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(54) Title: PRECIPITATED AND CALCINATED COMPOSITION BASED ON ZIRCONIUM OXIDE AND CERIUM OXIDE

(57) Abstract: The present invention concerns precipitated and calcinated compositions based on zirconium oxide and cerium oxide that exhibit a sufficiently high specific surface area after calcination and a very low maximum reduction temperature of the oxide after calcination. Compositions of the present invention may be notably used in various catalytic systems, such as for the treatment of exhaust gases from internal combustion engines.

PRECIPITATED AND CALCINATED COMPOSITION BASED ON ZIRCONIUM OXIDE AND CERIUM OXIDE

The present invention concerns precipitated and calcinated compositions based on zirconium oxide and cerium oxide that exhibit a sufficiently high specific surface area after calcination and a very low maximum reduction temperature of the oxide after calcination. Compositions of the present invention may be notably used in various catalytic systems, such as for the treatment of exhaust gases from internal combustion engines.

PRIOR ART

"Multifunctional" catalysts are currently used for the treatment of exhaust gases from internal combustion engines (automobile afterburning catalysis). The term "multifunctional" is understood to 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 ("three-way" catalysts). Zirconium oxide and cerium oxide today appear as two constituents which are particularly important and advantageous for this type of catalyst.

To be effective, these so-called washcoat materials high specific surface area at high temperature and a high oxygen storage capacity (OSC) with fast oxygen release. The notion of OSC is particularly relevant for this application. The H2-Temperature Programmed Reduction is a current method to check the OSC properties of the materials. It is generally accepted that the higher the H2 uptake

(expressed in mol of H2/g of oxide) and the lower the temperature of reduction, the better the catalytic properties.

WO2005/100249 A2 describes a composition based on zirconium oxide and on cerium oxide comprising tin oxide in a proportion of at most 25% by weight of oxide for the development of catalysts with improved reducibility at low temperature. However, such catalysts do not exhibit a satisfactory specific surface area at high temperature.

INVENTION

The subject matter of the invention is thus the development of a precipitated and calcinated composition with simultaneously improved maximum reduction temperature of the oxide and a high specific surface area at high temperature, and a high oxygen storage capacity (OSC) with fast oxygen release.

The present invention then concerns a precipitated and calcinated composition based on zirconium oxide and cerium oxide, characterized in that it comprises at least:

- lanthanum oxide in a proportion comprised between 0.1 and 10 by weight of oxide;
- yttrium and/or gadolinium oxide in a proportion comprised between 3 and 20 by weight of oxide; and
- tin oxide in a proportion comprised between 1 and 15 by weight of oxide;

Said composition exhibits:

- a specific surface area (SBET), after calcination at 1000°C for 6 hours, of at least 45 m^2/g; and

a specific surface area (SBET), after calcination at 1100°C for 6

hours, of at least 25 m^2/g.

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

Specific surface area (SBET), after calcination at 1000°C for 6 hours, is preferably superior or equal to 50 m^2/g, more preferably superior or equal to 55 m^2/g, notably superior or equal to 60 m^2/g. Specific surface area (SBET), after calcination at 1100°C for 6 hours, is preferably superior or equal to 30 m^2/g, more preferably superior or equal to 35 m^2/g, notably superior or equal to 40 m^2/g.

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.

The composition may also comprise praseodymium and/or neodymium oxide in a proportion comprised between 0 and 10 by weight of oxide.

The Ce/Zr molar ratio may be comprised between 0.10 and 4, more particularly between 0.15 and 2.25. The Ce/Zr molar ratio is preferably inferior or equal to 1.

The composition may exhibit a maximum reduction temperature, measured by temperature-programmed reduction (H_2-TPR), inferior or

equal to 500°C, preferably inferior or equal to 450°C, more preferably inferior or equal to 400°C, particularly inferior or equal to 350°C.

This H_2-TPR may be obtained as follows by using a OKURA RIKEN Co., LTD. TP-5000 device with a quarts reactor and a 500 mg sample which has been calcined beforehand at 1000°C for 6 hours under air. The gas is hydrogen at 10% by volume in argon and with a flow rate of 30 ml/min. The temperature rise takes place from ambient to 900°C at the rate of 10°C/min. The signal is detected with a thermal conductivity detector. Maximum reduction temperature, which was mentioned above, is measured using a thermocouple placed at the heart of the sample.

Definitions

Other characteristics, details and advantages of the invention will become even more fully apparent on reading the description which will follow and concrete but non limiting examples intended to illustrate it.

In the continuation 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 “The Journal of the American Chemical Society, 60, 309 (1938)”.

The term “rare earth metal” is understood to mean yttrium and the elements from the group consisting of the elements of the Periodic Table with an atomic number of between 57 and 71 inclusive.

It is specified that, in the continuation of the description, unless

otherwise indicated, the values at the limits are included in the ranges of values which are given.

The contents are given as oxides, unless otherwise indicated. The cerium oxide is in the form of ceric oxide (CeO_2) and the zirconium oxide is ZrO_2. The tin oxide is in the form of stannic oxide (SnO_2). The yttrium oxide is Y_2O_3. The gadolinium oxide is Gd_2O_3. The praseodymium oxide Pr_6O_{11}. The neodymium oxide is Nd_2O_3.

Process

The compositions 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 zirconium, of cerium, of tin, of lanthanum, of yttrium and/or gadolinium and, if appropriate other compounds. Such a 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.

It is notably possible to carry out a process comprising at least the following steps:

(a) a mixture comprising compounds of zirconium, of cerium, of tin, of lanthanum, of yttrium and/or gadolinium and, if appropriate other compounds, is formed;

(b) said mixture is brought into contact with a basic compound, whereby a precipitate is obtained;

(c) said precipitate is heated in an aqueous medium; and

(d) the precipitate thus obtained is calcined.

Such a process is notably described in detail in WO2005/100249 A1.

Optionally, an additive selected from anionic surfactants, nonionic surfactants, polyethylene glycols, carboxylic acids and their salts and surfactants of the carboxymethylated fatty alcohol ethoxylate type is added to the precipitate obtained in the step (c).

It is also possible to carry out a process comprising at least the following steps:

(a1) a mixture is formed comprising either zirconium and cerium compounds only or these compounds with one or more of the compounds of the present composition (ie. lanthanum compound, yttrium and/or gadolinium compound, and tin compound);

(b1) said mixture is brought together with a basic compound, with stirring;

(c1) the medium obtained in the preceding step is brought together, with stirring, with either the remaining compound(s) of the present composition if this or these compound(s) was (were) not present in step (a1), or the required remaining amount of said compound(s), the stirring energy used during step (c1) may be less than that used during step (b1);

(d1) said precipitate is heated in an aqueous medium;

optionally (e1) an additive selected from anionic surfactants, nonionic surfactants, polyethylene glycols, carboxylic acids and their salts and surfactants of the carboxymethylated fatty alcohol ethoxylate type is added to the precipitate obtained in the preceding step; and

(f1) the resulting precipitate is calcined.

Such a process is notably described in WO2011/138255 A1.

The first step of the process therefore consists in preparing a mixture of some of the compounds of the constituent elements of the composition that it is sought to prepare. The mixing is generally carried out in a liquid medium which is preferably water.

The compounds are preferably soluble compounds. They may in particular be zirconium, cerium, tin and rare earth salts. These compounds may be selected from the nitrates, sulfates, acetates, chlorides and ceric ammonium nitrate. By way of examples, mention may thus be made of zirconium sulfate, zirconyl nitrate or zirconyl chloride. The zirconyl sulfate may originate from placing crystalline zirconyl sulfate in solution. It may also have been obtained by dissolution of zirconium basic sulfate with sulfuric acid, or else by dissolution of zirconium hydroxide with sulfuric acid. In the same way, the zirconyl nitrate may originate from placing crystalline zirconyl nitrate in solution or else it may have been obtained by dissolution of zirconium basic carbonate or else by dissolution of zirconium hydroxide with nitric acid.

It may be advantageous to use a zirconium compound in the form of a combination or of a mixture of the above-mentioned salts. Mention may, for example, be made of the combination of zirconium nitrate with zirconium sulfate, or else the combination of zirconium sulfate with zirconyl chloride. The respective proportions of the various salts can vary to a large extent, from 90/10 to 10/90 for example, these proportions denoting the contribution of each of the salts in grams of total zirconium oxide.

For the cerium, mention may also in particular be made of cerium IV salts, such as the nitrate or ceric ammonium nitrate for example, which are particularly suitable here. Preferably, ceric nitrate is used. An aqueous solution of ceric nitrate can, for example, be obtained by reacting nitric acid with a ceric oxide hydrate prepared conventionally by reacting a solution of a cerous salt, for example cerous nitrate, and a solution of aqueous ammonia in the presence of aqueous hydrogen peroxide. Use may also preferably be made of a solution of ceric nitrate obtained according to the process of electrolytic oxidation of a cerous nitrate solution as described in FR-A-2570087, and which here constitutes an advantageous raw material.

It will be noted here that the aqueous solutions of cerium salts and of zirconyl salts can have a certain initial free acidity which can be adjusted by adding a base or an acid. It is, however, just as possible to use an initial solution of cerium and zirconium salts actually having a certain free acidity as mentioned above, as it is to use solutions that have been neutralized beforehand to a lesser or greater extent. This neutralization can be carried out by adding a basic compound to the abovementioned mixture so as to limit this acidity. This basic compound may, for example, be a solution of aqueous ammonia or else of alkali metal (sodium, potassium, etc.) hydroxides, but preferably a solution of aqueous ammonia.

It will be noted that, when the starting mixture contains cerium in form III, it is preferable to involve an oxidizing agent, for example aqueous hydrogen peroxide, during the process. This oxidizing agent may be used by adding it to the reaction medium during step (a1), during step

(b1) or else at the beginning of step (c1).

It is advantageous to use salts with a purity of at least 99.5% and more particularly of at least 99.9%.

Finally, it is also possible to use a sol as starting zirconium or cerium compound. The term "sol" denotes any system consisting of fine solid particles of colloidal dimensions, i.e. dimensions of between approximately 1 nm and approximately 200 nm, containing a zirconium or cerium compound, this compound generally being a zirconium or cerium oxide and/or oxide hydrate, in suspension in an aqueous liquid phase.

The mixture can without distinction be obtained either from compounds initially in the solid state, and will subsequently be introduced into a vessel heel of water for example, or else directly from solutions or suspensions of these compounds followed by mixing, in any order, of said solutions or suspensions.

According to the process of the invention, the mixture is brought together with a basic compound in order to react them. Products of the hydroxide type can be used as base or basic compound. Mention may be made of alkali metal or alkaline-earth metal hydroxides. Use may also be made of secondary, tertiary or quaternary amines. However, amines and aqueous ammonia may be preferred since they reduce the risks of pollution by alkali metal or alkaline-earth metal cations. Mention may also be made of urea.

The basic compound may be more particularly used in the form of a

solution. Finally, it may be used with a stoichiometric excess in order to be sure of optimum precipitation.

This bringing together is carried out with stirring. It can be carried out in any way, for example by adding a preformed mixture of the compounds of the above-mentioned elements to the basic compound in the form of a solution.

The next step (c1) of the process consists in bringing the medium resulting from the preceding step (b1) together with the remaining compounds of the compositions. This bringing together can be carried out in any way, for example by adding a preformed mixture of the remaining compounds to the mixture obtained at the end of step (b1). It is also carried out with stirring, but under conditions such that the stirring energy used during this step (c1) is less than that used during step (b1). More specifically, the energy used during step (c1) is at least 20% less than that of step (b1) and it may be more particularly less than 40% and even more particularly than 50% thereof.

The heating of the precipitate can be carried out directly on the reaction medium obtained at the end of step (b) or (c1) or on a suspension obtained after separating the precipitate from the reaction medium, optionally washing, and putting the precipitate back into water. The temperature to which the medium may be heated is at least 80°C, preferably at least 100°C and even more particularly at least 130°C. It can be between, for example, 100°C and 160°C. The heating operation can be carried out by introducing the liquid medium into a closed chamber (closed reactor of the autoclave type). Under the temperature conditions given above, and in an aqueous medium, it can

thus be specified, by way of illustration, that the pressure in the closed reactor can range between an upper value at 1 bar (10^5 Pa) and 165 bar (1.65×10^7 Pa), preferably between 5 bar (5×10^5 Pa) and 165 bar (1.65×10^7 Pa). The heating can also be carried out in an open reactor for temperatures of about 100°C.

The heating can be carried out either under air, or under an inert gas, preferably nitrogen.

The heating time can vary within broad limits, for example between 1 and 48 hours, preferably between 2 and 24 hours. Likewise, the increase in temperature is carried out at a rate which is not essential, and it is thus possible to reach the fixed reaction temperature by heating the medium for, for example, between 30 minutes and 4 hours, these values being given entirely by way of indication.

It is possible to carry out several heating operations. Thus, the precipitate obtained after the heating step and optionally washing can be resuspended in water and then a further heating of the resulting medium can be carried out. This further heating is carried out under the same conditions as those that were described for the first one.

It is also possible to add to the precipitate resulting from the preceding step, an additive which is selected from anionic surfactants, nonionic surfactants, polyethylene glycols and carboxylic acids and their salts and also surfactants of the carboxymethylated fatty alcohol ethoxylate type. With regard to this additive, reference may be made to the teaching of application WO-98/45212 and the surfactants described in this document may be used.

As surfactants of anionic type, mention may be made of ethoxycarboxylates, ethoxylated fatty acids, sarcosinates, phosphate esters, sulfates such as alcohol sulfates, alcohol ether sulfates and sulfated alkanolamide ethoxylates, and sulfonates such as sulfo-succinates, and alkylbenzene or alkylnapthalene sulfonates.

As nonionic surfactants, mention may be made of acetylenic surfactants, alcohol ethoxylates, alkanolamides, amine oxides, ethoxylated alkanolamides, long-chain ethoxylated amines, copolymers of ethylene oxide/propylene oxide, sorbitan derivatives, ethylene glycol, propylene glycol, glycerol, polyglyceryl esters and ethoxylated derivatives thereof, alkylamines, alkylimidazolines, ethoxylated oils and alkylphenol ethoxylates. Mention may in particular be made of the products sold under the brands Igepal®, Dowanol®, Rhodamox® and Alkamide®.

With regard to the carboxylic acids, it is in particular possible to use aliphatic monocarboxylic or dicarboxylic acids and, among these, more particularly saturated acids. Fatty acids and more particularly saturated fatty acids may also be used. Mention may thus in particular be made of formic acid, acetic acid, propionic acid, butyric acid, isobutyric acid, valeric acid, caproic acid, caprylic acid, capric acid, lauric acid, myristic acid and palmitic acid. As dicarboxylic acids, mention may be made of oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid and sebacic acid.

Salts of the carboxylic acids may also be used, in particular the

ammoniacal salts.

By way of example, mention may be made more particularly of lauric acid and ammonium laurate.

Finally, it is possible to use a surfactant which is selected from those of the carboxymethylated fatty alcohol ethoxylate type.

The expression "product of the carboxymethylated fatty alcohol ethoxylate type" is intended to mean products consisting of ethoxylated or propoxylated fatty alcohols comprising a CH_2-COOH group at the end of the chain.

These products may correspond to the formula:

$$R_1\text{-O-}(CR_2R_3\text{-}CR_4R_5\text{-O})_n\text{-}CH_2\text{-COOH}$$

in which R_1 denotes a saturated or unsaturated carbon-based chain of which the length is generally at most 22 carbon atoms, preferably at least 12 carbon atoms; R_2, R_3, R_4 and R_5 may be identical and may represent hydrogen or else R_2 may represent a CH_3 group and R_3, R_4 and R_5 represent hydrogen; n is a non-zero integer that may be up to 50 and more particularly between 5 and 15, these values being included. It will be noted that a surfactant may consist of a mixture of products of the formula above for which R_1 may be saturated or unsaturated, respectively, or alternatively products comprising both $-CH_2-CH_2-O-$ and $-C(CH_3)-CH_2-O-$ groups.

The surfactant can be added in two ways. It can be added directly to the suspension of precipitate resulting from the preceding heating step (d1). It can also be added to the solid precipitate after separation

thereof, by any known means, from the medium in which the heating took place.

The amount of surfactant used, expressed as percentage by weight of additive relative to the weight of the composition calculated as oxide, is generally between 5% and 100% and more particularly between 15% and 60%.

According to another advantageous variant of the invention, before implementing the calcination step of the process, washing of the precipitate is carried out after having separated it from the medium in which it was in suspension. This washing can be carried out with water, preferably with water at basic pH, for example aqueous ammonia solution.

In a final step of the process of the invention, the precipitate recovered is subsequently calcined. This calcination makes it possible to develop the crystallinity of the product formed and it can also be adjusted and/or selected according to the subsequent operating temperature intended for the composition according to the invention, this being done while taking into account the fact that the specific surface area of the product decreases as the calcination temperature used increases. Such a calcination is generally carried out under air, but a calcination carried out, for example, under inert gas or under a controlled atmosphere, oxidizing or reducing, is very clearly not excluded.

In practice, the calcination temperature is generally limited to a range of values of between 500°C and 900°C and more particularly between 700°C and 800°C.

The duration of the calcination is not critical and depends on the temperature. Purely by way of indication, it can be at least 2 hours and more particularly between 2 hours and 4 hours.

The compositions of the invention as described above or as obtained by means of the preparation process previously described are 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 compositions can be applied to any support commonly used 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.

The present invention also concerns a precipitated and calcinated composition based on zirconium oxide and cerium oxide susceptible to be obtained according to the above mentioned processes of the invention.

Application

The compositions of the invention may be used in catalytic systems. These catalytic systems can comprise a coating (wash coat), based on these compositions and with catalytic properties, on a 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 composition with the support, so as to form a suspension which can subsequently be deposited on the substrate.

These catalytic systems and more particularly the compositions of the invention can have a great many applications. They are therefore particularly well suited to, and thus usable in, the catalysis of various reactions, such as, for example, dehydration, hydrosulfurization, hydrodenitrification, desulfurization, hydrodesulfurization, dehydrohalogenation, reforming, steam reforming, cracking, hydrocracking, hydrogenation, dehydrogenation, isomerization, dismutation, oxychlorination, dehydrocyclization of hydrocarbons or 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°C, indeed even <100°C), catalytic oxidation of the soot emitted by internal combustion engines, such as diesel engines or petrol engines operating under lean burn conditions.

In the case of these uses in catalysis, the compositions 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 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 invention can thus be used in this case for three-way catalysis. More particularly still in the case of this use in three-way catalysis, the compositions can be employed in combination with an NOx (nitrogen oxides) trap for the treatment of exhaust gases from petrol engines operating with a lean burn mixture, for example in the three-way catalysis layer of such a trap. The compositions 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 which is characterized in that use is made, as catalyst, of a composition 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 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 NO_2), 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, 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.

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 composition or a catalytic system as described above or obtained by the processes described in detail above.

Concrete but non limiting examples will now be given.

EXPERIMENTAL PART

In these examples, the ability of capture hydrogen is measured by temperature-programmed reduction (H_2-TPR) in the following way. Use is made of a OKURA RIKEN Co., LTD. TP-5000 device with a quarts reactor and a 500 mg sample which has been calcined beforehand at 1000°C for 6 hours under air. The gas is hydrogen at 10% by volume in argon and with a flow rate of 30 ml/min. The temperature rise takes place from ambient to 900°C at the rate of 10°C/min. The signal is detected with a thermal conductivity detector. Maximum reduction temperature, which was mentioned above, is measured using a thermocouple placed at the heart of the sample.

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 1000°C for 6 hours or 1100°C for 6 hours under air.

Example 1

This example relates to the preparation of a composition based on cerium, zirconium, lanthanum, yttrium and tin oxides in the respective proportions by weight of oxide of 20%, 60%, 5%, 10% and 5%.

Two solutions of nitrates are prepared beforehand, one consisting of ceric nitrate, zirconyl nitrate and tin nitrate and the other of lanthanum nitrate and yttrium nitrate. Tin nitrate is prepared just before preparation of co-nitrate solutions. 34 ml of distilled water is introduced into a first beaker with 12 ml of nitric acid solution (13.1 mol/l). 2.0 g of metallic tin is introduced into the thus diluted nitric acid solution under stirring so as to obtain 52.5 g of tin nitrate solution. 150.4 g of zirconyl nitrate solution (290 g/l, expressed as oxide), 55.5 g of ceric nitrate solution (260 g/l, expressed as oxide), and 52.5 g of tin nitrate solution (54.4 g/l, expressed as oxide) that was prepared in the first beaker are introduced into a stirred second beaker. The mixture is subsequently made up with distilled water so as to obtain 425 ml of a first solution of nitrates of the cerium, zirconium and tin salts. 9.1 g of lanthanum nitrate solution (468 g/l, expressed as oxide), 32.3 g of yttrium nitrate solution (216 g/l, expressed as oxide) are introduced into a stirred third beaker. The mixture is subsequently made up with distilled water so as to obtain 75 ml of a second solution of nitrates of the lanthanum and yttrium salts. 114.4 ml of an aqueous ammonia solution (13.5 mol/l) is introduced into a stirred reactor and the volume is then made up with distilled water so as to obtain a total volume of 500 ml. The two solutions previously prepared are kept constantly stirring. The first solution of nitrates is introduced, over the course of 50 minutes, into the reactor stirred at a speed of 500 rpm, the second solution of nitrates is introduced over the course of 10 minutes

and the stirring is fixed at 200 rpm. The solution obtained is placed in a stainless steel autoclave equipped with a stirrer. The temperature of the medium is brought to 150°C for 2 hours with stirring. 16.5 g of lauric acid is added to the resulting suspension. The suspension is kept stirring for 1 hour. The suspension obtained is then filtered through a Büchner funnel, and then washed with 1 l of aqueous ammonia solution. The product obtained is calcined at 840°C for 2 hours under stationary conditions.

Example 2

This example relates to the preparation of a composition based on cerium, zirconium, lanthanum, yttrium and tin oxides in the respective proportions by weight of oxide of 20%, 55%, 5%, 15% and 5%.

Tin nitrate is prepared in the same way as in Example 1. 137.9 g of zirconyl nitrate solution (290 g/l, expressed as oxide), 55.5 g of ceric nitrate solution (260 g/l, expressed as oxide), 52.5 g of tin nitrate solution (54.4 g/l, expressed as oxide), 9.1 g of lanthanum nitrate solution (468 g/l, expressed as oxide), and 48.5 g of yttrium nitrate solution (216 g/l, expressed as oxide) are introduced into a stirred beaker. The mixture is subsequently made up with distilled water so as to obtain 500 ml of a solution of the cerium, zirconium, tin, lanthanum and yttrium salts. 116.8 ml of an aqueous ammonia solution (13.5 mol/l) is introduced into a stirred reactor and the volume is then made up with distilled water so as to obtain a total volume of 500 ml. The nitrate solution of the cerium, zirconium, tin, lanthanum and yttrium salts is introduced, over the course of 60 minutes, into the reactor stirred at a speed of 500 rpm. The operation is subsequently carried out as in example 1.

Example 3

This example relates to the preparation of the same composition as in Example 2, but the synthesis process is different.

The composite oxide is prepared in the same way as in Example 1 except that the quantity of zirconyl nitrate solution is 137.9 g instead of 150.4 g, the quantity of yttrium nitrate solution is 48.6 g instead of 32.3 g and the quantity of ammonia solution is 116.9 ml instead of 114.4 ml.

Comparative Example 1

This example relates to the preparation of a composition based on cerium, zirconium and tin oxides in the respective proportions by weight of oxide of 20%, 75% and 5%, which is prepared in accordance with the method disclosed in Patent Publication US2009/0185967 A1.

188.0 g of zirconyl nitrate solution (290 g/l, expressed as oxide), 55.5 g of ceric nitrate solution (260 g/l, expressed as oxide) and 5.8 g of tin (IV) chloride pentahydrate are introduced into a stirred beaker. The mixture is subsequently made up with distilled water so as to obtain 500 ml of a solution of the cerium, zirconium and tin salts. 98.1 ml of an aqueous ammonia solution (13.5 mol/l) is introduced into a stirred reactor and the volume is then made up with distilled water so as to obtain a total volume of 500 ml. The nitrate solution of the cerium, zirconium and tin salts is introduced, over the course of 60 minutes, into the reactor stirred at a speed of 500 rpm. The suspension thus obtained is filtered through a Büchner funnel, and then washed twice with 1000 ml of aqueous ammonia solution. The Precipitate is

subsequently resuspended in 657.5 ml of aqueous ammonia solution. The solution obtained is placed in a stainless steel autoclave equipped with a stirrer. The temperature of the medium is brought to 150°C for 2 hours with stirring. The suspension obtained is then filtered through a Büchner funnel, and then washed twice with 750 ml of aqueous ammonia solution. The operation is subsequently carried out as in example 1.

Comparative Example 2

This example relates to the preparation of a composition based on cerium, zirconium, lanthanum and tin oxides in the respective proportions by weight of oxide of 20%, 68%, 7% and 5%.

The composite oxide is prepared in the same way as in Example 2 except that the quantity of zirconyl nitrate solution is 170.5 g instead of 137.9 g, the quantity of lanthanum nitrate was 12.8 g instead of 9.1 g, the quantity of ammonia solution is 109.4 ml instead of 116.8 ml and introduction of the yttrium nitrate is deleted.

Comparative Example 3

This example relates to the preparation of a composition based on cerium, zirconium, lanthanum and neodymium oxides in the respective proportions by weight of oxide of 21%, 72%, 2% and 5%.

180.5 g of zirconyl nitrate solution (290 g/l, expressed as oxide), 58.2 g of ceric nitrate solution (260 g/l, expressed as oxide), 3.7 g of lanthanum nitrate solution (468 g/l, expressed as oxide) and 12.4 g of neodymium nitrate solution (297 g/l, expressed as oxide) are introduced into a stirred beaker. The mixture is subsequently made up

with distilled water so as to obtain 500 ml of a solution of the cerium, zirconium, lanthanum and neodymium salts. 98.0 ml of an aqueous ammonia solution (13.5 mol/l) is introduced into a stirred reactor and the volume is then made up with distilled water so as to obtain a total volume of 500 ml. The nitrate solution of the cerium, zirconium, lanthanum and neodymium salts is introduced, over the course of 60 minutes, into the reactor stirred at a speed of 500 rpm. The operation is subsequently carried out as in example 1.

The surfaces obtained after subsequent calcinations at different temperatures and the maximum reduction temperature of the oxide after subsequent calcination are expressed in the Table 1 below.

Table 1

Compositions	SBET 1000°C/6 h (m^2/g)	SBET 1100°C/6 h (m^2/g)	Maximum reduction temperature (°C)
Comparison 1: ZrCeSn 70/20/5	15	4	614
Comparison 2: ZrCeLaSn 68/20/7/5	40	20	380
Comparison 3: ZrCeLaNd 72/21/2/5	45	25	580
Invention 1: ZrCeLaYSn 60/20/5/10/5	62	33	348
Invention 2: ZrCeLaYSn 55/20/5/15/5	59	32	346
Invention 3: ZrCeLaYSn 55/20/5/15/5	64	38	331

It appears then that the compositions of the present invention provides higher specific surface are after calcination at high temperatures and a lower temperature-programmed reduction (H_2-TPR), in comparison with the precipitated and calcinated composition based on zirconium oxide and cerium oxide of the prior art that do not comprise lanthanum oxide, tin oxide and yttrium and/or gadolinium oxide.

CLAIMS

1. A precipitated and calcinated composition based on zirconium oxide and cerium oxide, characterized in that it comprises at least:

- lanthanum oxide in a proportion comprised between 0.1 and 10 by weight of oxide;
- yttrium and/or gadolinium oxide in a proportion comprised between 3 and 20 by weight of oxide; and
- tin oxide in a proportion comprised between 1 and 15 by weight of oxide;

Said composition exhibits:

- a specific surface area (SBET), after calcination at 1000°C for 6 hours, of at least 45 m^2/g; and

a specific surface area (SBET), after calcination at 1100°C for 6 hours, of at least 25 m^2/g.

2. Composition according to claim 1 wherein the specific surface area (SBET), after calcination at 1000°C for 6 hours, is superior or equal to 50 m^2/g.

3. Composition according to claim 1 or 2 wherein the specific surface area (SBET), after calcination at 1100°C for 6 hours, is superior or equal to 30 m^2/g.

4. Composition according to anyone of claims 1 to 3 wherein said composition also comprises praseodymium and/or neodymium oxide in a proportion comprised between 0 and 10 by weight of oxide.

5. Composition according to anyone of claims 1 to 4, wherein the

Ce/Zr molar ratio is comprised between 0.1 and 4.

6. Composition according to claims 5, wherein the Ce/Zr molar ratio is comprised between 0.15 and 2.25.

7. Composition according to claims 5, wherein the Ce/Zr molar ratio is inferior or equal to 1.

8. Composition according to anyone of claims 1 to 7, wherein said composition exhibits a maximum reduction temperature, measured by a temperature-programmed reduction (H_2-TPR), inferior or equal to 500°C.

9. Composition according to anyone of claims 1 to 8, wherein said composition exhibits a maximum reduction temperature, measured by a temperature-programmed reduction (H_2-TPR), inferior or equal to 400°C.

10. Process for the production of a precipitated and calcinated composition based on zirconium oxide and cerium oxide according to anyone of claims 1 to 9, comprising a calcination step of a precipitate comprising compounds of zirconium, of cerium, of tin, of lanthanum, of yttrium and/or gadolinium and, if appropriate other compounds.

11. Process for the production of a precipitated and calcinated composition based on zirconium oxide and cerium oxide according to anyone of claims 1 to 9, comprising at least the following steps:

(a) a mixture comprising compounds of zirconium, of cerium, of tin, of lanthanum, of yttrium and/or gadolinium and, if appropriate other

compounds, is formed;

(b) said mixture is brought into contact with a basic compound, whereby a precipitate is obtained;

(c) said precipitate is heated in an aqueous medium; and

(d) the precipitate thus obtained is calcined.

12. Process according to claim 11 wherein an additive selected from anionic surfactants, nonionic surfactants, polyethylene glycols, carboxylic acids and their salts and surfactants of the carboxymethylated fatty alcohol ethoxylate type is added to the precipitate obtained in the step (c).

13. Process for the production of a precipitated and calcinated composition based on zirconium oxide and cerium oxide according to anyone of claims 1 to 9, comprising at least the following steps:

(a1) a mixture is formed comprising either zirconium and cerium compounds only or these compounds with one or more of the compounds of said composition;

(b1) said mixture is brought together with a basic compound, with stirring;

(c1) the medium obtained in the preceding step is brought together, with stirring, with either the remaining compound(s) of the present composition if this or these compound(s) was (were) not present in step (a1), or the required remaining amount of said compound(s), the stirring energy used during step (c1) may be less than that used during step (b1);

(d1) said precipitate is heated in an aqueous medium;

optionally (e1) an additive selected from anionic surfactants, nonionic surfactants, polyethylene glycols, carboxylic acids and their salts and

surfactants of the carboxymethylated fatty alcohol ethoxylate type is added to the precipitate obtained in the preceding step; and

(f1) the resulting precipitate is calcined.

14. A precipitated and calcinated composition based on zirconium oxide and cerium oxide susceptible to be obtained by the process according to anyone of claims 10 to 13.

15. A catalytic system, comprising a composition as defined in anyone of claims 1 to 9.

16. A process for the treatment of exhaust gases from internal combustion.

17. 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 15.

18. 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 15.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/052188

A. CLASSIFICATION OF SUBJECT MATTER
INV. C01G25/00 B01J37/03 B01J23/00 B01J23/06 B01J23/10
B01D53/94
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)
C01G B01J B01D

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, BIOSIS, CHEM ABS Data, COMPENDEX, EMBASE, INSPEC, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2007/244002 A1 (KOZLOV ALEXANDR I [US] KOZLOV ALEXANDR I [US] ET AL) 18 October 2007 (2007-10-18)	1-10, 14-17
Y	paragraphs [0010], [0012], [0023]; examples 9-11	11-13,18

Y	WO 2005/100249 A1 (RHONE POULENC CHIMIE [FR]; DEMOURGUES ALAIN [FR]; VERDIER STEPHAN [FR]) 27 October 2005 (2005-10-27) cited in the application page 1, line 34 - page 2, line 33 page 6, line 10 - line 18 page 9, line 26 - page 10, line 23 page 11, line 31 - page 12, line 7	11,12,18

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
12 July 2013	23/07/2013

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INTERNATIONAL SEARCH REPORT

International application No
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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2011/138255 A2 (RHODIA OPERATIONS [FR]; IFRAH SIMON [FR]; LARCHER OLIVIER [US]) 10 November 2011 (2011-11-10) cited in the application page 6, line 13 - page 7, line 11 page 11, line 6 - page 12, line 2 -----	13

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2013/052188

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