacketed reactor with a 2 liters usable volume with an agitating device and a reagent introduction system (dosing pump), one introduces at 20°C, during 1 hour, simultaneously, 922 cm^3 of a cerous nitrate solution containing 179 g/l CeO and 38 cm^3 of a 200 volume hydrogen peroxide solution.

With a feeder linked to a pH regulation device, one adds during one hour, simultaneously, 860 cm^3 of a 3N ammonium hydroxide aqueous solution until the pH is 7.

After adding the reagents, the reactive medium is maintained at 70°C during one hour.

Then the precipitat[illegible]ation is effected on Buchner.

280 g of a ceric hydroxide with a molar ratio NO_3/Ce of 0,16 is obtained.

The RX diffraction analysis reveals that the ceric hydroxide presents crystallites with an average diameter of 5,5 nm (55 Å).

2. Ceric hydroxide autoclaving :

In a high shaped 100 cm^3 beaker, one introduces successively 30 cm^3 of deionised water and 30 g of the previously prepared ceric hydroxide.

After homogenisation of the latest in its medium, the beaker is placed in an autoclave with a usable volume of about 0,5 l.

The mixture is brought to 200°C, i.e. 16 bars (16.10^5.Pa), during four hours through an appropriate heating system.

At the end of this hydrothermal treatment, the precipate is filtered on Buchner.

An average crystallites diameter of 6,6 nm (65 Å) is determined by RX diffraction on the wet product.

It is then calcined at 350°C during 2 hours.

Then the ceric oxide specific surface and its porous volume lower than 60 nm (600 Å) are determined according to the methods defined in the description.

An x diffraction is also carried out to determine the size of the crystallites perpendicular to the 110 and 220 directions.

The obtained results are shown in Table I. As a comparison, it also shows the results of a ceric oxide prepared by a direct 2 hours calcination at 350°C of the ceric hydroxide synthetised under 1 (test A).

Table I

	specific surface m^2/g	porous volume cm^3/g	crystallites av.diameter nm (Å)
Example 1	101	0,06	7,0 (70)
Test A	54	0,04	7,5 (75)

It is observed that the ceric oxide obtained after an autoclaving treatment and calcined at 350 °C presents a specific surface twice larger and a smaller crystallites size.

Example 2

Test B

1. Ceric hydroxide synthesis

In a device as described in example 1, one introduces at 50 °C, 922 cm^3 of a 179 g/l CeO cerous nitrate solution and 38 cm^3 of a 200 volume hydrogen peroxide solution.

860 cm^3 of a 4,6 N aqueous ammonium hydroxide solution are added until reaching a 9,0 pH.

After adding the reagents, the reactive medium is kept at 70°C during one hour.

Then the separation of the precipitate is effected on Buchner.

515 g of a ceric hydroxyde presenting a 0,1 NO_3/Ce molar ratio are obtained.

The RX diffraction analysis reveals that the ceric hydroxide presents crystallites with an average diameter of 3 nm (30 Å).

2. Ceric hydroxide autoclaving

According to the operating procedure described in Example 1, one exposes 30 g of the above prepared ceric hydroxide placed in suspension in 30 cm^3 of deionised water to a 4 hour autoclaving treatment at 200°C.

. A 4,5 nm (45 Å) crystallite average diameter is determined by RX diffraction on the wet product.

At the end of this hydrothermal treatment, the precipitate is filtered on Buchner.

It is then calcined during 2 hours at 350 °C.

Then one determines the specific surface, the porous volume and the size of the ceric oxide crystallites having been exposed to the autoclaving treatment (example 2) and, as a comparison, of the ceric oxide prepared by a 2 hours direct calcination of the ceric hydroxide synthetised under 1 (Test B).

The obtained results are shown in Table II.

Table II

	specific surface m^2/g	porous volume cm^3/g	crystallites av. diameter nm (Å)
Example 2	100	0,26	5,0 (50)
Test B	70	0,20	6,5 (65)

One can observe, as in example 1, the beneficial effect of the autoclaving treatment on the specific surface and the porous colume of the ceric oxide obtained after a 350°C calcination.

Example 3

Test C

1. Ceric hydroxide synthesis

In a device as described in Example 1, one introduces at 50°C 922 cm^3 of a 179 g/l CeO cerous nitrate solution and38 cm^3 of a a 200 volume hydrogen peroxide solution.

825 cm^3 of a 4N aqueous ammonium hydroxide are added until reaching an 8,4 pH.

After adding the reagents, the reactive medium is kept at 70 °C during one hour.

Then the separation of the precipitate is effected on Buchner.

569 g of a ceric hydroxide presenting a o,1 NO_3/Ce molar ratio are obtained.

The RX diffraction analysis reveals that the ceric hydroxide presents crystallites with an average diameter of 3 nm (30 Å).

2. Ceric hydroxide autoclaving :

According to the operating procedure described in Example 1, one exposes 30 g of the above prepared ceric hydroxide placed in suspension in 30 cm^3 of desionised water to a 200 °C autoclavage treatment during 4 hours.

A 4,5 nm (45 Å) crystallites average diameter is determined by RX diffraction on the wet product.

At the end of this hydrothermal treatment, the precipitate is filtered on Buchner.

It is then calcined during 2 hours at 350°C.

Then one determines the specific surface, the porous volume and the size of the ceric oxide crystallites having been exposed to the autoclavage treatment (example 3) and, as a comparison, of a ceric oxide prepared by a 2 hours calcination at 350°C of the ceric oxide synthetised under 1 (test C).

The obtained are shown in Table III.

Table III

	specific surface m^2/g	porous volume cm^3/g	crystallites av. diameter nm (Å)
Example 3	110	0,20	5,0 (50)
Test C	46	0,16	6,5 (65)

One notes that the ceric oxide calcined at 350°C presents a larger specific surface and porous volume and a smaller size of the crystallites.

Example 4

Test D

1. Ceric hydroxide synthesis

In a device described in Example 1, one introduces at 50°C 922 cm^3 of a 179 g/l CeO cerous nitrate solution

and 38 cm^3 of a 200 volume hydrogen solution.
825 cm^3 of a 4 N aqueous ammonium hydrogen are added until reaching an 8,4 pH.

After adding the reagents, the reactive medium is kept at 70°C during one hour.
Then the separation of the precipitate is effected on Buchner.

The RX diffraction analysis reveals that the ceric hydroxide presents crystallites with an average diameter of 3,0 nm (30 Å).

2. Ceric hydroxide autoclaving

According to the operating procedure of Example 1, one exposes 30 g of the above prepared ceric hydroxide placed in suspension in 30 cm^3 of deionised water to a 200°C autoclave treatment during 4 hours.

A 4,5 nm (45 Å) crystallites average diameter is determined by RX diffraction on the wet product.

At the end of this hydrothermal treatment, the precipitate is filtered on Buchner.

It is then calcined during 2 hours at 800 °C.

Then one determines the specific surface, the porous volume and the size of the ceric oxide cristallites having been exposed to the autoclaving treatment (example 4) and, as a comparison, of a ceric oxide prepared by a 2 hours direct calcination at 800 °C of the ceric hydroxide synthetised under 1 (test D).

The results are shown in Table IV

Table IV

	specific surface m^2/g	porous volume cm^3/g	cryustallites av. diameter nm (Å)
Example 4	21	0,08	-
Test D	11	0,06	30 (300)

In comparison with Example 3, the ceric oxide is calcined at a higher temperature. One notes a decrease in the surface and the porous volume due to an important sintering which results into a considerable increase of the crystallites between 350 and 800°C.

Example 5

Test C

1. Ceric hydroxide Synthesis

It is carried out in accordance to the operating procedure of the Example 3-1.

2. Ceric hydroxide autoclaving

According to the operating procedure described in Example 1, one exposes 30 g of the above prepared ceric hydroxide placed in suspension in 30 cm^3 of a 1 N ammonium hydroxide aqueous solution to a 200°C autoclave treatment during 4 hours.

A 4,0 nm (40 Å) crystallites average diameter is determined by RX diffraction on the wet product.

At the end of this hydrothermal, the precipitate is filtered on Buchner.

It is then calcined during 2 hours at 350°C.

Then one determines the specific surface, the porous volume and the size of the ceric oxide crystallites having been exposed to the autoclaving treatment (example 5) and, as a comparison, of a ceric oxide prepared by a 2 hours direct calcination at 350°C of the ceric hydroxide synthesised under 1 (Test C).

The obtained results are shown in Table V.

Table V

	specific surface m^2/g	porous volume cm^3/g	crystallites av. diameter nm (Å)
Example 5	127	0,35	4,5 (45)
Test C	46	0,16	6,5 (65)

One can observed as in the previous examples the beneficial effects of the autoclaving on the specific surface and the porous volume of the ceric oxide obtained after an 800°C calcination.

Example 6

Test D

1. Ceric hydroxide synthesis

It is carried out according to the operating procedure of Example 4-1.

2. Ceric hydroxide autoclaving

According to the operating procedure described in Example 1, one exposes 30 g of the above prepared ceric hydroxide placed in suspension in 30 cm3 of a 1 N ammonium hydroxide aqueous solution to a 4 hours autoclaving treatment at 200°C.

A 4,0 nm (40 Å) crystallites average diameter is determined by RX diffraction on the wet product.

At the end of this hydrothermal treatment, the precipitate is filtered on Buchner.

It is then calcined during 2 hours at 800°C.

Then one determines the specific surface, the porous volume and the size of the ceric oxide crystallites having been exposed to the autoclaving treatment (example 6) and, as a comparison, of the ceric oxide prepared by a 2 hours direct calcination at 800°C of the ceric hydroxide synthetised under 1 (Test D).

The obtained results are shown in Table VI.

Table VI

	specific surface m²/g	porous volume cm³/g	crystallites av. diameter nm (Å)
Example 6	30	0,19	19 (190)
Test D	11	0,06	30 (300)

It is observed out that the ceric hydroxide autoclaving in an ammonium hydroxide medium allows to limit the sintering of the crystallites during calcination because of the size of the ceric oxide crystallites obtained after an 800°C calcination is not larger than 20 nm (200 Å).

Examples 7 and 8

1. Ceric hydroxide synthesis

It is carried out according to the operating procedure of Example 3-1.

2. Ceric hydroxide autoclaving

In a high shaped 100 cm^3 beaker, one introduces successively 25 cm^3 of a tetraethyl-ammonium hydroxide aqueous solution at 20 % and 15 g of the previously prepared ceric hydroxide.

After homogenisation of the medium, the beaker is placed into the autoclave.

The mixture is brought to 200°C, i.e. about 16 bars (16.10^5 Pa), during 3 hours through an appropriate heating system.

At the end of this thermal treatment, the precipitate is filtered on Buchner.

Then it is calcined in the following conditions :
2 hours at 350°C in Example 7 and 1 hour at 800°C in Example 8.

The specific surface and the porous volume of the obtained ceric oxides are then determined.

The results are shown in Table VII.

Table VII

	specific surface m^2/g	porous volume cm^3/g
Example 7	115	0,53
Example 8	29	0,23

Examples 9 to 20 :

Tests E and F

1. Ceric hydroxide synthesis

In a device as described in Example 1, one introduces at room temperature 922 cm^3 of a 150 g/l CeO_2 cerous nitrate solution and 38 cm^3 of a 200 volume hydrogen peroxide solution.

150 cm^3 of a 3 N aqueous ammonium hydroxide solution are

added by keeping the temperature at 8°C until reaching a pH of 9,5.

After adding the reagents, the reactive medium is kept at 8°C during 1 hour.

Then the separation of the precipitate is effected on Buchner, as well as a washing with water.

The RX diffraction analysis reveals that the ceric hydroxide presents crystallites with an average diameter of 3,5 nm (35 Å).

2. Ceric hydroxide autoclaving

A series of tests is carried at autoclavage temperatures varying from 160 to 330°C.

According to the same operating procedure described in the previous examples, one places 150 g of the above prepared ceric hydroxide in suspension in 150 cm3 of a 1 N aqueous ammonium hydroxide solution and exposes it to an autoclave treatment during 4 hours.

At the end of this thermal treatment, the precipitate is filtered on Buchner.

It is then calcined in the following conditions : 2 hours at 350 °C in the examples 9 to 14 and 2 hours at 800 °C in the examples 15 to 20.

Then the specific surface and the porous volume of the obtained ceric oxides are determined.

As a comparison, the results obtained with a ceric oxide prepared by a 2 hours direct calcination at 350 °C (Test E) and at 800 °C (Test F)of the ceric hydroxide synthetised under 1 are also given.

All the obtained results are shown in Table VIII.

Table VIII

	autoclaving temperature	calcination temperature	specific surface m^2/g	porous volume cm^3/g
Example 9	160°C	350°C	69	
Example 10	180°C	350°C	85	
Example 11	200°C	350°C	131	0,24
Example 12	250°C	350°C	126	0,27
Example 13	300°C	350°C	81	0,20
Example 14	330°C	350°C	73	0,25
Test E		350°C	65	0,12
Example 15	160°C	800°C	20	
Example 16	180°C	800°C	20	
Example 17	200°C	800°C	26	0,15
Example 18	250°C	800°C	27	0,14
Example 19	300°C	800°C	31	0,12
Example 20	330°C	800°C	45	0,17

Test F	800 °C	9,7	0,07

Example 21

Test G

1. Ceric hydroxide synthesis

In a double jacketed reactor in which circulates thermoregulated water at 20 °C, with a usable capacity of 2000 cm³, equipped with a agitating device and a reagent introduction system, one introduces simultaneously and continuously :

- an aqueous ceric nitrate solution containing mole/litre of cerium IV, 0,06 mole/litre of cerium III, with a 0,5 N free acidity, prepared according to FR-A 2 570 087 (no.84 13641), at the rate of 0,92 litre/hour.
- a 3 N aqueous ammonium hydroxide solution at the rate of 1,08 litre/hour.

The mixture is done by agitating at 300

revolutions/minute during 60 minutes.

The rates of flow of the added solutions are regulated in such a way that the pH be maintained at 5,5.

The precipitate is separated by filtration on Buchner.

The product obtained contains 42 % of CeO_2 and presents a crystallite size smaller than 3 nm (30 Å).

2. Ceric hydroxide autoclaving

In a 0,5 l usable volume autoclave, one introduces successively 300 cm^3 of NH_4OH 1 N and 100 g of the ceric oxide previously prepared.

After homogenisation of the latest in its medium, the mixture is brought to 200 °C, i.e. about 16 bars (16.10^5 Pa), during 3 hours, through the appropriate heating system.

At the end of this hydrothermal treatment, the precipitate is filtered on Buchner.

It is then calcined in the following conditions : 3 hours at 350 °C and 1 hour at 800 °C.

Then the specific surface and the porous volume of the obtained ceric oxide are determined according to the methods defined in the description.

The obtained results are shown in Table IX. As a comparison, one gives also the results of a ceric oxide prepared by a 2 hours direct calcination at 350°C and a 1 hour direct calcination at 800°C of the ceric hydroxide synthetised under 1.

Table IX

	Calcination temperature °C	specific surface m²/g	porous volume cm³/g
Example 21	350	135	0,21
	800	7	0,08
Test G	350	46	0,09
	800	3,5	0,04

Example 22

Test H

1. Ceric hydroxide synthesis

In a double jacketed reactor in which circulates thermoregulated water at 20°C with a 2000 cm³ usable capacity, equipped with an agitating device and a reagent introduction system, one introduces simultaneously and continuously :

- an aqueous ceric nitrate solution containing 1 mole/litre of cerium IV, 0,06 mole/litre of cerium III, with a 0,5 N free acidity, prepared by electrolysis according to FR-A 2 570 087 (no.84 13641) at the rate of 0,78 litre/hour.
- a 3 N ammonium hydroxide aqueous solution, at the rate of 1,22 litres/hour.

The mixture is done by agitating at 300 revolutions/minutes during 60 minutes.

The rates of flow of the of the added solution are regulated in such a way that the pH is kept at 9,0.

The obtained precipitate is filtered on Buchner.

The obtained product contains 20 % of ceric oxide and presents a crystallites size smaller than 3 nm (30 Å).

2. Ceric hydroxide autoclaving

In a 0,1 l usable volume autoclave, one introduces successfully 300 cm³ of NH_4OH 1 N and 100 g of the ceric hydroxide previously prepared.

After homogenisation of the latest in its medium, the mixture is brought to 200° C, i.e. about 16 bars (16.10^5 Pa), during 3 hours through the appropriate heating system.

At the end of this hydrothermal treatment, the precipitate is filtered on Buchner.

It is then calcined in the following conditions : 2 hours at 350°C and 1 hour at 800 °C.

The obtained results are shown in Table X. As a comparison, the results of a ceric oxide prepared by a 2 hour direct calcination at 350°C and one hour at 800°C of the ceric hydroxide synthetised under 1 are also given.

Table X

	Calcination temperature °C	specific surface m^2/g	porous volume cm^3/g
Example 22	350	155	0,24
	800	17	0,06
Test H	350	53	0,05
	800	4,9	0,03

One can note the beneficial effect of the autoclaving on the specific surface and the porous volume of the ceric oxide obtained after an 800°C calcination.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

1. A method of preparing ceric oxide by calcination of a ceric hydroxide comprising the steps of solvothermally treating ceric hydroxide and then calcining the treated ceric hydroxide.

2. A method according to Claim 1 comprising the steps of:

- suspending the ceric hydroxide in a liquid medium,
- heating the ceric hydroxide suspension in a sealed area up to a temperature and a pressure respectively lower than the critical temperature and the pressure of the medium,
- cooling the reactive medium and bringing said medium back to atmospheric temperature,
- separating the treated ceric hydroxide, then
- calcining the treated ceric hydroxide.

3. A method according to Claim 2 wherein the ceric hydroxide corresponds to the formula (I):

$Ce(OH)_{4-ay}(A)_y \cdot nH_2O$ (I)

wherein:

A symbolizes a residual anion,
a is a whole number representing the anion charge,
y is a number between 0 and 2, and
n is a number between 0 and 20.

4. A method according to Claim 3 wherein "a" is lower than 3.

5. A method according to Claim 3 or 4 wherein "a" is equal to 1 or 2.

6. A method according to any one of Claims 3 to 5 wherein "y" is a number between 0 and 1.5.

7. A method according to any one of the Claims 3 to 6 wherein the residual anion is chloride, sulphate, nitrate, acetate or formate.

8. A method according to Claim 7 wherein the residual anion is chloride or nitrate.

9. A method according to any one of the Claims 3 to 8 wherein the ceric hydroxide is prepared by a) reacting a cerium salt solution and a base to obtain a precipitate and b) separating the precipitate.

10. A method according to Claim 9 wherein the cerium salt solution and base are reacted in the presence of an oxidiser.

11. A method according to Claim 9 or 10 wherein the separated precipitate is washed and/or dried.

12. A method according to any of the the Claims 9 to 11 wherein the cerium salt solution is a solution of cerous chloride or of cerium nitrate in a cerous or ceric state or a mixture of both.

13. A method according to Claim 12 wherein the cerium salt solution is an aqueous ceric nitrate solution or an aqueous solution of cerous nitrate used in the presence of an oxidiser.

14. A method according to Claim 13 wherein the cerium salt solution is an aqueous solution of ceric nitrate obtained by the electrochemical oxidation of a cerous nitrate or from the action of nitric acid on a hydrated

ceric oxide.

15. A method according to any one of Claims 9 to 14 wherein the base is an ammonium hydroxide solution.

16. A method according to any one of Claims 10 to 15 wherein the oxidiser is hydrogen peroxide.

17. A method according to any one of Claims 9 to 16 wherein the quantity of added base is such that the reactive medium pH is between 6 and 10.

18. A method according to Claim 17 wherein the pH is between 7.0 and 9.0.

19. A method according to any one of Claims 9 to 18 wherein the temperature of the reacting medium is between 5 and 95°C.

20. A method according to Claim 9 wherein temperature is between 40 and 70°C.

21. A method according to any one of Claims 11 to 20 wherein the separated ceric hydroxide precipitate is washed with water or with a basic solution.

22. A method according to Claim 1 wherein the liquid medium is water or a basic solution.

23. A method according to Claim 22 wherein the basic solution is an alkaline metal hydroxide solution or a solution of a base decomposable under the calcination conditions.

24. A method according to Claim 21 wherein the decomposable base is ammonium hydroxide, urea, ammonium hydrogenocarbonate, ammonium carbonate, a primary, secondary, tertiary or quaternary amine or a mixture

thereof.

25. A method according to Claim 24 wherein the decomposable base is ammonium hydroxide, a tetraalkylammonium hydroxide or their mixtures.

26. A method according to any one of Claims 22 to 25 wherein the concentration of the basic solution is between 1 and 10 N.

27. A method according to any one of the Claims 1 to 26 wherein the ceric hydroxide concentration expressed in CeO_2 is between 0.3 and 6 moles/litre.

28. A method according to Claim 27 wherein the concentration is between 2 and 3 moles/litre.

29. A method according to any one of the Claims 1 to 28 wherein the solvothermal treatment is autoclaving and the autoclaving temperature is between 100 and 350°.

30. A method according to Claim 29 wherein the temperature is between 150 and 350°C.

31. A method according to any of the Claims 1 to 30 wherein the pressure varies between $1(10^5$ Pa) and 165 bars (165.10^5 Pa).

32. A method according to Claim 31 wherein the pressure is between 5 (5.10^5 Pa) and 165 bars (165.10^5 Pa).

33. A method according to any one of the Claims 29 to 32 wherein the duration of autoclaving is between 30 minutes and 6 hours.

34. A method according to any one of the Claims 1 to 33 wherein the calcination temperature is between 300 and 1000°C.

35. A method according to Claim 32 wherein the temperature is between 350 and 800°C.

36. A method according to Claim 34 or 35 wherein the duration of calcination is between 2 and 6 hours.

37. A method of preparing ceric oxide substantially as herein described with reference to any one of examples 1-22.

DATED this 22nd day of January, 1991

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