

COMPOSITES OF MIXED METAL OXIDES FOR OXYGEN STORAGE

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority under 35 U.S.C. § 119(e) to U.S. Patent Application Ser. No. 61/660,315, filed June 15, 2012, which is hereby incorporated by reference in its entirety.

TECHNICAL FIELD

[0001] The present invention relates to materials used to prepare catalytic washcoats coated on substrates for emissions treatment systems and methods of making these materials. Also provided are methods for reducing contaminants in exhaust gas streams. Embodiments are directed to ceria-zirconia-alumina-based composite materials, optionally, promoted with rare earth metal oxides, that provide high surface area at low alumina content. Specifically, the mixed metal oxide materials of ceria-zirconia-alumina can be formed by using a soluble cerium salt, a soluble zirconium salt, a colloidal alumina suspension, and optionally at least one salt of rare earth metals other than cerium as precursors.

BACKGROUND

[0002] Three-way conversion (TWC) catalysts are used in engine exhaust streams to catalyze the oxidation of the unburned hydrocarbons (HCs) and carbon monoxide (CO) and the reduction of nitrogen oxides (NO_x) to nitrogen. The presence of an oxygen storage component (OSC) in a TWC catalyst allows oxygen to be stored during (fuel) lean conditions to promote reduction of NO_x adsorbed on the catalyst, and to be released during (fuel) rich conditions to promote oxidation of HCs and CO adsorbed on the catalyst. TWC catalysts typically comprise one or more platinum group metals (e.g., platinum, palladium, rhodium, and/or iridium) located upon a support such as a high surface area, refractory oxide support, e.g., a high surface area alumina or a composite support such as a ceria-zirconia composite. The ceria-zirconia composite can also provide oxygen storage capacity. The support is carried on a suitable carrier or substrate such as a monolithic carrier comprising a refractory ceramic or metal honeycomb structure, or refractory particles such as spheres or short, extruded segments of a suitable refractory material.

[0003] The integration of alumina as a diffusion barrier to OSC materials for improved thermostability has been practiced (e.g., Sugiura et al., Bull. Chem. Soc. Jpn., 2005, 78, 752; Wang et al., J. Phys. Chem. C, 2008, 112, 5113). In conventional synthetic approaches to such alumina-ceria-zirconia composites, a soluble aluminum salt, for instance, aluminum nitrate nonahydrate, is typically employed as the alumina precursor. The major contribution to the surface area of such materials is from the alumina component. Increased amounts of alumina in contact with the ceria-zirconia composite, however, can lead to interactions that inhibit efficiency of the oxygen storage function.

[0004] There is a continuing need in the art for catalytic materials that are thermally stable and whose ingredients are used efficiently.

SUMMARY

[0005] Provided are composites of mixed metal oxides, along with methods of making and using the same. The mixed metal oxide composites comprise: a ceria-zirconia-alumina composite, wherein the alumina is present in an amount in the range of 1 to less than 30% by weight of the composite and the mixed metal oxide composite, after 12 hours of hydrothermal aging at 1050°C, has reducibility of ceria of at least 50% in hydrogen temperature-programmed reduction (H₂-TPR) at a temperature up to 900°C. In one or more embodiments, the alumina is formed by using a colloidal alumina precursor. Moreover, the surface areas of these composites are greater than 24 m²/g after 12 hours of hydrothermal aging at 1050°C.

[0006] One aspect provides a mixed metal oxides where a ceria-zirconia solid solution is used that can optionally further comprise at least one rare earth oxide other than ceria, and the alumina formed by using a colloidal alumina precursor. The mixed metal oxide composite may be a random mixture of the ceria-zirconia solid solution and the alumina.

[0007] Another aspect is a method of making a composite of mixed metal oxides comprising ceria, zirconia, and alumina, the method comprising: forming an aqueous solution comprising a cerium salt, a zirconium salt, and optionally at least one rare earth metal salt other than cerium compound; providing a source of alumina in an amount that results in an alumina content in the range of 1 to less than 30% by weight in the composite; mixing the aqueous solution and the source of alumina to form a mixture; adjusting the pH of the mixture with a basic agent to form a raw precipitate; isolating the raw precipitate to obtain an isolated

precipitate; and calcining the isolated precipitate at a temperature of at least 600°C to form the composite of mixed metal oxides. In one or more embodiments, the source of alumina is a suspension of colloidal alumina.

[0008] In another aspect, provided are catalysts for treating engine exhaust comprising a catalytic material coated on a substrate, the catalytic material comprising: a mixed metal oxide as disclosed herein which is used as oxygen storage component or as a precious metal support, and a precious metal component selected from the group consisting of palladium, rhodium, platinum, and combinations thereof. Catalysts formed herein can be suitable for three-way conversions and/or diesel oxidation. Emissions after-treatment systems comprise the catalysts as disclosed herein. Methods of treating an exhaust stream comprising passing the exhaust stream through the catalysts disclosed herein.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] The disclosure may be more completely understood in consideration of the following detailed description of various embodiments of the disclosure in connection with the accompanying drawings, in which:

[0010] FIG. 1 provides a scanning electron microscope image of a mixed metal oxide composite according to an embodiment made from a colloidal alumina;

[0011] FIG. 2 provides a scanning electron microscope image of a comparative mixed metal oxide composite made from an aluminum precursor sourced from a soluble salt;

[0012] FIG. 3 provides a graph of cumulative pore volume as a function of pore radius by Hg porosimetry method for examples after 12 hours of hydrothermal aging at 1050°C;

[0013] FIG. 4 provides an X-ray diffraction pattern of one embodiment of a mixed metal oxide composite with the ceria-zirconia component crystallized in a cubic phase after hydrothermal aging at 1050 °C for 12 hours;

[0014] FIG. 5 provides an X-ray diffraction pattern of another embodiment of a mixed metal oxide composite with the ceria-zirconia component crystallized in a tetragonal phase after hydrothermal aging at 1050 °C for 12 hours;

[0015] FIG. 6 provides a graph of reducibility of ceria versus alumina content by the H₂-TPR method at a temperature up to 900°C for examples with the same contents of ceria and dopants after hydrothermal aging at 1050 °C for 12 hours; and

[0016] FIG. 7 provides a comparison of BET surface area for an inventive sample versus comparative examples with an analogous composition; and

[0017] FIG. 8 provides a graph of tailpipe NO_x, HC and CO emissions for a three-way conversion (TWC) catalyst made with a mixed metal oxide embodiment disclosed herein as compared to a TWC catalyst made with a comparative mixed metal oxide.

DETAILED DESCRIPTION

[0018] It is been found that the use of a soluble aluminum salt to prepare oxygen storage component (OSC) materials such as ceria-zirconia composites can deteriorate the oxygen storage capacity function of the composites, because the Al³⁺ ion of the salt precursor can damage the surface area of the ceria-zirconia component upon high temperature aging. In addition, a relatively high alumina content has to be used to retain a high surface area (alumina is thermally more stable than ceria-zirconia) in a trade-off of oxygen storage capacity. Use of colloidal alumina to form a diffusion barrier on the ceria-zirconia composite reduced the deleterious effects associated with the use of a soluble aluminum salt. Specifically, use of colloidal alumina results in composites having higher surface areas and pore volumes along with lower alumina loadings as compared composites formed with soluble aluminum salts. Mixed metal oxide composites prepared using colloidal alumina have higher thermal stability and oxygen storage capacity than comparative composites prepared using a soluble aluminum salt.

[0019] Without intending to be bound by theory, it is thought that, in conjunction with using colloidal alumina, treatment of raw precipitates with a surfactant such as a fatty acid aids in increasing intra-particle distance. In addition, hydrothermal treatment can assist in enhancing porosity of the raw precipitates. As such, mixed metal oxide composites prepared using colloidal alumina can have substantially more spherical morphologies as shown in FIG. 1, in contrast to mixed metal oxides prepared using a soluble aluminum salt as shown in FIG. 2, which has a more agglomerated morphology.

[0020] The following terms shall have, for the purposes of this application, the respective meanings set forth below.

[0021] "Colloidal alumina" refers to a suspension of nano-sized alumina particles comprising aluminum oxide, aluminum hydroxide, aluminum oxyhydroxide, or a mixture thereof. Anions such as nitrate, acetate and formate may coexist in a colloidal alumina

suspension. In one or more embodiments, the colloidal alumina is suspended in deionized water in solids loadings in the range of 5% to 50% by weight.

[0022] "Random mixture" refers to the absence of a deliberate attempt to load or impregnate one material with another. For example, incipient wetness is excluded from randomly mixing because of the choice to impregnate one ingredient with another.

[0023] "Ceria-zirconia solid solution" refers to a mixture of ceria, zirconia, and optionally one or more rare earth metal oxides other than ceria whereas the mixture exists in a homogeneous phase.

[0024] "Platinum group metal components" refer to platinum group metals or their oxides.

[0025] "Hydrothermal aging" refers to aging of a powder sample at a raised temperature in the presence of steam. In this invention, the hydrothermal aging was performed at 950°C or 1050°C in the presence of 10 vol. % of steam under air.

[0026] "Hydrothermal treatment" refers to the treatment of an aqueous suspension sample at a raised temperature in a sealed vessel. In one or more embodiments, the hydrothermal treatment is performed at temperatures at 80-300°C in a pressure-resistant steel autoclave.

[0027] "BET surface area" has its usual meaning of referring to the Brunauer-Emmett-Teller method for determining surface area by N₂-adsorption measurements. Unless otherwise stated, "surface area" refers to BET surface area.

[0028] "Rare earth metal oxides" refer to one or more oxides of scandium, yttrium, and the lanthanum series defined in the Periodic Table of Elements.

[0029] "Washcoat" is a thin, adherent coating of a catalytic or other material applied to a refractory substrate, such as a honeycomb flow through monolith substrate or a filter substrate, which is sufficiently porous to permit the passage there through of the gas stream being treated. A "washcoat layer," therefore, is defined as a coating that is comprised of support particles. A "catalyzed washcoat layer" is a coating comprised of support particles impregnated with catalytic components.

[0030] "TWC catalysts" comprise one or more platinum group metals (e.g., platinum, palladium, rhodium, rhenium and iridium) disposed on a support, which can be a mixed metal oxide as disclosed herein or a refractory metal oxide support, e.g., a high surface area alumina coating. The support is carried on a suitable carrier or substrate such as a

monolithic carrier comprising a refractory ceramic or metal honeycomb structure, or refractory particles such as spheres or short, extruded segments of a suitable refractory material. The refractory metal oxide supports may be stabilized against thermal degradation by materials such as zirconia, titania, alkaline earth metal oxides such as baria, calcia or strontia or, most
5 usually, rare earth metal oxides, for example, ceria, lanthana and mixtures of two or more rare earth metal oxides. For example, see U.S. Pat. No. 4,171,288 (Keith). TWC catalysts are formulated to include an oxygen storage component.

[0031] "Support" in a catalyst washcoat layer refers to a material that receives precious metals, stabilizers, promoters, binders, and the like through association, dispersion,
10 impregnation, or other suitable methods. Examples of supports include, but are not limited to, high surface area refractory metal oxides and composites containing oxygen storage components such as the mixed metal oxides disclosed herein. The high surface area refractory metal oxide supports preferably display other porous features including but not limited to a large pore radius and a wide pore distribution. As defined herein, such metal oxide supports
15 exclude molecular sieves, specifically, zeolites. High surface area refractory metal oxide supports, e.g., alumina support materials, also referred to as "gamma alumina" or "activated alumina", typically exhibit a BET surface area in excess of 60 square meters per gram (" m^2/g "), often up to about 200 m^2/g or higher. Such activated alumina is usually a mixture of the gamma and delta phases of alumina, but may also contain substantial amounts of eta, kappa
20 and theta alumina phases. Refractory metal oxides other than activated alumina can be used as a support for at least some of the catalytic components in a given catalyst. For example, bulk ceria, zirconia, alpha alumina and other materials are known for such use. Although many of these materials suffer from the disadvantage of having a considerably lower BET surface area than activated alumina, that disadvantage tends to be offset by a greater durability of the
25 resulting catalyst.

[0032] "Flow communication" means that the components and/or conduits are adjoined such that exhaust gases or other fluids can flow between the components and/or conduits.

[0033] "Downstream" refers to a position of a component in an exhaust gas stream
30 in a path further away from the engine than the component preceding component. For example, when a diesel particulate filter is referred to as downstream from a diesel oxidation catalyst, exhaust gas emanating from the engine in an exhaust conduit flows through the diesel

oxidation catalyst before flowing through the diesel particulate filter. Thus, "upstream" refers to a component that is located closer to the engine relate to another component.

[0034] In the present disclosure, "%" refers to "wt. %" or "mass %", unless otherwise stated.

5 Preparation of Mixed Metal Oxide Composites

[0035] In general terms, which will be exemplified below, the mixed metal oxide composites are prepared by mixing salts of cerium and zirconium along with salts of any other desired rare earth metals in water to form an aqueous solution at ambient temperature to 80°C. A source of alumina, such as a colloidal alumina suspension or gamma-alumina, is then added
10 to the aqueous solution to form a mixture. The pH of the mixture is adjusted with a basic agent to form a raw precipitate. An exemplary pH range is 6.0 to 11.0. The basic agent may comprises ammonia, ammonium carbonate, ammonium bicarbonate, an alkaline metal hydroxide, an alkaline metal carbonate, an alkaline metal bicarbonate, an alkaline earth metal hydroxide, an alkaline earth metal carbonate, an alkaline earth metal bicarbonate, or
15 combinations thereof. The raw precipitate is isolated or purified to form an isolated or purified precipitate. The isolated or purified precipitate is calcined to form the composite of mixed oxides. Calcining usually occurs under conditions of at least 600°C in a suitable oven or furnace. Another optional processing step is hydrothermally treating the raw precipitate at a temperature of at least 80°C or even 300°C. An optional further processing step includes
20 treatment of the raw precipitate with an organic agent such as an anionic surfactant, a cationic surfactant, a zwitterionic surfactant, a non-ionic surfactant, a polymeric surfactant, or combinations thereof.

[0036] Before describing several exemplary embodiments of the invention, it is to be understood that the invention is not limited to the details of construction or process steps set
25 forth in the following description. The invention is capable of other embodiments and of being practiced in various ways. In the following, preferred designs for the mixed metal oxide composites are provided, including such combinations as recited used alone or in unlimited combinations, the uses for which include catalysts, systems, and methods of other aspects of the present invention.

30 [0037] In embodiment 1, provided is a composite of mixed metal oxides comprising: a ceria-zirconia-alumina component, wherein the alumina is present in an amount

in the range of 1 to less than 30% by weight of the composite and wherein the mixed metal oxide composite, after 12 hours of hydrothermal aging at 1050°C, has a ceria reducibility of at least 50% in H₂-TPR at a temperature up to 900°C.

[0038] In embodiment 2, provided is a composite of mixed metal oxides comprising: a ceria-zirconia solid solution that optionally further comprises at least one rare earth oxide other than ceria; and alumina formed by using a colloidal alumina precursor in an amount in the range of 1 to less than 30% by weight of the composite; wherein the mixed metal oxide composite, after 12 hours of hydrothermal aging at 1050°C, is a random mixture of the ceria-zirconia solid solution and the alumina, and has a ceria reducibility of at least 50% in H₂-TPR at a temperature up to 900°C.

[0039] In embodiment 3, provided is a catalyst for treating engine exhaust comprising a catalytic material coated on a substrate, the catalytic material comprising: the composite of mixed metal oxide of embodiment 1 or embodiment 2, which is used as oxygen storage component or a precious metal support, and a precious metal component selected from the group consisting of palladium, rhodium, platinum, and combinations thereof. A detailed embodiment provides that the catalyst of claim comprises the composite of mixed metal oxides in the range of about 0.1 g/in³ to about 3.5 g/in³. The precious metal component can be present in the range of about 1 g/ft³ to about 300 g/ft³ (or 1.5-100 g/ft³ or even 2.0-50 g/ft³). Another detailed embodiment provides that the catalyst is a three-way conversion catalyst and the catalytic material is effective to substantially simultaneously oxidize hydrocarbons and carbon monoxide and reduce nitrogen oxides. Another detailed embodiment provides that the catalyst is a diesel oxidation catalyst and the catalytic material is effective to substantially simultaneously oxidize hydrocarbons and carbon monoxide.

[0040] In embodiment 4, provided is an emissions after-treatment system for treating an exhaust stream from an engine comprising the catalyst of embodiment 3 or any of its detailed embodiments in flow communication with the exhaust stream.

[0041] Any of embodiments 1-4 and methods of making or using the same, can have one or more of the following optional design features:

[0042] the morphology of the composite is substantially spherical as determined visually from a scanning electron microscope image;

[0043] the alumina content is in the range of 2 to 20 % by weight of the composite, or in the range of 5 to less than 20% by weight of the composite, or in the range of 10-18% by weight of the composite;

[0044] wherein the cumulative pore volume is at least 0.75 ml/g after 12 hours of hydrothermal aging at 1050°C;

[0045] the pore volume in the pore radius range of 30 to 1000 Å is 35 vol. % or more of the cumulative total pore volume after 12 hours of hydrothermal aging at 1050°C;

[0046] the surface area is in the range of 24 m²/g to 80 m²/g after 12 hours of hydrothermal aging at 1050°C;

[0047] the surface area is in the range of 24 m²/g to 60 m²/g after 12 hours of hydrothermal aging at 1050°C;

[0048] the surface area is in the range of 24 m²/g to 60 m²/g and the pore volume in the pore radius range of 30 to 1000 Å is 35 vol. % or more of the total pore volume after 12 hours of hydrothermal aging at 1050°C;

[0049] the hydrogen (H₂) consumption in H₂-TPR at a temperature of up to 900°C is 7 ml/g or greater;

[0050] the phase of the ceria-zirconia solid solution is cubic, tetragonal or a combination thereof;

[0051] ingredients by weight of the composite comprising: alumina in the range of 5% to less than 20%, ceria in the range of 1% to 50%, zirconia in the range of 10% to 70% by weight, rare earth oxides other than ceria in the range of 0% to 20%;

[0052] ingredients by weight of the composite comprising: alumina in the range of 10% to 18%, ceria in the range of 5% to 40%, zirconia in the range of 10% to 60% by weight, a rare earth oxide other than ceria in the range of 1% to 15%;

[0053] the composite comprising at least one rare earth oxide selected from the group consisting of yttria, praseodymia, lanthana, neodymia, samaria, and gadolinia; and/or

[0054] the composite comprising hafnia in the range of 0.01% to 10% by weight of the composite.

[0055] Embodiment 5 provides a method of making a composite of mixed metal oxides comprising ceria, zirconia, and alumina, the method comprising: forming an aqueous solution comprising a cerium salt, a zirconium salt, and optionally at least one rare earth metal salt other than cerium compound; providing a source of alumina in an amount in the range of 1

to less than 30% by weight in the composite; mixing the aqueous solution and the source of alumina to form a mixture; adjusting the pH of the mixture with a basic agent to form a raw precipitate; isolating the raw precipitate to obtain an isolated precipitate; and calcining the isolated precipitate at a temperature of at least 600°C to form the composite of mixed metal oxides. Embodiment 5 can include one or more of the following steps:

[0056] hydrothermally treating the raw precipitate at a temperature of at least 80°C;

[0057] treating the raw precipitate with an anionic surfactant, a cationic surfactant, a zwitterionic surfactant, a non-ionic surfactant, a polymeric surfactant, or combinations thereof;

[0058] the step of hydrothermally treating the raw precipitate is at a temperature of at least 80°C and treating the raw precipitate with an anionic surfactant, a cationic surfactant, a zwitterionic surfactant, a non-ionic surfactant, a polymeric surfactant, or combinations thereof;

[0059] the surfactant is a fatty acid or a salt of a fatty acid;

[0060] the step of hydrothermally treating the raw precipitate occurs in the presence of a basic agent comprising ammonia, ammonium carbonate, ammonium bicarbonate, an alkaline metal hydroxide, an alkaline metal carbonate, an alkaline metal bicarbonate, an alkaline earth metal hydroxide, an alkaline earth metal carbonate, or an alkaline earth metal bicarbonate; and/or

[0061] the pH is in the range of 6.0 to 11.0 and the basic agent comprises ammonia, ammonium carbonate, ammonium bicarbonate, an alkaline metal hydroxide, an alkaline metal carbonate, an alkaline metal bicarbonate, an alkaline earth metal hydroxide, an alkaline earth metal carbonate, or an alkaline earth metal bicarbonate.

[0062] In embodiment 6, provided is a method of treating an exhaust stream comprising passing the exhaust stream through the catalyst of any embodiment disclosed herein, wherein the precious metal component is selected from the group consisting of palladium, rhodium, platinum, and combinations thereof.

Preparation of Catalyst Washcoats

[0063] TWC catalysts may be formed in a single layer or multiple layers. In some instances, it may be suitable to prepare one slurry of catalytic material and use this slurry to form multiple layers on the carrier. The catalysts can readily prepared by processes well known in the prior art. A representative process is set forth below.

[0064] The catalyst can be readily prepared in layers on a carrier. For a first layer of a specific washcoat, finely divided particles of a high surface area refractory metal oxide such as gamma alumina are slurried in an appropriate vehicle, e.g., water. To incorporate components such as precious metals (e.g., palladium, rhodium, platinum, and/or combinations of the same), stabilizers and/or promoters, such components may be incorporated in the slurry as a mixture of water soluble or water-dispersible compounds or complexes. Typically, when palladium is desired, the palladium component is utilized in the form of a compound or complex to achieve dispersion of the component on the refractory metal oxide support, e.g., activated alumina. The term "palladium component" means any compound, complex, or the like which, upon calcination or use thereof, decomposes or otherwise converts to a catalytically active form, usually the metal or the metal oxide. Water-soluble compounds or water-dispersible compounds or complexes of the metal component may be used as long as the liquid medium used to impregnate or deposit the metal component onto the refractory metal oxide support particles does not adversely react with the metal or its compound or its complex or other components which may be present in the catalyst composition and is capable of being removed from the metal component by volatilization or decomposition upon heating and/or application of a vacuum. In some cases, the completion of removal of the liquid may not take place until the catalyst is placed into use and subjected to the high temperatures encountered during operation. Generally, both from the point of view of economics and environmental aspects, aqueous solutions of soluble compounds or complexes of the precious metals are utilized. For example, suitable compounds are palladium nitrate or rhodium nitrate.

[0065] A suitable method of preparing any layer of the layered catalyst composite of the invention is to prepare a mixture of a solution of a desired precious metal compound (e.g., palladium compound) and at least one support, such as the mixed metal oxide composites disclosed herein and/or a finely divided, high surface area, refractory metal oxide support, e.g., gamma alumina, which is sufficiently dry to absorb substantially all of the solution to form a wet solid which later combined with water to form a coatable slurry. In one or more embodiments, the slurry is acidic, having, for example, a pH of about 2 to less than about 7. The pH of the slurry may be lowered by the addition of an adequate amount of an inorganic or an organic acid to the slurry. Combinations of both can be used when compatibility of acid and raw materials is considered. Inorganic acids include, but are not limited to, nitric acid. Organic acids include, but are not limited to, acetic, propionic, oxalic, malonic, succinic,

glutamic, adipic, maleic, fumaric, phthalic, tartaric, citric acid and the like. Thereafter, if desired, water-soluble or water-dispersible compounds of oxygen storage components, e.g., cerium-zirconium composite, a stabilizer, e.g., barium acetate, and a promoter, e.g., lanthanum nitrate, may be added to the slurry.

- 5 **[0066]** In one embodiment, the slurry is thereafter comminuted to result in substantially all of the solids having particle sizes of less than about 20 microns, i.e., between about 0.1-15 microns, in an average diameter. The comminution may be accomplished in a ball mill or other similar equipment, and the solids content of the slurry may be, e.g., about 20-60 wt.%, more particularly about 30-40 wt.%.
- 10 **[0067]** Additional layers, i.e., the second and third layers may be prepared and deposited upon the first layer in the same manner as described above for deposition of the first layer upon the carrier.

AGING AND ANALYTICS OF COMPOSITES

- 15 **[0068]** For aging, powder samples were placed in high temperature resistant ceramic boats and heated in a horizontal tube furnace fit with a quartz tube. Aging was carried out under a flow of air and 10% steam controlled by a water pump. The temperature was ramped up to a desired temperature and remained at the desired temperature for a desired amount of time. A calibrated thermocouple was placed nearby the samples to control the aging temperature.
- 20 **[0069]** For X-Ray diffraction (XRD), data were collected on a PANalytical MPD X'Pert Pro diffraction system. Cu K_α radiation was used in the data collection with generator settings of 45 kV and 40 mA. The optical path consisted of a 1/4° divergence slit, 0.04 radian soller slits, 15 mm mask, 1/2° anti-scatter slits, the sample, 0.04 radian soller slits, Ni filter, and a PIXCEL position sensitive detector set to a 2.144° angular range. Samples were gently
- 25 ground in a mortar with a pestle and then packed in a round mount. The data collection from the round mount covered a 2θ range from 10° to 90° using a step scan with a step size of 0.026° and a count time of 600s per step. Jade Plus 9 Analytical X-Ray Diffraction Software was used for all steps of the data analysis. The phases present in each sample were identified by search and match of the data available from International Center for Diffraction Data
- 30 (ICDD).

[0070] Hydrogen temperature-programmed reduction (H₂-TPR) was carried out on a Micromeritics Autochem Series Instrument. A sample was pretreated under a flow of 4% O₂ in He at 450°C for 20 min and then cooled down to ambient temperature. The TPR experiment was run at a temperature-ramping rate of 10 °C/min from room temperature to 900 °C in 1.0% H₂ balanced with N₂ at a gas flow rate of 50 cc/min. The consumption of H₂ is accumulated at a temperature up to 900°C and is used to calculate the reducibility of ceria according to the following equation:

$$\text{Ceria Reducibility} = \frac{\text{Experimental H}_2 \text{ Consumption}}{\text{Theoretical H}_2 \text{ Consumption}} \times 100\%$$

wherein the theoretical H₂ consumption is calculated by assuming complete reduction of Ce(IV) to Ce(III) for one gram of the sample. The ceria reducibility reflects the efficiency of utilizing the ceria component of a mixed oxide composite under a reductive environment.

[0071] N₂-Adsorption/desorption measurements were carried out on a Micromeritics TriStar 3000 Series Instrument using American Standard Testing Method (ASTM) D3663. Samples were degassed for 4 hours at 300°C under a flow of dry nitrogen on a Micromeritics SmartPrep degasser.

[0072] Mercury porosimetry determinations were performed on a Micromeritics AutoPore IV Instrument on powder samples which were degassed overnight at 200°C. The porosity of the samples was analyzed from approximately 0.003 to 900 microns using a time-based equilibrium at specified pressures up to 60,000 psi. The operating parameters included a penetrometer constant of 22.07 µL/pF and a contact angle of 140.0 deg.

EXAMPLES OF COMPOSITES

[0073] The following examples illustrate the preparation and characterization of representative embodiments related to the present invention. However, the present invention is not limited to these examples.

EXAMPLE 1

[0074] This example describes the preparation of a composite of cerium, zirconium, lanthanum, yttrium, and aluminum oxides in respective mass proportions of 25%, 45%, 5%, 5%, and 20%.

[0075] To a beaker under stirring were sequentially charged 20 g of de-ioned water, 43.9 g of a zirconium oxynitrate solution (20.5% on a ZrO_2 basis), 3.4 g of yttrium nitrate hexahydrate crystals, 3.8 g of a lanthanum nitrate solution (26.5% on a La_2O_3 basis), and 17.2 g of a cerium nitrate solution (29.0% on a CeO_2 basis). A clear solution was formed, to which
5 was added 26.7 g of a 15.0% aqueous colloidal alumina (23N4-80 from Sasol) suspension, followed by addition of 16.0 g of a 30% aqueous hydrogen peroxide solution. The mixture was agitated for 5 minutes and the resulting suspension was transfer to a drop funnelTo another beaker under vigorous stirring were charged 60 g of a 29.4% aqueous ammonia solution and 40 g of de-ioned water. The nitrate-containing suspension prepared above was added dropwise
10 via the drop funnel to the ammonia solution over 1 hour. A pH of 9.8 was obtained upon completing the addition. The precipitate was collected by filtration and washed with de-ioned water to remove soluble nitrates. The frit was re-dispersed in de-ioned water to form a slurry of a solid percentage of 10%. The pH of the slurry was adjusted to 10 with an additional treatment of ammonia by using a 29.4% aqueous ammonia solution. Hydrothermal treatment
15 of the slurry was conducted in an autoclave at 150°C for 10 hours. After the hydrothermal treatment, the slurry was transferred to a beaker and then the temperature was raised to 70°C. Under stirring, the raw precipitate was treated with a surfactant by adding 9.0 g of lauric acid in small portions to the mixture which was kept at 70°C for 1 hour. The solid was collected by filtration and washed with de-ioned water. The washed frit was dried at 120°C overnight and
20 calcined at 650°C for 5 hours to give the target composite as a pale yellow powder in quantitative yield.

EXAMPLE 2

[0076] This example describes the preparation of a composite of cerium, zirconium, lanthanum, neodymium, and aluminum oxides in respective mass proportions of
25 25%, 45%, 5%, 5%, and 20%. The starting materials used in this preparation included 43.9 g of a zirconium oxynitrate solution (20.5% on a ZrO_2 basis), 3.7 g of a neodymium nitrate solution (27.4% on a Nd_2O_3 basis), 3.8 g of a lanthanum nitrate solution (26.5% on a La_2O_3 basis), 17.2 g of a cerium nitrate solution (29.0% on a CeO_2 basis), and 26.7 g of a 15.0% aqueous colloidal alumina (23N4-80) suspension. The procedure described in Example 1 was
30 followed and the target composite was obtained as a pale yellow powder in quantitative yield.

EXAMPLE 3

[0077] This example describes the preparation of a composite of cerium, zirconium, lanthanum, and aluminum oxides in respective mass proportions of 25%, 50%, 5%, and 20%. The starting materials used in this preparation included 48.8 g of a zirconium oxynitrate solution (20.5% on a ZrO_2 basis), 3.8 g of a lanthanum nitrate solution (26.5% on a La_2O_3 basis), 17.3 g of a cerium nitrate solution (29.0% on a CeO_2 basis), and 26.7 g of a 15.0% aqueous colloidal alumina (23N4-80) suspension. The procedure described in Example 1 was followed and the target composite was obtained as a pale yellow powder in quantitative yield.

EXAMPLE 4

[0078] This example describes the preparation of a composite of cerium, zirconium, lanthanum, yttrium, and aluminum oxides in respective mass proportions of 15%, 55%, 5%, 5%, and 20%. The starting materials used in this preparation included 53.7 g of a zirconium oxynitrate solution (20.5% on a ZrO_2 basis), 3.4 g of yttrium nitrate hexahydrate crystals, 3.8 g of a lanthanum nitrate solution (26.5% on a La_2O_3 basis), 10.4 g of a cerium nitrate solution (29.0% on a CeO_2 basis), and 26.7 g of a 15.0% aqueous colloidal alumina (23N4-80) suspension. The procedure described in Example 1 was followed and the target composite was obtained as a pale yellow powder in quantitative yield.

EXAMPLE 5

[0079] This example describes the preparation of a composite of cerium, zirconium, lanthanum, yttrium, and aluminum oxides in respective mass proportions of 10%, 62%, 5%, 5%, and 18%. The starting materials used in this preparation included 124.0 g of a zirconium oxynitrate solution (20.0% on a ZrO_2 basis), 13.3 g of a yttrium nitrate solution (15.0% on a Y_2O_3 basis), 7.6 g of a lanthanum nitrate solution (26.5% on a La_2O_3 basis), 13.8 g of a cerium nitrate solution (29.0% on a CeO_2 basis), and 48.0 g of a 15.0% aqueous colloidal alumina (23N4-80) suspension. The procedure described in Example 1 was followed and the target composite was obtained as a pale yellow powder in quantitative yield.

EXAMPLE 6

[0080] This example describes the preparation of a composite of cerium, zirconium, lanthanum, yttrium, and aluminum oxides in respective mass proportions of 25%, 50%, 5%, 5%, and 15%. The starting materials used in this preparation included 100.0 g of a zirconium oxynitrate solution (20.0% on a ZrO_2 basis), 13.3 g of a yttrium nitrate solution (15.0% on a Y_2O_3 basis), 7.6 g of a lanthanum nitrate solution (26.5% on a La_2O_3 basis), 34.5 g of a cerium nitrate solution (29.0% on a CeO_2 basis), and 40.0 g of a 15.0% aqueous colloidal alumina (23N4-80) suspension. The procedure described in Example 1 was followed and the target composite was obtained as a pale yellow powder in quantitative yield.

EXAMPLE 7

[0081] This example describes the preparation of a composite of cerium, zirconium, lanthanum, yttrium, and aluminum oxides in respective mass proportions of 25%, 55%, 5%, 5%, and 10%. The starting materials used in this preparation included 53.7 g of a zirconium oxynitrate solution (20.5% on a ZrO_2 basis), 3.4 g of yttrium nitrate hexahydrate crystals, 3.8 g of a lanthanum nitrate solution (26.5% on a La_2O_3 basis), 17.2 g of a cerium nitrate solution (29.0% on a CeO_2 basis), and 13.3 g of a 15.0% aqueous colloidal alumina (23N4-80) suspension. The procedure described in Example 1 was followed and the target composite was obtained as a pale yellow powder in quantitative yield.

EXAMPLE 8

[0082] This example describes the preparation of a composite of cerium, zirconium, lanthanum, praseodymium, and aluminum oxides in respective mass proportions of 28%, 47%, 5%, 2%, and 18%. The starting materials used in this preparation included 94.0 g of a zirconium oxynitrate solution (20.0% on a ZrO_2 basis), 5.2 g of a praseodymium nitrate solution (15.3% on a Pr_6O_{11} basis), 7.6 g of a lanthanum nitrate solution (26.5% on a La_2O_3 basis), 38.6 g of a cerium nitrate solution (29.0% on a CeO_2 basis), and 48.0 g of a 15.0% aqueous colloidal alumina (23N4-80) suspension. The procedure described in Example 1 was followed and the target composite was obtained as an orange powder in quantitative yield.

EXAMPLE 9

COMPARATIVE

[0083] This example describes the preparation of a composite of cerium, zirconium, lanthanum, yttrium, and aluminum oxides in respective mass proportions of 25%, 35%, 5%, 5%, and 30%. The starting materials used in this preparation included 34.2 g of a zirconium oxynitrate solution (20.5% on a ZrO_2 basis), 3.4 g of yttrium nitrate hexahydrate crystals, 3.8 g of a lanthanum nitrate solution (26.5% on a La_2O_3 basis), 17.3 g of a cerium nitrate solution (29.0% on a CeO_2 basis), and 40.7 g of a 15.0% aqueous colloidal alumina (23N4-80) suspension. The procedure described in Example 1 was followed and the target composite was obtained as a pale yellow powder in quantitative yield.

EXAMPLE 10

COMPARATIVE

[0084] This example describes the preparation of a composite of cerium, zirconium, lanthanum, yttrium, and aluminum oxides in respective mass proportions of 25%, 15%, 5%, 5%, and 50%. The starting materials used in this preparation included 15.1 g of a zirconium oxynitrate solution (20.0% on a ZrO_2 basis), 6.7 g of a yttrium nitrate solution (15.0% on a Y_2O_3 basis), 3.8 g of a lanthanum nitrate solution (26.5% on a La_2O_3 basis), 17.3 g of a cerium nitrate solution (29.0% on a CeO_2 basis), and 50.0 g of a 15.0% aqueous colloidal alumina (23N4-80) suspension. The procedure described in Example 1 was followed and the target composite was obtained as a pale yellow powder in quantitative yield.

EXAMPLE 11

COMPARATIVE

[0085] This example describes the preparation of a composite of cerium, zirconium, lanthanum, yttrium, and aluminum oxides in respective mass proportions of 25%, 50%, 5%, 5%, and 15% (the same composition to Example 6) using aluminum nitrate nonahydrate as the alumina precursor. To a beaker under stirring were sequentially charged 40 g of de-ioned water, 100.0 g of a zirconium oxynitrate solution (20.0% on a ZrO_2 basis), 13.3 g of a yttrium nitrate solution (15.0% on a Y_2O_3 basis), 7.6 g of a lanthanum nitrate solution (26.5% on a La_2O_3 basis), 34.5 g of a cerium nitrate solution (29.0% on a CeO_2 basis), 44.1 g of aluminum nitrate nonahydrate crystals, and 32.0 g of a 30% aqueous hydrogen peroxide solution. The mixture was agitated for 5 minutes and the resulting solution was transfer to a drop funnel. To another beaker under vigorous stirring were charged 120 g of a 29.4%

aqueous ammonia solution and 80 g of de-ioned water. The nitrate solution prepared above was added dropwise via the drop funnel to the ammonia solution over 2 hour. A pH of 9.4 was obtained upon completing the addition. Further workup as described in Example 1, expect for using 18 g of lauric acid, gave the target composite as a pale yellow powder in quantitative yield.

EXAMPLE 12

COMPARATIVE

[0086] A physical mixture containing 3.0 g of a high surface area gamma-alumina (surface area after hydrothermal aging at 1050°C for 12 hours: 33.8 m²/g) and 17.0 g of a high surface area, doped ceria-zirconia material (composition: 30% CeO₂, 60% ZrO₂, 5% La₂O₃ and 5% Y₂O₃; surface area after hydrothermal aging at 1050°C for 12 hours: 29.8 m²/g) was prepared. The mixture has a final composition of cerium, zirconium, lanthanum, yttrium, and aluminum oxides in respective mass proportions of 25.5%, 51%, 4.3%, 4.3%, and 15%. The composition of Comparative Example 12 is closely analogous to the composition of Example 6.

TESTING OF COMPOSITES

[0087] The compositions of Examples 1-8 and Comparative Examples 9-12 are summarized in Table 1.

Table 1

Sample	Composition, wt. %						
	CeO ₂	ZrO ₂	La ₂ O ₃	Y ₂ O ₃	Nd ₂ O ₃	Pr ₆ O ₁₁	Al ₂ O ₃
EXAMPLE 1	25	45	5	5	-	-	20
EXAMPLE 2	25	45	5	-	5	-	20
EXAMPLE 3	25	50	5	-	-	-	20
EXAMPLE 4	15	55	5	5	-	-	20
EXAMPLE 5	10	62	5	5	-	-	18
EXAMPLE 6	25	50	5	5	-	-	15
EXAMPLE 7	25	55	5	5	-	-	10
EXAMPLE 8	28	47	5	-	-	2	18

EXAMPLE 9 COMPARATIVE	25	35	5	5	-	-	30
EXAMPLE 10 COMPARATIVE	25	15	5	5	-	-	50
EXAMPLE 11 COMPARATIVE	25	50	5	5	-	-	15
EXAMPLE 12 COMPARATIVE	25.5	51	4.3	4.3	-	-	15

[0088] Table 2 provides data obtained by hydrogen temperature-programmed reduction (TPR) for the samples hydrothermally aged at 1050°C for 12 hours. The ceria reducibility of Examples 1, 6 and 7, and Comparative Examples 9 and 10 are plotted in FIG. 6.

- 5 These five samples have the same contents of ceria (25%) and dopants (5% La₂O₃ and 5% La₂O₃) but different contents of alumina (10-50%) and balance zirconia. It is clearly shown that the reducibility of ceria increases upon decreasing the content of alumina in this series of samples. One unique feature of the current invention is that, by choosing a relatively low content of alumina (< 30%), the inventive composites exhibit a reducibility of ceria greater
- 10 than 50%.

Table 2

Sample ^a	H ₂ -TPR	
	H ₂ Consumption, ml/g	CeO ₂ Reducibility, %
EXAMPLE 1	8.8	54
EXAMPLE 2	9.2	57
EXAMPLE 3	11.1	68
EXAMPLE 4	6.4	66
EXAMPLE 5	5.6	86
EXAMPLE 6	9.7	60
EXAMPLE 7	9.7	60
EXAMPLE 8	12.0	66
EXAMPLE 9 COMPARATIVE	7.3	45
EXAMPLE 10 COMPARATIVE	3.7	23

^a Samples hydrothermally aged at 1050°C for 12 hours.

[0089] Table 3 provides data of the BET surface area determined by the standard N₂-adsorption/desorption method. The samples were analyzed as-is as well as after being aged at high temperatures (950°C and 1050°C) for 12 hours in air and 10 vol. % of steam. The data acquired upon aging at 1050°C are discussed in the following. Examples 1-8 exhibit a surface area ranging from 24.8 to 40.5 m²/g after aging. Comparative Examples 9 and 10 have a surface area of 41.3 and 43.4 m²/g, respectively. However, the relatively large surface area is mainly contributed by the higher content of alumina. FIG. 7 shows a comparison of the BET surface area of Example 6 and Comparative Examples 11 and 12 with an analogous composition. The data reveal that Example 6 prepared using the colloidal alumina as the precursor has notably higher thermal stability than Comparative Example 11 prepared using a soluble aluminum salt (27.8 m²/g versus 15.8 m²/g). Moreover, in comparison with Comparative Example 12 which is a physical mixture of a high surface area alumina and a high surface area ceria-zirconia of a similar composition, Example 6 still displays higher surface area (27.8 m²/g versus 20.8 m²/g) upon high temperature aging.

Table 3

Sample	BET Surface Area, m ² /g		
	Fresh (as is)	950°C, 12 hrs ^a	1050°C, 12 hrs ^a
EXAMPLE 1	155	57.1	35.3
EXAMPLE 2	155	61.4	31.2
EXAMPLE 3	148	53.9	40.5
EXAMPLE 4	150	53.3	31.5
EXAMPLE 5	153	50.4	30.8
EXAMPLE 6	153	46.3	27.8
EXAMPLE 7	158	44.5	24.8
EXAMPLE 8	142	46.7	28.9
EXAMPLE 9	159	55.1	41.3
COMPARATIVE			
EXAMPLE 10	154	57.0	43.4
COMPARATIVE			
EXAMPLE 11	66.0	32.8	15.8
COMPARATIVE			

EXAMPLE 12	-	-	20.8
COMPARATIVE			

^a Hydrothermal aging conditions.

[0090] Table 4 provides pore volumes of Examples 1-8 and Comparative Examples 11 acquired by the mercury porosimetry method after 12 hours of hydrothermal aging at 1050°C. FIG. 3 provides a graph of cumulative pore volume as a function of pore radius for Example 6 and Comparative Example 11. These data demonstrate that the inventive examples have a total pore volume of 0.78-1.10 ml/g, substantially larger than the comparative example. The difference in the total pore volume is mainly contributed by the pores with a diameter of 30 to 1000 Å. For Examples 1-8, the pore volume of the pores with a diameter of 30 to 1000 Å accounts for more than 35% of the corresponding total pore volume. This percentage is significantly less for the comparative example prepared using a soluble aluminum salt as the precursor.

Table 4

Sample ^a	Hg Porosimetry	
	Total Pore Volume, ml/g	Pore Volume (30-1000 Å), ml/g
EXAMPLE 1	1.05	0.42
EXAMPLE 2	0.88	0.35
EXAMPLE 3	0.90	0.36
EXAMPLE 4	0.78	0.36
EXAMPLE 5	1.06	0.50
EXAMPLE 6	1.08	0.46
EXAMPLE 7	0.77	0.32
EXAMPLE 8	1.10	0.55
EXAMPLE 11	0.66	0.12
COMPARATIVE		

^a Samples hydrothermally aged at 1050°C for 12 hours.

[0091] Mixed metal oxide composites prepared using the colloidal alumina can have substantially more spherical morphologies as shown in FIG. 1, which is a scanning

electron microscope image of Example 1, in contrast to mixed metal oxides prepared by using a soluble aluminum salt and having a more agglomerated morphology as shown in FIG. 2.

[0092] The XRD patterns of Examples 1-8 are consistent with the coexistence of a single homogeneous solid solution of the doped ceria-zirconia component and multiple transitional alumina phases. The phase of the doped ceria-zirconia component has either a cubic zirconia structure or a tetragonal zirconia structure. FIG. 4 shows the X-ray diffraction pattern of an exemplary mixed metal oxide composite prepared using a colloidal alumina and hydrothermally aged at 1050°C for 12 hours, which crystallizes in the cubic structure. FIG. 5 shows the X-ray diffraction pattern of another exemplary mixed metal oxide composite prepared using a colloidal alumina and hydrothermally aged at 1050°C for 12 hours, which crystallizes in the tetragonal structure. The doped ceria-zirconia component of the mixed metal oxide composite exists as a single homogeneous solid solution, indicating the material is thermally stable upon aging at 1050°C.

EXAMPLES OF CATALYSTS

EXAMPLE 13

[0093] This example demonstrates the preparation of a three-way conversion (TWC) catalyst comprising a single layered washcoat architecture using the inventive composite Example 5 as one of supports for a platinum group metal (PGM). Four PGM-containing supports were prepared by a standard wetness incipient impregnation method followed by calcination at 550°C for 2 hours. The first impregnated support was prepared by adding a diluted rhodium nitrate solution to 1.00 g/in³ of Example 6 resulting in 2.25 g/ft³ Rh. The second impregnated support was prepared by adding a diluted rhodium nitrate solution to 0.47 g/in³ of a high surface area gamma-alumina (BET surface area: 150 m²/g) resulting in 0.75 g/ft³ Rh. The third impregnated support was prepared by adding a diluted palladium nitrate solution to 1.45 g/in³ of a stabilized ceria-zirconia composite (CeO₂: 30 wt. %) resulting in 25.85 g/ft³ Pd. The fourth impregnated support was prepared by adding a diluted palladium nitrate solution to 0.47 g/in³ of a high surface area gamma-alumina resulting in 21.25 g/ft³ Pd. The four PGM-impregnated supports were dispersed in de-ioned water containing barium acetate of 0.10 g/in³ BaO and zirconium oxynitrate of 0.10 g/in³ ZrO₂. The resulting suspension was adjusted with acetic acid and then milled to give the coating slurry. The slurry

was coated onto a ceramic monolith substrate, dried at 110°C, and calcined at 550°C in air to give a total washcoat loading of 3.61 g/in³.

EXAMPLE 14

5 COMPARATIVE

[0094] This example demonstrates the preparation of a three-way conversion (TWC) catalyst comprising a single layered washcoat architecture using conventional supports for PGM. Four PGM-containing supports were prepared by a standard wetness incipient impregnation method followed by calcination at 550°C for 2 hours. The first impregnated support was prepared by adding a diluted rhodium nitrate solution to 1.00 g/in³ of a stabilized ceria-zirconia composite (CeO₂: 10 wt. %) resulting in 2.25 g/ft³ Rh. The second impregnated support was prepared by adding a diluted rhodium nitrate solution to 0.47 g/in³ of a high surface area gamma-alumina (BET surface area: 150 m²/g) resulting in 0.75 g/ft³ Rh. The third impregnated support was prepared by adding a diluted palladium nitrate solution to 1.45 g/in³ of a second stabilized ceria-zirconia composite (CeO₂: 30 wt. %) resulting in 25.85 g/ft³ Pd. The fourth impregnated support was prepared by adding a diluted palladium nitrate solution to 0.47 g/in³ of a high surface area gamma-alumina resulting in 21.25 g/ft³ Pd. The four PGM-impregnated supports were dispersed in de-ioned water containing barium acetate of 0.10 g/in³ BaO and zirconium oxynitrate of 0.10 g/in³ ZrO₂. The resulting suspension was adjusted with acetic acid and then milled to give the coating slurry. The slurry was coated onto a ceramic monolith substrate, dried at 110°C, and calcined at 550°C in air to give a total washcoat loading of 3.61 g/in³.

AGING AND TESTING OF CATALYSTS

25 [0095] Example 13 and Comparative Example 14, 61.2 in³ in volume each, were loaded separately in a converter can, mounted in parallel in an exhaust line of a gasoline engine, and aged at a maximum bed temperature of 980°C for 80 hour using a fuel-cut aging cycle. The aged catalysts were tested on another gasoline engine operating New European Drive Cycles (NEDC) following certified procedures and tolerances. FIG. 8 provides tailpipe NO_x, HC and CO emissions during the NEDC tests. The data show that the three tailpipe emissions are reduced for Example 13 relative to Comparative Example 14.

[0096] Reference throughout this specification to "one embodiment," "certain embodiments," "one or more embodiments" or "an embodiment" means that a particular feature, structure, material, or characteristic described in connection with the embodiment is included in at least one embodiment of the invention. Thus, the appearances of the phrases
5 such as "in one or more embodiments," "in certain embodiments," "in one embodiment" or "in an embodiment" in various places throughout this specification are not necessarily referring to the same embodiment of the invention. Furthermore, the particular features, structures, materials, or characteristics may be combined in any suitable manner in one or more embodiments.

10 [0097] While this invention has been described with an emphasis upon preferred embodiments, it will be obvious to those of ordinary skill in the art that variations in the preferred devices and methods may be used and that it is intended that the invention may be practiced otherwise than as specifically described herein. Accordingly, this invention includes all modifications encompassed within the spirit and scope of the invention as defined by the
15 claims that follow.

What is claimed:

1. A composite of mixed metal oxides comprising:

a ceria-zirconia solid solution that optionally further comprises at least one rare earth oxide other than ceria; and

alumina in an amount in the range of 1 to less than 30% by weight of the composite;

wherein the mixed metal oxide composite, after 12 hours of hydrothermal aging at 1050°C, has a reducibility of ceria of at least 50% in H₂-TPR at a temperature up to 900°C.

2. The composite of mixed metal oxides of claim 1, wherein the alumina formed by using a colloidal alumina precursor.

3. The composite of mixed metal oxides of claim 1, wherein the alumina content is in the range of 5 to less than 20% by weight of the composite.

4. The composite of mixed metal oxides of claim 1, wherein the pore volume in the pore radius range of 30 to 1000 Å is 35 vol. % or more of the cumulative total pore volume after 12 hours of hydrothermal aging at 1050°C.

5. The composite of mixed metal oxides of claim 1, wherein the surface area is in the range of 24 m²/g to 80 m²/g after 12 hours of hydrothermal aging at 1050°C.

6. The composite of mixed metal oxides of claim 1 comprising, by weight of the composite:

alumina in the range of 5% to less than 20%;

ceria in the range of 1% to 50%;

zirconia in the range of 10% to 70% by weight;

rare earth oxides other than ceria in the range of 0% to 20%.

7. A method of making a composite of mixed metal oxides comprising ceria, zirconia, and alumina, the method comprising:

forming an aqueous solution comprising a cerium salt, a zirconium salt, and optionally at least one rare earth metal salt other than cerium compound;

providing a source of alumina in an amount that results in an alumina content in the range of 1 to less than 30% by weight in the composite;

- 5 mixing the aqueous solution and the source of alumina to form a mixture;
 adjusting the pH of the mixture with a basic agent to form a raw precipitate;
 isolating the raw precipitate to obtain an isolated precipitate; and
 calcining the isolated precipitate at a temperature of at least 600°C to form the
10 composite of mixed metal oxides.

8. The method of claim 7, wherein the source of alumina is a suspension of colloidal alumina.

9. The method of claim 7, further comprising hydrothermally treating the raw precipitate at a temperature of at least 80°C.

15 10. The method of claim 7, further comprising treating the raw precipitate with an anionic surfactant, a cationic surfactant, a zwitterionic surfactant, a non-ionic surfactant, a polymeric surfactant, or combinations thereof.

11. A catalyst for treating engine exhaust comprising a catalytic material coated on a substrate, the catalytic material comprising:

20 the composite of mixed metal oxide of claim 1 which is used as oxygen storage component or a precious metal support, and
 a precious metal component selected from the group consisting of palladium, rhodium, platinum, and combinations thereof.

25 12. The catalyst of claim 11, wherein the catalyst is a three-way conversion catalyst and the catalytic material is effective to substantially simultaneously oxidize hydrocarbons and carbon monoxide and reduce nitrogen oxides.

13. The catalyst of claim 11, wherein the catalyst is a diesel oxidation catalyst and the catalytic material is effective to substantially simultaneously oxidize hydrocarbons and carbon monoxide.

14. An emissions after-treatment system for treating an exhaust stream from an engine
5 comprising the catalyst of claim 11 in flow communication with the exhaust stream.

15. A method of treating an exhaust stream comprising passing the exhaust stream through the catalyst of claim 11.