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(54) Title: COMPOSITE OXIDE BASED ON CERIUM OXIDE, SILICON OXIDE AND TITANIUM OXIDE

(57) Abstract: The present invention concerns a composite oxide based on cerium, oxide, silicon oxide and titanium oxide. The present invention also concerns a process to obtain these composites, a catalytic system comprising said composite oxides and their use for the treatment of exhaust gases from internal combustion, notably by bringing into contact exhaust gases from internal combustion engines with these catalytic systems.



COMPOSITE OXIDE BASED ON CERIUM OXIDE,
SILICON OXIDE AND TITANIUM OXIDE

5 The present invention concerns a composite oxide based on cerium oxide, silicon oxide and titanium oxide. The present invention also concerns a process to obtain these composites, a catalytic system comprising said composite oxides and their use for the treatment of exhaust gases from internal combustion, notably by bringing into
10 contact exhaust gases from internal combustion engines with these catalytic systems.

PRIOR ART

The following discussion of the prior art is provided to place the
15 invention in an appropriate technical context and enable the advantages of it to be more fully understood. It should be appreciated, however, that any discussion of the prior art throughout the specification should not be considered as an express or implied admission that such prior art is widely known or forms part of common general knowledge in the
20 field.

"Multifunctional" catalysts are currently used for the treatment of exhaust gases from internal combustion engines (automobile afterburning catalysis). The term "multifunctional" is understood to
25 mean catalysts capable of carrying out not only oxidation, in particular of carbon monoxide and hydrocarbons present in exhaust gases, but also reduction, in particular of nitrogen oxides also present in these gases. Cerium oxides today appear as constituents which are particularly important and advantageous for this type of catalyst,

notably for the conversion of noxious gases released by diesel engines either from mobiles sources or stationary sources.

The reduction of nitrogen oxide (NO_x) such as nitric oxide (NO),
5 nitrogen dioxide (NO₂), and nitrous oxide (N₂O), in exhaust gas is a widely addressed problem as a result of environmental concerns and mandated government emissions regulations, particularly in the transportation industry. One approach uses catalysts to treat the exhaust gases of spark-ignited gasoline internal combustion engines
10 for the reduction of NO_x emissions, since the exhaust contains minimal oxygen.

In addition to the NO_x, the exhaust gases typically contain sulfur compounds such as sulfur dioxide (SO₂) gas, which are produced by
15 the burning of sulfur contained in the fuel. The NO_x catalyst oxidizes sulfur dioxide to sulfur trioxide in oxygen-rich atmospheres. Still further, SO₃ reacts readily with water vapor, which is also contained in the exhaust gases, to produce sulfite ions and sulfate ions. The sulfite ions and sulfate ions react with the NO_x catalyst to produce sulfites
20 and sulfates. The resulting sulfites and sulfates adversely affect the NO_x storage reaction. Thus, such sulfites and sulfates are commonly referred to as NO_x poisons that degrade exhaust purification as they are irreversibly adsorbed at the surface of the washcoat materials, such as alumina, ceria or barium oxides.

25

TiO₂ containing support materials were also reported to suppress the sulfur poisoning (H.Y. Huang, R.Q. Long, R.T. Yang, Appl. Catal. B 33 (2001) 127). This effect is associated with the surface acidity of TiO₂, inhibiting the adsorption of acidic SO_x species (T. Takahashi, A.

Suda, I. Hachisuka, M. Sugiura, H. Sobukawa, H. Shinjoh, Appl. Catal. B 72 (2007) 187). In order to prevent SOx poisoning, it would be then possible to provide dopants to increase acidity on the CeO₂ surface by using for instance TiO₂ (Wenqing Xu, Yunbo Yu, Changbin Zhang, Hong He, Catal. Comm. 9 (2008) 1453). However it appears that CeTi exhibits a dramatically drop of the specific surface area (SBET) at high temperatures and can not be used in said application.

Otherwise, it is also known that a silicon-containing cerium composite oxide comprising 2 to 20 mass % silicon in terms of SiO₂, exhibits a higher specific surface area even in use in a high temperature environment as expressed in Patent Publication US2012/0316059. However it appears that this CeSi does not provide a sufficient acidity on the CeO₂ surface.

Therefore, there is a need to develop sulfur resistant materials which show the best trade-off between thermal stability and sulfur resistance in order to achieve the most severe regulation limits of diesel engines.

20 INVENTION

The subject matter of the invention is thus the development of a composite oxide with simultaneously improved high specific surface area at high temperature and a high acidity leading to low SOx adsorption and easier “desulfation properties” – ie. a SOx desorption in a lower temperature range than the existing materials. Indeed, it appears that the cerium composite oxide comprising silicon oxide and titanium oxide of the invention is sufficiently acid to provide a sulfur resistance and may notably be used in the formulation of sulfur resistant diesel catalyst. The above-described and other disadvantages

of the prior art are then overcome by the composition of the invention.

The present invention then concerns a cerium composite oxide comprising at least:

- 5 - silicon oxide in a proportion comprised between 1 and 15 % by weight of oxide, preferably in a proportion comprised between 5 and 15 % by weight of oxide; and
- titanium oxide in a proportion comprised between 1 and 20 % by weight of oxide, preferably in a proportion comprised between 5 and
10 15 % by weight of oxide.

The present invention also concerns a process to obtain these composite oxides, a catalytic system comprising said composite oxides and the use of them for the treatment of exhaust gases from internal
15 combustion, notably by bringing into contact exhaust gases from internal combustion engines with these catalytic systems.

Preferably, the present invention concerns a precipitated and calcined composition based on cerium oxide, silicon oxide and titanium oxide
20 as described.

Other characteristics, details and advantages of the invention will emerge even more fully upon reading the description which follows.

25 Throughout the description, including the claims, the term "comprising one" should be understood as being synonymous with the term "comprising at least one", unless otherwise specified, and "between" should be understood as being inclusive of the limits.

In the remainder of the description, the term “specific surface” is understood to mean the BET specific surface determined by nitrogen adsorption in accordance with standard ASTM D 3663-78 laid down from the Brunauer-Emmett-Teller method described in the periodical
5 “The Journal of the American Chemical Society, 60, 309 (1938)”.

It is specified that, in the remainder of the description, unless otherwise indicated, the values at the limits are included in the ranges of values which are given.

10

The contents are given as oxides, unless otherwise indicated. The cerium oxide is in the form of ceric oxide (CeO_2). Silicon oxide is SiO_2 and titanium oxide is TiO_2 .

15 Composite oxides of the invention may exhibit a pH inferior or equal to 7, more preferably inferior or equal to 6, more preferably a pH comprised between 1 and 6; wherein pH is measured in an aqueous solution comprising 3 % by weight of this composition, at 25°C pH may notably be measured according to the following protocol:
20 a composite oxide powder is dried at 200°C for 1 hour and the dried oxide powder is hold in a desiccator for 30 minutes. 3.0 g of thus obtained oxide powder is then added into a 100 ml of deionized water under stirring. After 1 minute of stirring, a pH meter (HORIBA D-51) is put into the slurry. The pH value is collected after 3 minutes of
25 putting the pH meter.

Preferably said oxide composites exhibit a specific surface area (SBET), after calcination at 800°C for 2 hours, comprised between 70 and 120 m^2/g ; notably comprised between 85 and 110 m^2/g .

Said oxide composites may also exhibit a specific surface area (SBET), after calcination at 900°C for 5 hours, comprised between 40 and 85 m²/g, notably comprised between 50 and 70 m²/g.

5

This specific surface area may be obtained as follows by using a MOUNTECH Co., LTD. Macsorb analyzer with a 200 mg sample which has been calcined beforehand at subjected temperature under air.

- 10 Cerium composite oxide of the present invention may also comprise at least one rare earth element oxide, other than cerium oxide, notably in a proportion comprised between 1 and 15 % by weight of oxide, preferably in a proportion comprised between 1 and 10 % by weight of oxide. Several rare earth element oxides, other than cerium oxide, may
15 be used in the cerium composite oxide of the invention.

- Rare earth element (REE) or rare earth metal is one of a set of seventeen chemical elements in the periodic table, specifically the fifteen lanthanides plus scandium and yttrium. Preferably, rare earth
20 element oxide are chosen in the group consisting of: lanthanum oxide (La₂O₃), praseodymium oxide (Pr₆O₁₁), neodymium oxide (Nd₂O₃) and yttrium oxide (Y₂O₃).

- Preferably the cerium composite oxide of the invention comprises at
25 least:

- cerium oxide, preferably in a proportion comprised between 60 and 95 % by weight of oxide ;
- silicon oxide in a proportion comprised between 1 and 15 % by weight of oxide, preferably in a proportion comprised between 5 and

15 % by weight of oxide;

- titanium oxide in a proportion comprised between 1 and 20 % by weight of oxide, preferably in a proportion comprised between 5 and 15 % by weight of oxide; and

- 5 - a rare earth element oxide, other than cerium oxide, in a proportion comprised between 1 and 15 % by weight of oxide, preferably in a proportion comprised between 1 and 10 % by weight of oxide.

10 Cerium oxide typically accounts for at least 50 % by weight of the oxide. Preferably cerium oxide is at least 60 % by weight. Cerium oxide typically does not exceed 98% by weight of the total weight of the oxide, preferably it does not exceed 95 % by weight.

Process

- 15 The composite oxides of the present invention may be obtained according to several possible processes.

Usually, the process consists in a calcination of a precipitate comprising compounds of cerium and other compounds. Such a
20 precipitate is generally obtained by the addition of a basic compound. It is notably possible to heat the precipitate in an aqueous medium before to dry and calcine the precipitate. Compounds of silicon and titanium may notably be added before or after the precipitation of the cerium compound.

25

The composition of the invention may notably be obtained by a method for producing a composition comprising the steps of:

(a) providing a cerium solution, in which preferably not less than 90 mol % of which cerium ions are tetravalent,

- (b) heating and maintaining said cerium solution obtained from step (a) up to and at not lower than 60°C,
- (c) adding a precipitant to a cerium suspension obtained through said heating and maintaining to obtain a precipitate,
- 5 (d) calcining said precipitate to obtain a cerium oxide,
- (e) impregnating said cerium oxide obtained through said calcination with a solution of a silicon oxide precursor and titanium oxide precursor, and
- (f) calcining said cerium oxide impregnated with said solution of a
- 10 silicon oxide precursor and titanium oxide precursor.

A water-soluble cerium compound which may be used in step (a) may be, for example, a ceric nitrate solution or ammonium ceric nitrate, with the ceric nitrate solution being particularly preferred.

15

In step (a), the initial concentration of the cerium solution may be adjusted to usually 5 to 100 g/L cerium, preferably 5 to 80 g/L, more preferably 10 to 70 g/L in terms of CeO_2 .

- 20 Preferably step (a) provides a cerium solution in which not less than 90 mol % of which cerium ions are tetravalent.

Usually water is used for the adjustment of the concentration of the cerium solution, and deionized water is particularly preferred. If the

25 initial concentration is too high, the crystallinity of the precipitate is not sufficiently high and sufficient pores for impregnation with the solution of silicon oxide precursor and titanium oxide precursor cannot be formed, resulting in insufficient heat resistance and reducibility of the ultimate composite oxide. Too low an initial concentration leads to

low productivity, which is not industrially advantageous.

It is notably possible to add in step (a) a rare earth element compound, for example a rare earth element in the form of nitrate, chloride, oxide, carbonate, halide, oxyhalide, oxynitrate, and/or sulfate.

In the first method, step (b) of heating and maintaining the cerium solution obtained from step (a) up to and at not lower than 60°C is carried out to cause reaction of the cerium solution. A reactor to be used in step (b) may either be a sealed- or open-type vessel. An autoclave reactor may preferably be used.

In step (b), the temperature at which the cerium solution is heated and maintained is not lower than 60°C, preferably 60 to 200°C, more preferably 80 to 180°C, most preferably 90 to 160°C. The duration of heating and maintaining is usually 10 minutes to 48 hours, preferably 30 minutes to 36 hours, more preferably 1 hour to 24 hours. With insufficient heating and maintaining, the crystallinity of the precipitate is not sufficiently high and a sufficient volume of pores for impregnation with the solution of silicon oxide precursor and titanium oxide precursor cannot be formed, resulting in insufficient heat resistance of the ultimate composite oxide. Too long a period of heating and maintaining affects little the heat resistance and is not industrially advantageous.

The first method further includes step (c) of adding a precipitant to the cerium suspension obtained through the heating and maintaining in step (b) to obtain a precipitate.

The precipitant used in step (c) may be a base, for example, sodium hydroxide, potassium hydroxide, aqueous ammonia, ammonia gas, or a mixture thereof, with the aqueous ammonia being particularly preferred.

5

The precipitant may be added, for example, by preparing an aqueous solution of the precipitant at a suitable concentration and adding the solution to the cerium suspension obtained from step (b) under stirring, or in the case of ammonia gas, by bubbling the cerium suspension with the ammonia gas in the reactor under stirring. The amount of the precipitant to be added may easily be determined by monitoring the pH change of the suspension. Usually, the amount for generating a precipitate in the cerium suspension at pH 7 to 9, preferably pH 7 to 8.5, is sufficient.

15

Step (c) may be carried out after the cerium suspension obtained through the heating and maintaining in step (b) is cooled. Such cooling may usually be carried out under stirring according to a commonly known method. The cooling may either be natural cooling by leaving the suspension to stand, or forced cooling with cooling tubes. The cooling may be carried out down to usually 40°C or lower, preferably a room temperature of 20 to 30°C.

25

Through the precipitation reaction in step (c), a slurry containing a precipitate of cerium oxide hydrate with grown crystals is obtained. The precipitate may be separated by, for example, the Nutsche method, centrifugation, or filter-pressing. The precipitate may optionally be washed with water as needed. Further, in order to improve the efficiency in the following step (d), the precipitate may optionally be

dried to a suitable level.

The first method includes step (d) of calcining the precipitate to obtain a cerium oxide. The temperature for the calcining is usually 250 to
5 500°C, preferably 280 to 450°C.

The cerium oxide obtained through calcination in step (d) is in the form of a porous body having pores of sufficient volume for impregnation with a solution of a silicon oxide precursor and titanium
10 oxide precursor. This facilitates impregnation with a solution of a silicon oxide precursor and titanium oxide precursor and improves the heat resistance of the ultimate composite oxide.

The duration of the calcination may usually be 30 minutes to 36 hours,
15 preferably 1 hour to 24 hours, more preferably 3 hours to 20 hours.

The first method includes step (e) of impregnating the cerium oxide obtained through calcination with a solution of a silicon oxide precursor and a titanium oxide precursor.

20

The silicon oxide precursor used in step (e) may be any compound which may be converted to a silicon oxide through an oxidation treatment, such as calcining, as long as the calcined cerium oxide porous body may be impregnated with the compound dissolved in a
25 solvent. Examples of the precursor may include silicates, such as sodium silicate, silane compounds, such as tetraethyl orthosilicate, silyl compounds, such as trimethylsilyl isocyanate, quaternary ammonium silicates, such as tetramethyl ammonium silicate, and colloidal silica.

The colloidal silica is a commercially-available product, such as for example AT-20Q provided by ADEKA with the following characteristics: acid stabilized type, %SiO₂ = 20, primary particle size = 10-15 nm.

5

The titanium oxide precursor used in step (e) may be any compound which may be converted to a titanium oxide through an oxidation treatment, such as calcining, as long as the calcined cerium oxide porous body may be impregnated with the compound dissolved in a solvent. Examples of the precursor may include titanium sulfate, titanium oxysulfate, titanium tetrachloride, titanium oxychloride, titanium nitrate, titanium tetra-methoxide, titanium tetra-ethoxide, titanium tetra-propoxide, titanium tetra-butoxide, titanium tetra-acetylacetonate, quaternary ammonium titanate sol and colloidal titania.

15

The colloidal titania is a commonly-available product, such as for example TKS-202 provided by TAYCA with the following characteristics: acid stabilized type, % TiO₂ = 33%, primary particle size = 6 nm.

20

The solvent to be used for dissolving the silicon oxide precursor and the titanium oxide precursor may be selected depending on the kind of the precursor to be used, and may be, for example, water or organic solvents, such as alcohol, xylene, hexane, or toluene.

25

The concentration of the solution of the silicon oxide precursor is not particularly limited as long as the cerium oxide may be impregnated with the solution, and may usually be 1 to 300 g/L, preferably about 10

to 200 g/L of the silicon oxide precursor in terms of SiO_2 for workability and efficiency.

The concentration of the solution of the titanium oxide precursor is not particularly limited as long as the cerium oxide may be impregnated with the solution, and may usually be 1 to 300 g/L, preferably about 10 to 200 g/L of the silicon oxide precursor in terms of TiO_2 for workability and efficiency.

In step (e), the amount of the silicon oxide precursor is usually 1 to 15 mass %, preferably 5 to 15 mass % of silicon oxide precursor in terms of SiO_2 with respect to the total amount of the silicon oxide precursor in terms of SiO_2 , the titanium oxide precursor in terms of TiO_2 and the cerium in terms of CeO_2 .

In step (e), the amount of the titanium oxide precursor is usually 1 to 20 mass %, preferably 5 to 15 mass % of titanium oxide precursor in terms of TiO_2 with respect to the total amount of the silicon oxide precursor in terms of SiO_2 , the titanium oxide precursor in terms of TiO_2 and the cerium in terms of CeO_2 .

In step (e), the impregnation of the cerium oxide with the solution of the silicon oxide precursor and titanium oxide precursor may be carried out, for example, by pore-filling, adsorption, or evaporation to dryness. The pore-filling may be effected by measuring in advance the total pore volume of the cerium oxide, and adding the same volume of the solution of the silicon oxide precursor and titanium oxide precursor so that the surface of the cerium oxide is evenly wetted.

It is notably possible to add in step (e) a rare earth element compound, for example a rare earth element in the form of nitrate, chloride, oxide, carbonate, halide, oxyhalide, oxynitrate, and/or sulfate. A rare earth element compound may be then added in step (a) and/or (e).

5

The first method includes step (f) of calcinating the cerium oxide thus impregnated with the solution of the silicon oxide precursor and titanium oxide precursor. The temperature of the calcination is usually 300 to 900°C, preferably 450 to 750°C. The duration of calcination in

10 step (f) may suitably be determined in view of the calcination temperature, and may usually be 1 to 10 hours.

15

In the first method, after step (e) and before step (f), the cerium oxide impregnated with the solution of the silicon oxide precursor and titanium oxide precursor may optionally be dried at about 60 to 200°C. With such a drying step, the efficiency of the calcination in step (f) may be improved.

20

In the first method, after step (f), the cerium oxide impregnated with the solution of the silicon oxide precursor and titanium oxide precursor may optionally be milled. The milling may usually be carried out by commonly known method such as hammer milling or jet milling.

25

Alternatively the inventive composition may be prepared according to a method comprising the steps of:

(A) providing a cerium solution, in which preferably not less than 90 mol % of which cerium ions are tetravalent,

(B) heating and maintaining said cerium solution obtained from step (A) up to and at not lower than 60°C,

- (C) adding a silicon oxide precursor and a titanium oxide precursor to a cerium suspension obtained through said heating and maintaining,
- (D) heating and maintaining said cerium suspension containing said silicon oxide precursor and titanium oxide precursor up to and at not
- 5 lower than 100°C,
- (E) adding a precipitant to said cerium suspension containing said silicon oxide precursor and titanium oxide precursor obtained through said heating and maintaining, to obtain a precipitate, and
- (F) calcining said precipitate.

10

The second method according to the present invention includes step (A) of providing a cerium solution not less than 90 mol % of which cerium ions are tetravalent.

- 15 A water-soluble cerium compound which may be used in step (A) may be, for example, a ceric nitrate solution or ammonium ceric nitrate, with the ceric nitrate solution being particularly preferred.

- In step (A), the initial concentration of the cerium solution not less
- 20 than 90 mol % of which cerium ions are tetravalent, may be adjusted to usually 5 to 100 g/L cerium, preferably 5 to 80 g/L, more preferably 10 to 70 g/L in terms of CeO₂. Usually water is used for the adjustment of the concentration of the cerium solution, and deionized water is particularly preferred.

25

It is notably possible to add in step (A) a rare earth element compound, for example a rare earth element in the form of nitrate, chloride, oxide, carbonate, halide, oxyhalide, oxynitrate, and/or sulfate.

In the second method, step (B) of heating and maintaining the cerium solution obtained from step (A) up to and at not lower than 60°C is carried out next.

- 5 A reactor to be used in step (B) may either be a sealed- or open-type vessel, and an autoclave reactor may preferably be used.

In step (B), the temperature at which the cerium solution is heated and maintained is not lower than 60°C, preferably 60 to 200°C, more
10 preferably 80 to 180°C, most preferably 90 to 160°C. The duration of heating and maintaining is usually 10 minutes to 48 hours, preferably 15 minutes to 36 hours, more preferably 30 minutes to 10 hours.

The second method further includes step (C) of adding a silicon oxide
15 precursor and a titanium oxide precursor to a cerium suspension obtained from step (B).

In step (C), the silicon oxide precursor to be added to the cerium suspension may be any compound which may be converted to a silicon
20 oxide through an oxidation treatment, such as calcination, and may be, for example, colloidal silica, siliconate, or quaternary ammonium silicate sol, with the colloidal silica being particularly preferred in view of the production cost and reduction of environmental burden.

25 In step (C), the titanium oxide precursor to be added to the cerium suspension may be any compound which may be converted to a titanium oxide through an oxidation treatment, such as calcination, and may be, for example, colloidal titania, titanium sulfate, titanium oxysulfate, titanium tetrachloride, titanium oxychloride, titanium

nitrate, titanium tetra-methoxide, titanium tetra-ethoxide, titanium tetra-propoxide, titanium tetra-butoxide, titanium tetra-acetylacetonate or quaternary ammonium titanate sol, with the colloidal titania being particularly preferred in view of the production cost and reduction of environmental burden.

In step (C), the amount of the silicon oxide precursor is usually 1 to 15 mass % of the silicon oxide precursor, preferably 5 to 15 mass %, in terms of SiO_2 with respect to the total amount of the silicon oxide precursor in terms of SiO_2 , the titanium oxide precursor in terms of TiO_2 and the cerium in terms of CeO_2 .

In step (C), the amount of the titanium oxide precursor is usually 1 to 20 mass % of the titanium oxide precursor, preferably 5 to 15 mass %, in terms of TiO_2 with respect to the total amount of the silicon oxide precursor in terms of SiO_2 , the titanium oxide precursor in terms of TiO_2 and the cerium in terms of CeO_2 .

In step (C), before adding the silicon oxide precursor and the titanium oxide precursor, the salt concentration of the cerium suspension may be adjusted by removing the mother liquor from the cerium suspension or by adding water. The removal of the mother liquor may be effected, for example, by decantation, Nutsche method, centrifugation, or filter-pressing. In this case, a slight amount of cerium is removed with the mother liquor, so the amount of the silicon oxide precursor and titanium oxide precursor and water to be added next may be adjusted, taking this removed amount of cerium into consideration.

Step (C) may be carried out after the cerium suspension obtained

through the heating and maintaining in step (B) is cooled. Such cooling may usually be carried out under stirring according to a commonly known method. The cooling may either be natural cooling by leaving the suspension to stand, or forced cooling with cooling tubes. The
5 cooling may be carried out down to usually 40°C or lower, preferably a room temperature of 20 to 30°C.

It is notably possible to add in step (C) a rare earth element compound, for example a rare earth element in the form of nitrate, chloride, oxide,
10 carbonate, halide, oxyhalide, oxynitrate, and/or sulfate. A rare earth element compound may be then added in step (A) and/or (C).

The second method includes step (D) of heating and maintaining the cerium suspension containing the silicon oxide precursor and titanium
15 oxide precursor up to and at not lower than 100°C, preferably 100 to 200°C, more preferably 100 to 150°C.

In step (D), the duration of the heating and maintaining may be usually 10 minutes to 6 hours, preferably 20 minutes to 5 hours, more
20 preferably 30 minutes to 4 hours. In step (D) of heating and maintaining, at lower than 100°C, the crystallinity of the precipitate is not sufficiently high, resulting in insufficient heat resistance of the ultimate composite oxide.

25 The second method includes step (E) of adding a precipitant to the cerium suspension containing the silicon oxide precursor and titanium oxide precursor obtained through the heating and maintaining to obtain a precipitate.

The precipitant used in step (E) may be a base, for example, sodium hydroxide, potassium hydroxide, aqueous ammonia, ammonia gas, or a mixture thereof, with the aqueous ammonia being particularly preferred. The amount of the precipitant to be added in step (E) may
5 easily be determined by monitoring the pH change of the cerium suspension containing the silicon oxide precursor and titanium oxide precursor. Usually, the amount for generating a precipitate in the cerium suspension at pH 7 to 9, preferably pH 7 to 8.5, is sufficient.

10 Step (E) may be carried out after the cerium suspension obtained through the heating and maintaining in step (D) is cooled. Such cooling may usually be carried out under stirring according to a commonly known method. The cooling may either be natural cooling by leaving the suspension to stand, or forced cooling with cooling
15 tubes. The cooling may be carried out down to usually 40°C or lower, preferably a room temperature of 20 to 30°C.

The precipitate may be separated by, for example, the Nutsche method, centrifugation, or filter-pressing. The precipitate may optionally be
20 washed with water as needed.

The second method includes step (F) of calcining the precipitate thus obtained. The temperature for the calcining is usually 300 to 900°C, preferably 450 to 750°C. The duration of the calcination may usually
25 be 1 to 48 hours, preferably 1 to 24 hours, more preferably 3 to 20 hours.

In the second method, after step (F), the cerium based composite oxide may optionally be milled. The milling may usually be carried out by

commonly known method such as hammer milling or jet milling.

The composite oxides of the invention as described above or as obtained by means of the preparation process previously described are
5 in the form of powders, but they can optionally be formed so as to be in the form of granules, pellets, foams, beads, cylinders or honeycombs of variable dimensions.

These composite oxides can be applied to any support commonly used
10 in the field of catalysis, that is to say in particular thermally inert supports. This support can be chosen from alumina, titanium oxide, cerium oxide, zirconium oxide, silica, spinels, zeolites, silicates, crystalline silicoaluminum phosphates or crystalline aluminum phosphates.

15

The present invention also concerns a composite oxide susceptible to be obtained according to the above mentioned processes of the invention.

Application

The composite oxides of the invention may be used in catalytic systems. These catalytic systems can comprise a coating (wash coat), based on these composite oxides and with catalytic properties, on a
5 substrate of the metal or ceramic monolith type, for example. Such a monolith type can be a filter type based on silicon carbide, cordierite or aluminium titanate, for instance. The coating can itself also comprise a support of the type of those mentioned above. This coating is obtained by mixing the composite oxides with the support, so as to form a
10 suspension which can subsequently be deposited on the substrate.

These catalytic systems and more particularly the composite oxides of the invention can have a great many applications. They are therefore particularly well suited to, and thus usable in, the catalysis of various
15 reactions, such as, for example, dehydration, hydrosulfurization, hydrodenitritication, desulfurization, hydrodesulfurization, dehydrohalogenation, reforming, steam reforming, cracking, hydrocracking, hydrogenation, dehydrogenation, isomerization, dismutation, oxychlorination, dehydrocyclization of hydrocarbons or
20 other organic compounds, oxidation and/or reduction reactions, the Claus reaction, treatment of exhaust gases from internal combustion engines, demetallation, methanation, the shift conversion, oxidation of CO, purification of air by low-temperature oxidation ($<200^{\circ}\text{C}$, indeed even $<100^{\circ}\text{C}$), catalytic oxidation of the soot emitted by internal
25 combustion engines, such as diesel engines or petrol engines operating under lean burn conditions.

In the case of these uses in catalysis, the composite oxides of the invention can be employed in combination with precious metals. The

nature of these metals and the techniques for the incorporation of the latter in these compositions are well known to a person skilled in the art. For example, the metals can be platinum, rhodium, palladium, gold or iridium and they can, in particular, be incorporated in the
5 compositions by impregnation.

Among the uses mentioned, the treatment of exhaust gases from internal combustion engines (automobile afterburning catalysis) is a particularly advantageous application. The compositions of the
10 invention can thus be used in this case for catalysis. More particularly still in the case of this use in catalysis, the compositions can be employed in combination with an NO_x (nitrogen oxides) trap for the treatment of exhaust gases from petrol engines operating with a lean burn mixture, for example in the catalysis layer of such a trap. The
15 composite oxides of the invention can be incorporated in oxidation catalysts for diesel engines.

For this reason, the invention also relates very particularly to a process for the treatment of exhaust gases from internal combustion engines
20 which is characterized in that use is made, as catalyst, of a composite oxide or of a catalytic system as described above.

Another advantageous use is the purification of air at temperatures of less than 200°C, indeed even of less than 100°C, this air comprising at
25 least one compound of the carbon monoxide, ethylene, aldehyde, amine, mercaptan or ozone type and generally of the type of the volatile organic compounds or atmospheric pollutants, such as fatty acids, hydrocarbons, in particular aromatic hydrocarbons, and nitrogen oxides (for the oxidation of NO to give NO₂), and of the malodorous

compounds type.

The present invention also concerns then a process for the purification of air, said air comprising carbon monoxide, ethylene, aldehyde,
5 amine, mercaptan, ozone, volatile organic compounds, atmospheric pollutants, fatty acids, hydrocarbons, aromatic hydrocarbons, nitrogen oxides or malodorous compounds, comprising the step of bringing into contact said gases with the catalytic system of the invention.

10 Mention may more particularly be made, as compounds of this type, of ethanethiol, valeric acid and trimethylamine. This treatment is carried out by bringing the air to be treated into contact with a composite oxide or a catalytic system as described above or obtained by the processes described in detail above.

15

Concrete but non limiting examples will now be given.

EXPERIMENTAL PART

Example 1

20 This example relates to a composite oxide of cerium oxide, silicon oxide and titanium oxide at a mass ratio of 92.8:5.1:2.1.

50 g of a ceric nitrate solution in terms of CeO_2 containing not less than 90 mol % tetravalent cerium ions was measured out, and adjusted
25 to a total amount of 1 L with deionized water. The obtained solution was heated to 100°C , maintained at this temperature for 30 minutes, and allowed to cool down to the room temperature, to thereby obtain a cerium suspension. After the mother liquor was removed (2.6 g of cerium in terms of CeO_2 was removed-with the mother liquor) from the

cerium suspension thus obtained, 12.9 g of a colloidal silica (2.6 g in terms of SiO_2) and 3.2 g of a colloidal titania (1.1 g in terms of TiO_2) were added, and the total volume was adjusted to 1 L with deionized water.

5

Then the cerium suspension containing a precursor of silicon oxide and titanium oxide was maintained at 120°C for 2 hours, allowed to cool, and neutralized to pH 8.5 with aqueous ammonia.

10 The obtained slurry was subjected to solid-liquid separation through a Nutsche filter to obtain a filter cake. The cake was calcined in the air at 700°C for 10 hours to obtain composite oxide powder mainly composed of cerium oxide with 5.1 mass % of silicon oxide and 2.1 mass % of titanium oxide.

15

The obtained composite oxide powder was measured of the specific surface area by the BET method after calcination at 800°C for 2 hours and at 900°C for 5 hours. Further, the pH in the aqueous solution comprising 3 % by weight of this composite oxide was measured.

20

The results are shown in Table 1.

Example 2

This example relates to a composite oxide of cerium oxide, silicon
25 oxide and titanium oxide at a mass ratio of 90.0:5.0:5.0.

A composite oxide powder mainly composed of cerium oxide with 5.0 mass % of silicon oxide and 5.0 mass % of titanium oxide was

prepared in the same way as in Example 1 except that the amount of a colloidal titania was 8.0 g (2.6 g in terms of TiO_2).

The properties of the composite oxide powder thus obtained were evaluated in the same way as in Example 1 and the results are shown in Table 1.

Example 3

This example relates to a composite oxide of cerium oxide, silicon oxide and titanium oxide at a mass ratio of 85.7:4.8:9.5.

A composite oxide powder mainly composed of cerium oxide with 4.8 mass % of silicon oxide and 9.5 mass % of titanium oxide was prepared in the same way as in Example 1 except that the amount of a colloidal titania was 16.0 g (5.3 g in terms of TiO_2).

The properties of the composite oxide powder thus obtained were evaluated in the same way as in Example 1 and the results are shown in Table 1.

20

Example 4

This example relates to a composite oxide of cerium oxide, silicon oxide and titanium oxide at a mass ratio of 85.0:10.0:5.0.

A composite oxide powder mainly composed of cerium oxide with 10.0 mass % of silicon oxide and 5.0 mass % of titanium oxide was prepared in the same way as in Example 1 except that the amount of a colloidal silica was 27.8 g (5.6 g in terms of SiO_2) and the amount of a colloidal titania was 8.1 g (2.8 g in terms of TiO_2).

The properties of the composite oxide powder thus obtained were evaluated in the same way as in Example 1 and the results are shown in Table 1.

Example 5

This example relates to a composite oxide of cerium oxide, silicon oxide and titanium oxide at a mass ratio of 90.0:5.0:5.0 and prepared by a method different from Example 2.

A cerium oxide powder was prepared in accordance with the method disclosed in Patent Publication WO2003/022740.

20 g of a ceric nitrate solution in terms of CeO_2 containing not less than 90 mol % tetravalent cerium ions was measured out, and adjusted to a total amount of 1 L with deionized water. The obtained solution was heated to 100°C, maintained at this temperature for 24 hours, and allowed to cool down to the room temperature. Then aqueous ammonia was added to neutralize to pH 8 to obtain cerium oxide hydrate in the form of the slurry. The slurry was then subjected to solid-liquid separation with a Nutsche to obtain a filter cake. The cake was calcined in the air at 300°C for 10 hours to obtain cerium oxide powder.

47.4 g of the cerium oxide powder (45.0 g in terms of CeO_2) thus obtained was placed in a beaker, to which an ethanol solution of 8.39 g of tetraethylorthosilicate (2.5 g in terms of SiO_2) and 8.90 g of titanium n-Propoxide (2.5 g in terms of TiO_2) in a total amount of 28.5 mL was

added to impregnate the cerium oxide with a solution of silicon oxide precursor and titanium oxide precursor by pore-filling.

Then the cerium oxide impregnated with the solution of silicon oxide precursor and titanium oxide precursor was dried at 120°C for 10 hours, and calcined in the air at 700°C for 10 hours to obtain composite oxide powder mainly composed of cerium oxide with 5.0 mass % of silicon oxide and 5.0 mass % of titanium oxide.

The properties of the composite oxide powder thus obtained were evaluated in the same way as in Example 1 and the results are shown in Table 1.

Example 6

This example relates to a composite oxide of cerium oxide, silicon oxide, titanium oxide and lanthanum oxide at a mass ratio of 80.0:5.0:10.0:5.0.

A composite oxide powder mainly composed of cerium oxide with 5.0 mass % of silicon oxide, 10.0 mass % of titanium oxide and 5.0 mass % of lanthanum oxide was prepared in the same way as in Example 1 except that the amount of a colloidal silica was 14.8 g (3.0 g in terms of SiO_2), the amount of a colloidal titania was 18.2 g (5.9 g in terms of TiO_2) and 18.0 g of lanthanum nitrate solution (3.0 g in terms of La_2O_3) was added.

Comparative example 1

This example relates to a cerium oxide without silicon oxide and titanium oxide, which was obtained by calcination at 700°C for 10

hours before the impregnation with the solution of a silicon oxide precursor and a titanium oxide precursor in Example 4.

The properties of the oxide powder thus obtained were evaluated in the same way as in Example 1 and the results are shown in Table 1.

Comparative example 2

This example relates to a composite oxide of cerium oxide and titanium oxide at a mass ratio of 98.0:2.0.

10

A composite oxide powder mainly composed of cerium oxide with 2.0 mass % of titanium oxide was prepared in the same way as in Example 1 except that the amount of a colloidal titania was 2.9 g (1.0 g in terms of TiO_2) and colloidal silica was not added.

15

The properties of the composite oxide powder thus obtained were evaluated in the same way as in Example 1 and the results are shown in Table 1.

Comparative example 3

20

This example relates to a composite oxide of cerium oxide and titanium oxide at a mass ratio of 95.0:5.0.

A composite oxide powder mainly composed of cerium oxide with 5.0 mass % of titanium oxide was prepared in the same way as in Example 1 except that the amount of a colloidal titania was 7.6 g (2.5 g in terms of TiO_2) and colloidal silica was not added.

25

The properties of the composite oxide powder thus obtained were evaluated in the same way as in Example 1 and the results are shown in Table 1.

5 **Comparative example 4**

This example relates to a composite oxide of cerium oxide and titanium oxide at a mass ratio of 90.0:10.0.

10 A composite oxide powder mainly composed of cerium oxide with 10.0 mass % of titanium oxide was prepared in the same way as in Example 1 except that the amount of a colloidal titania was 16.0 g (5.3 g in terms of TiO_2) and colloidal silica was not added.

15 The properties of the composite oxide powder thus obtained were evaluated in the same way as in Example 1 and the results are shown in Table 1.

20 **Comparative example 5**

This example relates to a composite oxide of cerium oxide and silicon oxide at a mass ratio of 95.0:5.0.

25 A composite oxide powder mainly composed of cerium oxide with 5.0 mass % of silicon oxide was prepared in the same way as in Example 1 except that colloidal titania was not added.

The properties of the composite oxide powder thus obtained were evaluated in the same way as in Example 1 and the results are shown in Table 1.

Table 1

Compositions	SBET 800°C/2 h (m²/g)	SBET 900°C/5 h (m²/g)	pH in the aqueous suspension
Invention 1: CeSiTi 92.8/5.1/2.1	104	64	5.9
Invention 2: CeSiTi 90.0/5.0/5.0	94	60	5.5
Invention 3: CeSiTi 85.7/4.8/9.5	92	58	5.8
Invention 4: CeSiTi 85.0/10.0/5.0	118	72	5.6
Invention 5: CeSiTi 90.0/5.0/5.0	88	53	5.7
Comparison 1: Ce 100	61	46	9.8
Comparison 2: CeTi 98.0/2.0	13	7	8.2
Comparison 3: CeTi 95.0/5.0	31	14	6.5
Comparison 4: CeTi 90.0/10.0	16	10	6.7
Comparison 5: CeSi 95.0/5.0	113	72	6.4

Description of analysis method

SBET: The Specific surface area is measured by BET method in the following way. Use is made of a MOUNTECH Co., LTD. Macsorb

analyzer with a 200 mg sample which has been calcined beforehand at 800°C for 2 hours or 900°C for 5 hours under air.

pH in the aqueous suspension: The pH in the aqueous solution comprising 3% by weight of the oxide powder is measured in the following way. An oxide powder is dried at 200°C for 1 hour. The dried oxide powder is hold in the desiccator for 30 minutes. 3.0 g of thus obtained oxide powder is added into a 100 ml of deionized water under stirring. After 1 minute of stirring, a pH meter (HORIBA D-51) is put into the slurry. The pH value is collected after 3 minutes of putting the pH meter.

While preferred embodiments have been shown and described, various modifications and substitutions may be made thereto without departing from the spirit and scope of the invention. Accordingly, it is to be understood that the system and method have been described by way of illustration only, and such illustrations and embodiments as have been disclosed herein are not to be construed as limiting to the claims.

CLAIMS

1. A cerium composite oxide comprising at least:
 - cerium oxide;
 - 5 - silicon oxide in a proportion comprised between 1 and 15 % by weight of oxide; and
 - titanium oxide in a proportion comprised between 1 and 20 % by weight of oxide.
- 10 2. Cerium composite oxide according to claim 1 wherein it comprises silicone oxide in a proportion comprised between 5 and 15 % by weight of oxide.
3. Cerium composite oxide according to claim 1 or 2 wherein it
- 15 comprises titanium oxide in a proportion comprised between 5 and 15 % by weight of oxide.
4. Cerium composite oxide according to anyone of claims 1 to 3 wherein it exhibits a pH inferior or equal to 7, wherein pH is measured
- 20 in an aqueous solution comprising 3 % by weight of this composition, at 25°C.
5. Cerium composite oxide according to anyone of claims 1 to 4 wherein it exhibits a specific surface area, after calcination at 800°C
- 25 for 2 hours, comprised between 70 and 120 m²/g.
6. Cerium composite oxide according to anyone of claims 1 to 5 wherein it exhibits a specific surface area, after calcination at 900°C for 5 hours, comprised between 40 and 85 m²/g.

7. Cerium composite oxide according to anyone of claims 1 to 6 wherein it comprises a rare earth element oxide, other than cerium oxide, in a proportion comprised between 1 and 15 % by weight of oxide, preferably in a proportion comprised between 1 and 10 % by weight of oxide.

8. Process to produce a cerium composite oxide according to anyone of claims 1 to 7 comprising the steps of:

- 10 (a) providing a cerium solution,
- (b) heating and maintaining said cerium solution obtained from step (a) up to and at not lower than 60°C,
- (c) adding a precipitant to a cerium suspension obtained through said heating and maintaining to obtain a precipitate,
- 15 (d) calcining said precipitate to obtain a cerium oxide,
- (e) impregnating said cerium oxide obtained through said calcination with a solution of a silicon oxide precursor and titanium oxide precursor, and
- (f) calcining said cerium oxide impregnated with said solution of a silicon oxide precursor and titanium oxide precursor.
- 20

9. Process according to claim 8 wherein a rare earth element compound may be added in step (a) and/or (e).

- 25 10. Process to produce a cerium composite oxide according to anyone of claims 1 to 6 comprising the steps of:
 - (A) providing a cerium solution,
 - (B) heating and maintaining said cerium solution obtained from step (A) up to and at not lower than 60°C,

(C) adding a silicon oxide precursor and a titanium oxide precursor to a cerium suspension obtained through said heating and maintaining,

(D) heating and maintaining said cerium suspension containing said silicon oxide precursor and titanium oxide precursor up to and at not

5 lower than 100°C,

(E) adding a precipitant to said cerium suspension containing said silicon oxide precursor and titanium oxide precursor obtained through said heating and maintaining, to obtain a precipitate, and

(F) calcining said precipitate.

10

11. Process according to claim 10 wherein a rare earth element compound may be then added in step (A) and/or (C).

15

12. Process according to claim 8 or 10 wherein step (a) or (A) provides a cerium solution in which not less than 90 mol % of which cerium ions are tetravalent.

13. A catalytic system comprising a cerium composite oxide according to anyone of claims 1 to 7.

20

14. A process for the treatment of exhaust gases from internal combustion engines, comprising the step of bringing into contact said gases with the catalytic system as claimed in claim 13.

25

15. A process for the purification of air, said air comprising carbon monoxide, ethylene, aldehyde, amine, mercaptan, ozone, volatile organic compounds, atmospheric pollutants, fatty acids, hydrocarbons, aromatic hydrocarbons, nitrogen oxides or malodorous compounds, comprising the step of bringing into contact said gases with the

catalytic system as claimed in claim 13.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/062950

A. CLASSIFICATION OF SUBJECT MATTER

INV. B01J23/00 B01J23/10 B01J21/08 B01J21/06 B01D53/94
F24F3/16 B01D53/86 B01J37/02 B01J35/10

ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B01J B01D F24F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	TAKAHASHI ET AL: "Sulfur durability of NOx storage and reduction catalyst with supports of TiO₂, ZrO₂ and ZrO₂-TiO₂ mixed oxides", APPLIED CATALYSIS B: ENVIRONMENTAL, ELSEVIER, AMSTERDAM, NL, vol. 72, no. 1-2, 13 February 2007 (2007-02-13), pages 187-195, XP005885860, ISSN: 0926-3373, DOI: 10.1016/J.APCATB.2006.10.014 the whole document ----- -/-	1-15



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/062950

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	XU ET AL: "Selective catalytic reduction of NO by NH₃ over a Ce/TiO₂ catalyst", CATALYSIS COMMUNICATIONS, ELSEVIER SCIENCE, AMSTERDAM, NL, vol. 9, no. 6, 31 December 2007 (2007-12-31), pages 1453-1457, XP022490071, ISSN: 1566-7367, DOI: 10.1016/J.CATCOM.2007.12.012 the whole document -----	1-15
A	US 2012/316059 A1 (OHTAKE NAOTAKA [JP] ET AL) 13 December 2012 (2012-12-13) the whole document -----	1-15
A	ZHANG J ET AL: "Synthesis of Ti-Ce-Si Binary and Ternary Nanocomposite Photocatalyst by Supercritical Fluid Drying Technology", JOURNAL OF RARE EARTHS, INTERNATIONAL ACADEMIC PUBLISHERS, BEIJING, CN, vol. 24, no. 2, 1 January 2006 (2006-01-01), pages 182-187, XP022933730, ISSN: 1002-0721, DOI: 10.1016/S1002-0721(06)60090-2 [retrieved on 2006-01-01] the whole document -----	1-15
A	CUI H ET AL: "Highly Efficient Inorganic Transparent UV-Protective Thin-Film Coating by Low Temperature Sol-Gel Procedure for Application on Heat-Sensitive Substrates", ADVANCED MATERIALS, WILEY VCH VERLAG, DE, vol. 20, no. 1, 1 January 2008 (2008-01-01), pages 65-68, XP009173941, ISSN: 0935-9648, DOI: 10.1002/ADMA.200701960 [retrieved on 2007-12-07] the whole document PAge 67: "Experimental" -----	1-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2014/062950

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2012316059	A1	13-12-2012	CA 2781794 A1 03-06-2011
			CN 102711983 A 03-10-2012
			EP 2505262 A1 03-10-2012
			KR 20120098794 A 05-09-2012
			RU 2012125963 A 27-12-2013
			US 2012316059 A1 13-12-2012
			WO 2011065416 A1 03-06-2011
