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(54) CERIA-BASED MIXED-METAL OXIDE STRUCTURE, INCLUDING METHOD OF MAKING AND USE

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(57) ABSTRACT

A homogeneous ceria-based mixed-metal oxide, useful as a catalyst support, a co-catalyst and/or a getter, is described. The mixed-metal oxide has a relatively large surface area per weight, typically exceeding 150 m^2/g, a structure of nanocrystallites having diameters of less than 4 nm, and including pores larger than the nanocrystallites and having diameters in the range of 4 to about 9 nm. The ratio of the pore volumes, V_P, to skeletal structure volumes, V_S, is typically less than about 2.5, and the surface area per unit volume of the oxide material is greater than 320 m^2/cm^3, such that the structural morphology supports both a relatively low internal mass transfer resistance and large effective surface area for reaction activity of interest. The mixed metal oxide is made by co-precipitating a dilute metal salt solution containing the respective metals, which may include Zr, Hf, and/or other metal constituents in addition to Ce, replacing water in the co-precipitate with a water-miscible low surface-tension solvent, and relatively quickly drying and calcining the co-precipitate at moderate temperatures. A highly dispersive catalyst metal, such as Pt, may be loaded on the mixed metal oxide support from a catalyst-containing solution following a selected acid surface treatment of the oxide support. The mixed metal oxide, as catalyst support, co-catalyst or getter, is applied in various reactions, and particularly water gas shift and/or preferential oxidation reactions as associated with fuel processing systems, as for fuel cells and the like.

CERIA-BASED MIXED-METAL OXIDE STRUCTURE, INCLUDING METHOD OF MAKING AND USE

TECHNICAL FIELD

[0001] This invention relates to mixed metal oxides, and more particularly to ceria-based mixed-metal oxide structures, for use as catalyst supports, as co-catalysts, as getters, and the like. The invention relates further to methods of preparing such ceria-based mixed-metal oxide structures, and further still to metal loading of such structures. The invention relates still further to the application of such mixed-metal oxide structures as catalyst supports, co-catalysts, and/or getters in, for instance, fuel processing systems.

BACKGROUND ART

[0002] Various metal oxides have found use in chemically reactive systems as catalysts, supports for catalysts, gettering agents and the like. As used herein, a gettering agent, or getter, is a substance that sorbs or chemically binds with a deleterious or unwanted impurity, such as sulfur. In those usages, their chemical characteristics and morphologies may be important, as well as their ease and economy of manufacture. One area of usage that is of particular interest is in fuel processing systems. Fuel processing systems catalytically convert hydrocarbons into hydrogen-rich fuel streams by reaction with water and oxygen. The conversion of carbon monoxide and water into carbon dioxide and hydrogen through the water gas shift (WGS) reaction is an essential step in these systems. A preferential oxidation (PROX) of the WGS product using such catalysts may also be part of the process, as in providing hydrogen fuel for a fuel cell. Industrially, copper-zinc oxide catalysts, often containing alumina and other products, are effective low temperature shift catalysts. These catalysts are less desirable for use in fuel processing systems because they require careful reductive activation and can be irreversibly damaged by air after activation.

[0003] Recent studies of automotive exhaust gas “three-way” catalysts (TWC) have described the effectiveness of a component of such catalysts, that being noble metal on cerium oxide, or “ceria” (CeO_2), for the water gas shift reaction because of its particular oxygen storing capacity (OSC). Indeed, the ceria may even act as a “co-catalyst” with the noble metal loading in that it, under reducing conditions, acts in concert with the noble metal, providing oxygen from the CeO_2 lattice to the noble metal surface to oxidize carbon monoxide or hydrocarbons adsorbed and activated on the surface. In many cases the ceria component of these catalysts is not pure ceria, but cerium oxide mixed with zirconium oxide and optionally, other oxides such as rare earth oxides. It has been determined that the reduction/oxidation (redox) behavior of the cerium oxide is enhanced by the presence of ZrO_2 and/or selected dopants. Robustness at high temperatures is an essential property of TWC’s, and thus, such catalysts do not typically have either sustainable high surface areas, i. e., greater than 100 m^2/g, or high metal dispersion (very small metal crystallites), even though such features are generally recognized as desirable in other, lower temperature, catalytic applications.

[0004] Ceria-zirconia mixed oxide materials having relatively large surface area per unit weight may be particularly well suited in various catalytic, gettering and/or sulfur sorbing applications, as might be typified by, but not limited to, the WGS reaction. Indeed, such ceria-based mixed metal oxides may be used first in a WGS system as a getter to adsorb sulfur-containing compounds from the gas stream to protect more sensitive/valuable components downstream that use such oxides as catalysts in the WGS reaction. In that general regard, it is deemed desirable that the mixed oxide material comprises small crystallites agglomerated to form porous particles having relatively large surface areas per unit weight as a result of significant pore diameters and pore volumes. Large pore diameters facilitate mass transfer during catalytic reactions or gettering applications, by minimizing mass transfer resistance. On the other hand, however, excessive pore volumes may act to minimize the amount of effective surface area in a given reactor volume, for a given final form of catalyst or getter, thereby limiting the catalytic or gettering action in a given reactor volume. Thus, the ratio of pore volume to the structural mass, as well as crystallite size and pore diameters, can be optimized within a range. In this regard then, the particular morphology of the ceria mixed oxide material may be important to efficient operation of the material as a catalyst or getter in particular reactions and/or under particular operating conditions and geometries.

[0005] A variety of techniques have been used to provide ceria-zirconia mixed oxide materials. These techniques include conventional co-precipitation, homogeneous coprecipitation, the citrate process, and a variety of sol-gel techniques. However, as far as can be determined, the surface areas of the mixed metal oxides resulting from these techniques are typically less than about 130 m^2/g.

[0006] Surface areas as great as 235 m^2/g for such materials have been reported by D Terribile, et al, in an article entitled “The preparation of high surface area CeO2-ZrO2 mixed oxides by a surfactant-assisted approach” appearing in *Catalysis Today* 43 (1998) at pages 79-88, however, the process for their production is complex, sensitive, and slow. The process for making these oxides requires the use of a surfactant and a lengthy aging, or maturing, interval of about 90 hours at 90° C. Moreover, the initial precipitate must be washed repeatedly with water and acetone to remove the free surfactant (cetyltrimethylammonium bromide) before the material can be calcined, thereby contributing to delays and possible other concerns. Still further, the mean particle sizes of those oxides appears to be at least 4-6 nm or more. The pore volume is stated to be about 0.66 cm^3/g. This relatively large pore volume per gram is not consistent with that required for a ceria-based mixed metal oxide which, while thermally robust, should tend to maximize both the available surface area in a given reactor volume and the mass transfer characteristics of the overall structure as well as the appropriate reactivity of that surface area, as is desired in the applications under consideration. Assuming the density, D, of this particular material is about 6.64 g/cm^3, the skeleton has a volume, V_S, of 1/D, or about 0.15 cm^3/g, such that the total volume, V_T, of that gram of that material is the sum of the pore volume, P_V, (0.66 cm^3/gm)+skeletal volume, V_S, which equals about 0.81 cm^3/gm. Hence, 235 $m^2/gm/0.81\ cm^3/gm$ equals about 290 m^2/cm^3. Because of the relatively large pore volume, the surface area per unit volume of a material of such density has a reduced value that may not be viewed as optimal.

[**0007**] It is desirable to provide ceria-based mixed-metal oxide materials having the aforementioned positive properties and avoiding the limitations, for use in reactions/gettering generally, and fuel processing reactions/gettering more specifically. Even more particularly, it is desirable to provide such ceria-based mixed-metal oxide materials for use in, for example, water gas shift reactions employed in fuel processing systems for the production of hydrogen-rich feed stock.

[**0008**] Accordingly, it is an object of the invention to provide ceria-based mixed metal oxides having the aforementioned desirable properties of relatively stable, high surface areas, relatively small crystallites, and meso-pores and pore volumes sized to optimally balance the reduction of mass transfer resistance and the provision of sufficient effective surface area in a given reactor volume, particularly for use as a catalyst support or co-catalyst, though not limited thereto.

[**0009**] It is a further object of the invention to provide such ceria-based mixed-metal oxide having enhanced redox capability.

[**0010**] It is an even further object of the invention to provide a catalyst including the ceria-based mixed metal-oxide as support, in accordance with the forgoing objects.

[**0011**] It is a still further object of the invention to provide an efficient and economical process for making such ceria-based mixed-metal oxide catalyst support, catalyst, and/or getter in accordance with the forgoing objects.

[**0012**] It is yet a further object of the invention to utilize a catalyst employing a ceria-based mixed metal oxide as support, co-catalyst, or getter, made in accordance with the forgoing objects, in a fuel processing system in, for example, a water gas shift reaction.

DISCLOSURE OF INVENTION

[**0013**] The present invention relates to a ceria-based mixed-metal oxide material, and more particularly to such material having a relatively high surface area per unit of weight, relatively small crystallite diameters, pore diameters that normally exceed the particle diameters, and having an aggregate particle morphology that is thermally robust, and that optimizes available surface area per unit volume, mass transfer characteristics, and the reactivity of that surface area. The invention also relates to the selection of metal constituents in the metal oxide mix with the ceria base, for providing the aforementioned characteristics, and may preferably include one or more of the relatively redox tolerant ions Zr^{+4}, Hf^{+4} and Ti^{+4}, and the aliovalent ions such as typical lanthanide ions La^{+3} and Yb^{+3}.

[**0014**] The invention further relates to the process(s) for making such ceria-based oxides, to the use of such ceria-based oxides as catalyst supports, co-catalysts, getters and the like, and to the catalyst supported thereby and the process for its manufacture. The invention also relates to the use of such ceria-based mixed metal oxide support and catalyst particularly in water gas shift (WGS) and/or PROX oxidation reactions in fuel processing systems, as for fuel cells.

[**0015**] According to the invention, there is provided a material of homogeneous cerium-based binary, ternary or quarternary mixed-oxides that are nano-crystalline, the average crystallite size less than 4 nm after calcinations at 500° C. or less, and which after calcination in air for 1-6 hours, and preferably 2-4 hours, at temperatures in the range of about 250°-600° C., and preferably 350°-500° C., have high (large) surface areas greater than 150 m^2/g after calcinations at 500° C., a skeletal density of about 6.5 g/cm^3, pore volumes of moderate size such that the surface area per unit volume of the porous material is greater than 320 m2/cm3, and preferably greater than 420 m^2/cm^3, and an average pore diameter normally greater than the nano-crystallites, typically being greater than 4 nm but less than about 9 nm in keeping with pore volumes of moderate size. As used herein, the term "homogeneous" refers to the elemental composition of the individual nanocrystallites that reflects the overall elemental composition.

[**0016**] This combination of surface area and average pore diameter translates into relatively low internal mass transfer resistance. However, if that value becomes too small because of excessive pore size and/or volume, the effective number of sites per crystallite aggregate necessarily decreases and the amount of effective surface area per unit reactor volume also decreases. As described earlier, for a porous material of given density, D, the skeletal volume, V_S, is 1/D, such that the total volume of a gram of material, V_T, is the sum of the pore volume, V_P, +skeletal volume, V_S. From this, the surface area/gram/V_T yields the surface area per unit volume of material, and it is this value which the invention seeks to maximize. Accordingly, it has been determined that the surface area per unit volume of material should be greater than 320 m^2/cm^3, and preferably greater than 420 m^2/cm^3. In this respect, because the pore diameter and pore volume are related, it has been determined that the pore diameter should be moderate and in the range of more than 4 nm but less than 9 nm. Viewed yet another way, it has been determined that the ratio of pore volume, V_P, to the particle, or skeletal volume, V_S, should not exceed about 2.5.

[**0017**] In addition to the cerium oxide, the other oxides in the mix are derived from one or more constituents from the group which includes Zr (zirconium), Hf (hafnium), Nb (niobium), Ta (tantalum), La (lanthanum), Pr (praseodymium), Nd (neodymium), Sm (samarium), Eu (europium), Gd (gadolinium), Tb (terbium), Dy (dysprosium), Ho (holmium), Er (erbium), Tm (thullium), Yb(ytterbium), Lu (lutetium), Mo (molybdenum), W (tungsten), Re (rhenium), Rh (rhodium), Sb (antimony), Bi (bismuth), Ti (titanium), V (vanadium), Mn (manganese), Co (cobalt), Cu (copper), Ga (gallium), Ca (calcium), Sr (strontium), and Ba (barium). In addition to Ce, the other element(s) in the mixed-metal oxide most typically include Zr and/or Hf. Further, on a metals-only atomic percent basis, the sum of Ce and one or more optional constituents selected from the group consisting of La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Mo, W, Re, Rh, Sb, Bi, V, Mn, Co, Cu, Ga, Ca, Sr, and Ba is at least 60%, and the sum of Zr, Hf, Nb, Ta, and Ti is 40% or less. With respect to the sum of these latter five constituents, at least about 75% of that sum is Zr and/or Hf, with Nb, Ta, and/or Ti comprising 25% or less of that sum, or less than 10% of the total. For purposes of the discussion herein, if a constituent in the mixed metal oxide is present in an amount less than about 10% of the total, it may be referred to as a "dopant". It will be understood by those skilled in the art that not all of the listed dopants are equally effective or even desirable for all processes in which these ceria-based oxides may be used. For instance, some dopants such as Ga and Bi may not be desirable in Pt/$CeZrO_2$ catalysts if for use in WGS reactions.

[0018] The inventive process for making the Ce-based mixed metal oxide material having the constituents, properties and morphology of the invention avoids the need for using surfactants and lengthy aging steps, and includes the steps of 1)dissolving salts of the cerium and at least one other constituent in water to form a dilute metal salt solution; 2) adding urea, either as a solid or aqueous solution; 3) heating the solution of metal salt and urea to near boiling (which may include boiling) to coprecipitate homogeneously a mixed-oxide of the cerium and the one or more other constituent(s) as a gelatinous coprecipitate; 4)optionally maturing the gelatinous coprecipitate in accordance with a thermal schedule; 5) replacing water in the solution with a water miscible, low surface-tension solvent, such as dried 2-propanol; 6) drying the coprecipitate and solvent to remove substantially all of the solvent; and 7) calcining the dried coprecipitate at an effective temperature, typically moderate, for an interval sufficient to remove adsorbed species and strengthen the structure against premature aging. In the dilute metal salt solution, the metal concentration is less than 0.16 mol/L, is preferably less than about 0.02 mol/L, and is most preferably less than about 0.016 mol/L, and the urea concentration is relatively high, being greater than 0.5 mol/L and preferably at least about 2 mol/L. The maturing of the coprecipitate is accomplished in less than 72 hours, and preferably less than about 24 hours, for example in the range of 3 to 8 hours. The calcining of the dried coprecipitate occurs for 1-6 hours, and preferably 2-4 hours, at a heating rate of about 2° C./min with a final calcining temperature in the range of 250°-600° C., and preferably in the range of 350°-500° C.

[0019] The ceria-based mixed-metal oxide material of, and made in accordance with, the invention finds particular utility as a catalyst support in a catalytic fuel processing system. A highly dispersive catalyst metal is loaded on the described mixed-metal oxide support to a concentration in the range of 0.1 to 5 wt %. The catalyst metal is chosen to have crystallites that are predominantly less than 2.5 nm in size, and preferably less than 2.0 nm. The catalyst metal may typically be a noble metal, with platinum being preferred. The process for loading the catalyst comprises the steps of 1) surface treating the support in a solution containing an acid from the group consisting of amino acids, hydroxy dicarboxylic acids, hydroxy polycarboxylic acids, and keto polycarboxylic acids; and 2) loading the catalyst metal by submerging the surface-treated support in a solution containing the catalyst metal. The acid for surface treating the support is preferably malic acid or citric acid. The solution containing the catalyst metal may be a solution of tetraamineplatinum nitrate having about 1 weight percent platinum, 1 weight percent ammonia hydroxide and 15 weight percent 2-propanol, and the surface-treated support is submerged therein for about 2 hours at room temperature, following which it is filtered and dried. The catalyst-loaded support is then calcined for up to 4 hours at a heating rate of about 2° C./min to a calcining temperature in the range of 250°-600° C., and more preferably in the range of 400°-500° C. The resulting catalyst is then used, in accordance with another aspect of the invention, in a water gas shift reactor and/or a preferential oxidizer in a fuel processing system.

[0020] The foregoing features and advantages of the present invention will become more apparent in light of the following detailed description of exemplary embodiments thereof.

BEST MODE FOR CARRYING OUT THE INVENTION

[0021] The invention relates to a ceria-based mixed-metal material, useful as a catalyst support, a co-catalyst and/or a getter, and to the catalyst supported thereby in the instance of catalyst usage. The invention also relates to the processes associated with making such ceria-based metal-oxide materials, as support, catalyst, and getter or sulfur sorber. The invention further relates to use of such ceria-based mixed metal oxides as catalysts, or catalyst supports, in fuel processing systems. As used herein, a supported catalyst, or simply catalyst, comprises the combination of a catalyst support and a catalyst metal dispersed thereon. The catalyst metal may be referred to as being loaded on the catalyst support, and may, in instances herein, be referred to simply as "the catalyst", depending on the context of usage. Because the ceria-based mixed metal oxide material and process of the invention find particular utility as a catalyst support, though is not limited to such use, the following discussion of that oxide material and the process by which it is made is in the context of such a support. Thus, reference to "the support" is synonymous with the oxide material of the invention and will typically be used for simplicity.

[0022] It is desirable to efficiently maximize the effective surface area of a catalyst support, particularly for use in water gas shift (WGS) reactions and/or PROX oxidation reactions to process hydrocarbon feedstocks into hydrogen-rich fuels for fuel cells, in order to make the resulting reaction as efficient as possible. Consequently, the proper combination of relatively high surface area per unit skeletal density coupled with relatively, though not excessively, large pores that minimize internal mass transfer resistance without creating excessive pore volume, results in a highly effective catalyst that increases catalyst efficiency by maximizing the amount of effective surface area within a given reactor volume. By increasing the efficiency of a catalyst in such a reaction, it is possible then to either increase the reaction flow for a given reactor volume or to decrease the reactor volume for a given reaction flow, or a combination of the two. The use of such fuel processing systems in mobile applications places considerable emphasis on reducing size/volume, as will be understood. The improved catalyst support/catalyst/getter of the invention contribute to this objective.

[0023] The process(es) and product(s) of the invention involve the formation of high surface area ceria-based mixed-metal oxides as catalyst supports and catalysts of the type particularly suited for use in WGS reactions and PROX oxidation reactions, as for the fuel processing system associated with providing a hydrogen-rich fuel supply to a fuel cell. Moreover, those supports and catalysts are formed by processes that are efficient and effective. Consideration will first be given to the formation of the high surface area ceria-based mixed-metal oxide material of the catalyst support, and then to the formation/loading of the catalyst on that support.

[0024] The support is a homogeneous structure of cerium oxide and at least one other metal oxide constituent that are all nano-crystalline, that is, less than about (<) 4 nm. For binary mixed oxides, the other constituents preferably are selected from the group consisting of zirconium and hafnium. Further still, some advantage may be derived from homogeneous ternary and/or quaternary cerium-zirconium or cerium-hafnium based mixed oxides that provide the same small nano-crystalline structure. In providing the homogeneous ternary and/or quarternary mixed oxides of cerium and either zirconium or hafnium, the additional constituents, or dopants, are selected from the group of metals consisting of rare earth metals La (lanthanum), Pr (praseodymium), Nd (neodymium), Sm (samarium), Eu (europium), Gd (gadolinium), Tb (terbium), Dy (dysprosium), Ho (holmium), Er (erbium), Tm (thullium), Yb(ytterbium), Lu (lutetium), and non-rare earth metals of Cu (copper), Mo (molybdenum), W (tungsten), Re (rhenium), Rh (rhodium), Sb (antimony), Bi (bismuth), V (vanadium), Mn (manganese), Co (cobalt), Ga (gallium), Ca (calcium), Sr (strontium, and Ba (barium) for association with the cerium, and are selected from the group consisting of Ti (titanium), Nb (niobium), and Ta (tantalum), for association with the zirconium and/or hafnium. In the formulations in which zirconium and/or hafnium are mixed with cerium to provide the mixed oxides, the total metals-only, atomic-percentage basis of cerium and, optionally, one or more of the constituents (dopants) listed above in association with it, is at least 60%, while the total percentage of zirconium and/or hafnium and optional constituents/dopants therewith, is 40% or less. That 40% or less of zirconium and/or hafnium may optionally include up to 8%-10% of the dopants listed above in association with those two metals. Stated another way, the atomic percentage of dopants in association with the Zr and/or Hf is less than about 25% of the sum of the Zr and/or Hf and the dopants.

[0025] It will be understood and appreciated that by using the process of the invention, these cerium-based mixed-metal oxides form support structures that have a nano-crystalline structure that, on average, is less than about 4 nm, as determined by powder x-ray line broadening; a high B.E.T. surface area that exceeds 150 m^2/g after calcination at about 450° C. for about 4 hours, and typically is about 180 m^2/g or more; and relatively large pores as determined by nitrogen adsorption, the average pore size as determined by the maximum in the pore size distribution curve for the material being greater than 4 nm, and typically 5 nm or greater, to about 9 nm, and thus normally larger than the crystallite size. These characteristics tend to maximize and optimize the surface for interaction with the gas phase, by combining relatively high surface area per unit skeletal density coupled with relatively, though not excessively, large pores that minimize internal mass transfer resistance without creating excessive pore volume, to result in a highly effective catalyst that increases catalyst efficiency by maximizing the amount of effective surface area within a given reactor volume. They also make the material very well suited for the support of small, i. e., less than about 2.0-2.5 nm metal clusters or crystallites. Thus the ceria-based mixed-metal oxide with this morphology and bearing these small metal particles on its surface is ideally suited for use as a catalyst in the WGS reaction where, it is reported, the CO chemisorbed on the surface of the metal particles undergoes nucleophilic attack by oxide ions from the mixed metal oxide, converting it to CO_2 and reducing the mixed metal oxide which is reoxidized by the reaction of the oxide with water, a reaction that liberates hydrogen.

[0026] Referring to the process by which supports having the aforementioned structure and characteristics are formed, a novel method of synthesis by homogeneous coprecipitation is used. While homogeneous coprecipitation methods are known, including the use of urea as in the present invention, the steps and parameters of the process of the invention are specific and unique, and yield the improved ceria-based mixed-metal oxide support in a novel and efficient manner. The synthesis method used in the invention has the advantage of relatively short aging, or maturing, time, the avoidance of expensive reagents like alcoxides, and the avoidance of super-critical solvent removal.

[0027] An important part of the support-forming method is that the coprecipitation is performed in a very dilute metal salt solution, which is believed to prevent particles/nuclei from some agglomeration. The total metal concentration in the solution is less than 0.16 mol/L, is preferably less than about 0.02 mol/L, and most preferably, is less than about 0.016 mol/L. The solution, in addition to the metal salt(s), also includes urea. Another important aspect is that the urea concentration must be high, at least 0.1 mol/L, and preferably being about 2 mol/L. The solution, containing the appropriate amounts of metallic salt and urea to attain the requisite concentrations, is heated to near boiling, which may include boiling, while stirring, to cause the hydrolysis of the urea and thus the reaction of the soluble metal ions with the urea hydroloysis products to form a cloudy suspension of nanocrystals. The heating is continued until substantially all of the desired elements added as soluble salts are incorporated into the nanocrysrtallites. The coprecipitation of the various metal oxides quickly begins and is completed, typically in less than a minute. The resulting coprecipitate is gelatinous. While stirring is continued, the mixture of coprecipitate (hereinafter referred to sometimes simply as "precipitate") and solution may optionally be aged, or matured. The step of aging the coprecipitate mixture is relatively fast, being less than 72 hours, preferably less than about 24 hours, and most typically being in the range of 3 to 8 hours. The aging step comprises heating, or maintaining the heating of, the mixture to, or near, its boiling temperature for about, for example, 7 hours, and then continuing to stir and allowing to cool to ambient room temperature for an additional period of, for example, about 16 hours. The continued heating after the formation of the nanocrystalline suspension has been completed is neither particularly helpful nor harmful, nor is an extended period of stirring during and after cool down.

[0028] The mixture is then filtered, and the resulting filter cake is washed, typically twice, with de-ionized water at about boiling temperature. Importantly, the water associated with the filter cake is then replaced with a water-miscible, low surface-tension solvent. This serves to reduce the capillary pressure exerted by the solvent on the solid oxide during a subsequent drying step. That water-miscible, low surface-tension solvent may be an alcohol with 4 carbons or less, and preferably 3 carbons or less, or a ketone or an ester, each with 4 carbons or less. A preferred such solvent is dried 2-propanol, with other examples including propanone (acetone), methyl ethyl ketone, and 1-propanol. This may be accomplished in various ways, but preferred herein is first washing the filter cake several times with the water-miscible, low surface-tension solvent at room temperature, and then mixing fresh, dried, water-miscible, low surface-tension solvent with the precipitate and heating to reflux for about 45 minutes. The need for the reflux wash will be determined by the effectiveness of the prior lower temperature washes in replacing the water. The washed precipitate may be freed from excess solvent by any of the several means known in the art including filtration, centrifugation, spray drying, etc. Alternatively, the washed precipitate may be effectively suspended in a sufficient amount of liquid and that suspension used either directly or after the addition of a binder or binder components, to wash coat monoliths, foams, and/or other substrate objects. In a more concentrated form, the washed precipitate may be extruded, as by a syringe or the like.

[0029] The resulting coating or extrudate then undergoes a drying step to remove the remaining solvent. This may be accomplished by any of the variety of means known in the art, but vacuum oven drying at about 70° C. for about 3 hours is effective, and the extrudate may then remain in the oven at that same temperature, but without vacuum, for an additional period that may be about 16 hours.

[0030] Following drying, the oxide, or the aforedescribed formed and dried mixed metal oxide may be calcined at 250° C.-600° C., and preferably about 350° C. -500° C., for an interval sufficient to remove adsorbed species and strengthen the structure against premature aging. Lower temperatures typically mean more physisorbed and chemisorbed solvent and/or carbonates, while higher temperatures and longer times mean the reverse. In an exemplary process, the calcining required about 4 hours with a heating rate of about 2° C./minute. The calcining process typically begins at a temperature of about 70° C., and the calcining temperature selected is a balance of increased surface area at the lower end of the time/temperature range vs. assured removal of contaminants at the upper end.

[0031] Following calcination, the precipitate possesses the properties desired of the support of the invention, to wit, homogeneous mixed oxides of at least cerium and typically zirconium, hafnium, and/or various constituents, that are nano-crystalline, typically less than 4 nm for calcinations at 500° C. or less, and that collectively define a structure having large pores, typically of more than 4 nm, in the range of more than 4 nm to less than about 9 nm, and thereby have a large surface area greater than 150 m^2/g, typically 180 m^2/g or greater. This combination of surface area and average pore diameter translates into relatively low internal mass transfer resistance. However, if that value becomes too small because of excessive pore size and/or volume, the effective number of sites per crystallite aggregate necessarily decreases and the amount of effective surface area per unit reactor volume also decreases. For a porous material of given density, D, the skeletal volume, V_S, is 1/D, such that the total volume of a gram of material, V_T, is the sum of the pore volume, V_P, +skeletal volume, V_S. From this, the surface area/gram/V_T yields the surface area per unit volume of material, and it is this value which the invention seeks to maximize. Accordingly, it has been determined that the surface area per unit volume of material should be greater than 320 m^2/cm^3, and preferably greater than 420 m^2/cm^3. Viewed yet another way, it has been determined that the ratio of pore volume, V_P, to the particle, or skeletal volume, V_S, should not exceed about 2.5. It is important to realize that skeletal volume is more appropriate than mass when dealing with a high skeletal or crystallite density like CeO_2, (7.132 g/cm^3). For example, a given surface area/g of CeO_2 will translate to about 2½ times the surface area, m^2, per unit volume, cm^3, than for the same given surface area/g of a the less-dense catalyst support material SiO_2, which has a crystallite density of 2.65 g/cm^3.

[0032] At this point the mixed metal oxide as described, is complete as to its chemical and micro-morphology, although if necessary its macro-morphology (>several microns) may be adjusted. If the mixed metal oxide is to be loaded with precursors of what will become a highly dispersed catalytically-active metallic phase, further treatment steps may be necessary as will be described following in connection with further aspects of the invention. Immediately following are examples in which the above-described process or some variants thereof, are described in detail for illustrative or comparative purposes. These examples are of mixed metal oxides used as catalyst supports, and are intended to be illustrative, and not limiting.

[0033] It is helpful at this juncture to identify and/or describe the techniques used to identify crystallite size, support surface area, pore volume, and average pore diameter herein.

[0034] Average crystallite size was determined by X-ray diffraction line broadening using powder X-ray diffraction patterns (PXRD) and the Scherrer equation:

$t=(0.9*\lambda)/B \text{ Cos } \theta_B$, where:

[0035] t=Crystallite thickness;

[0036] 0.9 or 1.0=crystal shape factor;

[0037] λ=Wave length of Radiation (angstroms);

[0038] B=breadth of diffraction peak (radians);

[0039] θ_B=Bragg angle (degree).

[0040] The surface area of the mixed metal oxide support was determined by first determining nitrogen adsorption-desorption isotherms at liquid nitrogen boiling temperature by the classical volumetric method with a Micromeretics ASAP 2010 instrument, and then calculating the surface area using the well-known BET method.

[0041] Pore volume was determined by the volume of the adsorbate taken at a relative pressure of $P/P_0=0.98955093$.

[0042] Pore size distribution data and curves were calculated from the desorption branch of the isotherm using the BJH method.

[0043] The average pore diameter was determined by dividing the pore volume by the surface area, the result being multiplied by a factor depending on the pore shape. The equation 4V/A was used for cylindrical pores where V and A are, respectively, the pore volume and the surface area as determined above.

EXAMPLE 1

[0044] A $Ce_{0.65}Zr_{0.35}O_2$ catalyst support is prepared by dissolving 26.7 g of $(NH_4)_2Ce(NO_3)_6$, 7.2 g of $ZrO(NO_3)_2.xH_2O$ and 576 g of urea in 4800 mL of de-ionized water. The solution is heated to its boiling temperature while stirring until the coprecipitation is observed. The mixture is then aged at boiling temperature for 7 hours and then is left stirring at room temperature for 16 hours. The mixture is filtered on in a Büchner funnel. The resulting filter cake is washed twice with 500 mL of de-ionized water at boiling temperature while stirring for 10 minutes, and then filtered again after each washing step. Then the filter cake is washed three times with 100 mL of dried 2-propanol while in the Büchner funnel. Then, if necessary, the precipitate is mixed with 400 mL of dried 2-propanol and heated to reflux for 45 minutes and then filtered again before being extruded, as through a syringe. The extrudates are dried in a vacuum oven at 70° C. for 3 hours and then left in the oven at 70° C. (overnight) for 16 hours without vacuum. The extrudates are then calcined at 500° C. for 4 hours with a heating rate of 2° C./min.

[0045] After calcination at 500° C., the surface area of the support (Sample UR 27) is 180 m^2/g and has an average crystallite size of 34.1 Å (3.41 nm). The pore volume is 0.25 cm^3/g and the average pore diameter is 55 Å (5.5 nm). Another support (Sample UR 17) prepared with essentially the same parameters has a surface area of 187 m^2/g and an average crystallite size of 32.3 Å (3.23 nm).

COMPARATIVE EXAMPLE 2

[0046] A $Ce_{0.65}Zr_{0.35}O_2$ catalyst support is prepared by dissolving 26.7 g of $(NH_4)_2Ce(NO_3)_6$, 7.2 g of $ZrO(NO_3)_2$. xH_2O and 60 g of urea in 500 mL of de-ionized water. The solution is heated to its boiling temperature while stirring until the coprecipitation is observed. The mixture is then aged at boiling temperature for 7 hours and then is left stirring at room temperature for 16 hours. The mixture is filtered in a Büchner funnel. The resulting filter cake is washed twice with 500 mL of de-ionized water at boiling temperature while stirring for 10 minutes, and then filtered again after each washing step. Then the filter cake is washed three times with 100 mL of dried 2-propanol while in the Büchner funnel. Then, if necessary, the precipitate is mixed with 400 mL of dried 2-propanol and heated to reflux for 45 minutes and then filtered again before being extruded, as through a syringe. The extrudates are dried in a vacuum oven at 70° C. for 3 hours and then left in the oven at 70° C. (overnight) for 16 hours without vacuum. The extrudates are then calcined at 500° C. for 4 hours with a heating rate of 2° C./min.

[0047] After calcinations at 500° C., the surface area of the support (Sample UR 48) is 144 m^2/g, the pore volume is 0.22 cm^3/g, and the average pore diameter is 60 Å. Thus it is seen that the lower dilution of the solution of Example 2 relative to the higher dilution of Example 1, yields an Example 2 support having small surface area that is unsatisfactory.

COMPARATIVE EXAMPLE 3

[0048] A $Ce_{0.65}Zr_{0.35}O_2$ catalyst support is prepared by dissolving 26.7 g of $(NH_4)_2Ce(NO_3)_6$, 7.2 g of $ZrO(NO_3)_2$. xH_2O and 576 g of urea in 4800 mL of de-ionized water. The solution is heated to its boiling temperature while stirring until the coprecipitation is observed. The mixture is then aged at boiling temperature for 7 hour and then is left stirring at room temperature for 16 hour. The mixture is filtered in a Büchner funnel. The resulting filter cake is washed twice with 500 mL of de-ionized water at boiling temperature while stirring for 10 minutes, and then filtered again after each washing step. However, at this point there is no replacement of water, as with a low surface-tension solvent or otherwise. The filter cake is extruded through a syringe. The extrudates are dried in a vacuum oven at 70° C. for 3 hours and then left in the oven at 70° C. overnight without vacuum. The extrudates are finally calcined at 500° C. for 4 hours with a heating rate of 2° C./min.

[0049] After calcinations at 500° C., the surface area of the support (Sample UR 19) is 116 m^2/g. Thus, it can be clearly seen that when water is not displaced or exchanged by a low surface-tension solvent, a significantly reduced surface results and is undesirable.

EXAMPLE 4

[0050] A $Ce_{0.625}Zr_{0.325}Pr_{0.05}O_2$ catalyst support is prepared by dissolving 25.7 g of $(NH_4)_2Ce(NO_3)_6$, 6.7 g of $ZrO(NO_3)_2$. xH_2O, 1.63 g of $Pr(NO_3)_3$ $6H_2O$ and 576 g of urea in 4800 mL of de-ionized water. The solution is heated to its boiling temperature while stirring until the coprecipitation is observed. The mixture is then aged at boiling temperature for 7 hours and then is left stirring at room temperature for 16 hours. The mixture is filtered in a Büchner funnel. The resulting filter cake is washed twice with 500 mL of de-ionized water at boiling temperature while stirring for 10 minutes, and then filtered after each washing step. Then the filter cake is washed three times with 100 mL of dried 2-propanol while in the Büchner funnel. Then, if necessary, the precipitate is mixed with 400 mL of dried 2-propanol and heated to reflux for 45 minutes and then filtered again before being extruded, as through a syringe. The extrudates are dried in a vacuum oven at 70° C. for 3 hours and then left in the oven at 70° C. (overnight) for 16 hours without vacuum. The extrudates are then calcined at 500° C. for 4 hours with a heating rate of 2° C./min.

[0051] After calcinations at 500° C., the surface area of the support (Sample UR 26) is 182 m^2/g, the pore volume is 0.26 cm^3/g, and the average pore diameter is 56 Å (5.6 nm). Thus, there is provided an example of a ternary mixed metal oxide in accordance with the invention.

EXAMPLE 5

[0052] A $Ce_{0.625}Zr_{0.325}La_{0.05}O_2$ catalyst support is prepared by dissolving 25.7 g of $(NH_4)_2Ce(NO_3)_6$, 6.7 g of $ZrO(NO_3)_2$. xH_2O, 1.62 g of $La(NO_3)_3$ $6H_2O$ and 576 g of urea in 4800 mL of de-ionized water. The solution is heated to its boiling temperature while stirring until the coprecipitation is observed. The mixture is then aged at boiling temperature for 7 hours and then is left stirring at room temperature for 16 hours. The mixture is filtered in a Büchner funnel. The resulting filter cake is washed twice with 500 mL of de-ionized water at boiling temperature while stirring for 10 minutes, and then filtered after each washing step. Then the filter cake is washed three times with 100 mL of 2-propanol while in the Büchner funnel. Then, if necessary, the precipitate is mixed with 400 mL of dried 2-propanol and heated to reflux for 45 minutes and then filtered again before being extruded, as through a syringe. The extrudates are dried in a vacuum oven at 70° C. for 3 hours and then left in the oven at 70° C. (overnight) for 16 hours without vacuum. The extrudates are then calcined at 450° C. for 4 hours with a heating rate of 2° C./min.

[0053] After calcinations at 450° C., the surface area of the support (Sample UR 37) is 204 m^2/g, the pore volume is

0.25 cm^3/g, and the average pore diameter is 49.9 Å (4.9 nm). The average crystallite size is 28.6 Å (2.86 nm). This provides another example of a ternary mixed metal oxide in accordance with the invention.

EXAMPLE 6

[0054] A $Ce_{0.80}Gd_{0.20}O_2$ catalyst support is prepared by dissolving 32.89 g of $(NH_4)_2Ce(NO_3)_6$, 6.77 g of $Gd(NO_3)_3 . 6H_2O$ and 576 g of urea in 4800 mL of de-ionized water. The solution is heated to its boiling temperature while stirring until the coprecipitation is observed. The mixture is then aged at boiling temperature for 7 hours and then is left stirring at room temperature for 16 hours. The mixture is filtered in a Büchner funnel. The resulting filter cake is washed twice with 500 mL of de-ionized water at boiling temperature while stirring for 10 minutes, and then filtered after each washing step. Then the filter cake is washed three times with 100 mL of dried 2-propanol while in the Büchner funnel. Then, if necessary, the precipitate is mixed with 400 mL of dried 2-propanol and heated to reflux for 45 minutes and then filtered again before being extruded, as through a syringe. The extrudates are dried in a vacuum oven at 70° C. for 3 hours and then left in the oven at 70° C. (overnight) for 16 hours without vacuum. The extrudates are then calcined at 450° C. for 4 hours with a heating rate of 2° C./min.

[0055] After calcinations at 450° C., the surface area of the support (Sample UR 78) is 222 m^2/g, the pore volume is 0.37 cm^3/g, and the average pore diameter is 67 Å (6.7 nm). In this example, it is seen that the use of yet another rare earth dopant, in this instance Gd (gadolinium), in combination with cerium, but in the absence of zirconium or hafnium, yields a particularly large surface area, pore volume on a unit weight basis, and pore diameter. However, on an activity-per-surface area basis, the performance of this catalyst support was deficient, and reflects the likelihood that water gas shift activity is positively affected by the presence of Zr, and the reverse by its absence.

EXAMPLE 7

[0056] A $Ce_{0.65}Hf_{0.35}O_2$ catalyst support was prepared by dissolving 26.67 g of $(NH_4)_2Ce(NO_3)_6$, 9.70 g of $HfO(NO_3)_2 . 5H_2O$ and 576 g of urea in 4800 mL of de-ionized water. The further steps were generally in accordance with EXAMPLE 1 above, however the extrudate was calcined at 400° C. (2° C./min ramp up) for 4 hours. Following calcination, the surface area of the support (Sample UR 94) was 180 m^2/g, the pore volume was 0.21 cm^3/g, and the average pore diameter was 46.2 Å (4.62 nm). The average crystallite diameter was 26.0 Å (2.6 nm). This oxide, after subsequently being loaded with Pt, was tested and found to be active for water gas shift catalysis.

[0057] In addition to the aforementioned Examples of seven or eight Samples, the following Table 1 includes seven additional Samples of ternary mixed-oxides and their respective relevant properties:

TABLE 1

Sample	Ce	Zr	Popant	Amount	Clcn Temp ° C.	Srfc Area m^2/g	Avg Pore Dia Å	Pore Vol cm^3/g	Avg Crys Size Å
UR39	0.625	0.325	Sm	0.05	450	185	55	0.26	31
UR43	0.625	0.325	Eu	0.05	450	188	56	0.26	34
UR38	0.625	0.325	Gd	0.05	450	196	54	0.26	32
UR46	0.625	0.325	Tb	0.05	450	202	53	0.27	33
UR47	0.625	0.325	Yb	0.05	450	182	58	0.26	37
UR76	0.700	0.200	Mo	0.10	450	191	55	0.26	33
UR70	0.750	0.200	Nb	0.05	450	175	65	0.28	38

[0058] The Samples of Table 1 each contain, on metals-only basis, 62.5 atomic %, or greater, of Ce, 32.5 atomic %, or less, of Zr, and the remainder is one of several different dopants in the amount of 5 atomic %, or more. All of those Samples were calcined at 450° C., and resulted in mixed metal oxides having surface areas of 175 to 202 m_2/g, average pore diameters of 53 to 65 Å (5.3-6.5 nm), pore volumes in the range of 0.25-0.28 cm^3/g, , and average crystallite sizes, as determined by the Jade program, of 31-38 Å. Though not shown in Table 1, the lattice parameters of these samples were in the range of 5.33 to 5.38 Å. The earlier-mentioned Samples of Examples 1-7 serve to expand those ranges somewhat, with the lattice parameter, which is an indication of homogeneity, in particular expanding its range to 5.32-5.42 Å., the surface area increasing to 222 m^2/g, the average pore diameter range increasing to 50-67 Å, and the average crystallite size range extending to 29 Å. The pore volumes of relevant Examples 1, 4 and 5 were similar to those of Table 1; the Example 7, with Hf instead of Zr, had a pore volume of 0.21 cm3/g,; whereas the non-Zr, non-Hf, Example 6 had a pore volume of 0.37 cm^3/g.

[0059] Consideration will now be given to the data presented in Table 2, wherein the identifiers UR86, UR87, and UR88 represent three mixed metal oxides of the invention, with differing amounts of Ce and Zr, and CZ68 and CZ80 represent Ce and Zr oxides made in accordance with the teachings of the article by Terribile, et al referenced earlier in the Background Art section. The numbers immediately following the identifiers are the temperatures (° C.) at which they were calcined. The CeO had a density of 7.132 and the ZrO density was 5.6 g/cm^3. From left to right, beginning with the fourth column, there is surface area (SA); pore volume (V_P); Average Pore diameter; total volume (V_T), which is the sum of V_P and V_S; Surface Area per V_T; Density of Ce/Zr skeleton (D); volume of skeleton (V_S); and the ratio of V_P to V_S (V_P/V_S).

TABLE 2

#	% Ce 7.132	% Zr 5.6	SA SA m2 gr	V_p cm3 per gram	Ave Pore dia nm	V(t) cm3 of gram	SA/Vt m2 cm3	D(s) g/cm3 skel	Vs cm3/g	Vp/Vs
UR88-450	0.8	0.2	215	0.27	5.02	0.42	516	6.83	0.147	1.84
UR88-550	0.8	0.2	175	0.24	5.49	0.39	453	6.83	0.147	1.64
UR88-650	0.8	0.2	126	0.21	6.67	0.36	353	6.83	0.147	1.43
UR87-450	0.75	0.25	214	0.29	5.42	0.44	488	6.75	0.148	1.96
UR87-550	0.75	0.25	164	0.26	6.34	0.41	402	6.75	0.148	1.75
UR87-650	0.75	0.25	127	0.23	7.24	0.38	336	6.75	0.148	1.55
UR86-450	0.68	0.32	197	0.27	5.48	0.42	468	6.64	0.151	1.79
UR86-550	0.68	0.32	156	0.25	6.41	0.40	389	6.64	0.151	1.66
UR86-650	0.68	0.32	116	0.22	7.59	0.37	313	6.64	0.151	1.46
CZ80-450	0.8	0.2	208	0.86	16.54	1.01	207	6.83	0.147	5.87
CZ80-650	0.8	0.2	163	0.56	13.74	0.71	231	6.83	0.147	3.82
CZ68-450	0.68	0.32	235	0.66	11.23	0.81	290	6.64	0.151	4.38
CZ68-650	0.68	0.32	170	0.42	9.88	0.57	298	6.64	0.151	2.79

[0060] A review of Table 2 shows the decrease in surface areas as a function of calcining temperature, with the more desirable surface areas being for calcinations below about 500° C.; relatively smaller pore volumes for the mixed oxides of the invention and relatively larger for the other; pore diameters less than about 8 or 9 nm for the material of the invention and larger for the other; relatively smaller total volumes for the invention and larger for the other; relatively larger surface areas per total volume (typically greater than 320-420 m^2/cm^3) for the materials of the invention; and V_p/V_S ratios under 2.5 for the material of the invention.

[0061] Attention is now given to the facet of the invention concerned with loading a highly dispersive catalyst metal on the mixed metal oxide support just described, including the associated process and the resulting product. Although the following discussion and examples will use Pt (platinum) as the catalyst metal loaded on the support, it will be understood that other metals, and particularly noble metals, are well-suited alternatives to Pt, such as Pd, Rh, Ir, Ru, and Os, as well as alloys or mixed metal clusters containing nobel metal including Group 1B metals and/or Re. The highly dispersed platinum, that is, Pt crystallites that are typically less than 3 nm in diameter, preferably less than 2.5 nm in diameter, and most preferably less than 2 nm in diameter, as applied to the mixed oxide support of the invention and in the manner and formulation of the invention, has a concentration in the range from about 0.1 to about 5% by weight, as metal, based on the final weight of the dried oxide and supported metal. While "low" metal loadings below about 1.0 wt % may be acceptable or even desirable in some situations, such as catalyst use at temperatures above 400° C., high loadings of about 5 wt % may be needed to obtain the desired catalytic activity and life time at lower temperatures, for instance 200° C. Such loading of a catalyst, such as Pt, on a large surface area, ceria-based support results in a catalyst that is particularly effective and efficient for use in WGS and PROX reactions.

[0062] To load the highly dispersed platinum on the support, several steps are involved, two of which are particularly important to the invention. Those important steps include, firstly, surface treating the ceria-based support and secondly, selecting an/the appropriate formulation for loading the support. A preliminary step, which may also be accomplished as a final step in the formation of the support, involves forming the oxide into a suitable form. This form may be that of a fine powder (<200 mesh), 50 to 100 mesh granules, extrudates, pellets, with or without added binder extrusion aides, etc., or a wash coat or other coating on a ceramic or metallic monolith, foam or wire mesh, again with or without a suitable binder.

[0063] The 50-200 mesh, ceria-based metal oxide support particles, preparatory to being metal-loaded, undergo surface treatment by being heated in an acid solution containing one or more acids from the group consisting of amino acids, hydroxy dicarboxylic acids, hydroxy polycarboxylic acids and keto carboxylic acids, of which citric acid from the hydroxy polycarboxylic acid group and malic acid from the hydroxy dicarboxylic acid group are preferred, with malic acid being particularly preferred. These acids are selected to provide a mild reaction and serve to react with the oxide surface, forming sites that bind noble metal-containing cations such as $[Pt(NH_3)_4]^{+2}$. It is believed these sites are sufficiently separated from each other as to yield after either calcinations, calcinations and reduction, or reduction, very high noble metal dispersion, that is noble metal particles typically less than 2.5 nm. The support particles are heated in an alcohol solution, typically of ethanol, containing a selected acid, such as malic or citric acid, at about 50° C. for 2-3 hours. The support particles are then rinsed with ethanol until a pH greater than 4 is attained.

[0064] After the surface treatment rinse, the support particles are submerged or immersed in a suitable solution containing the catalyst metal, in this instance a tetraamineplatinum nitrate solution of Pt, ammonia hydroxide and propanol, for 2-3 hours at room temperature. Platinum tetraamine nitrate or analogous salts of other noble metals are usually chosen because they provide sufficiently stable, soluble noble metal cations to react with the treated surface, are halogen or sulfur free, are available at a reasonable cost, and on further treatment such as calcination smoothly decompose leaving no unwanted residue. Platinum(II) tetraamine chloride, bromide, etc. would work but they contain halogens. For some noble metals, like Pd, other ligands like ethanolamine can be substituted for ammonia, and the resulting water containing solution contains a mixture of complexes of the type M(II) $[(NH_3)_{4-(x+n)}(\text{ethanolamine})_x(H_2O)_n]$, where x+n is equal to or less than 4. Care must also be taken that the noble metal salt chosen doesn't undergo either spontaneous or light induced redox reactions causing the noble metal to come out of solution.

[0065] Thereafter, the support particles are filtered with a 10 μm membrane filter and vacuum dried overnight (about 16 hours). Finally, the dried and metal-loaded catalyst support is calcined at a temperature in the range of 400°-500° C. for about 3-4 hours at a heating rate of about 2° C./min, to provide the finished catalyst. The essence of this phase of the process is to convert the metal-loaded proto-catalyst to a stable form, through some appropriate combination of drying, calcining and/or reduction.

[0066] Following are 5 examples (7-11) in which the above-described process, or some variants thereof, are described in detail for illustrative and comparative purposes, however it will be understood that these examples are not intended to be limiting.

EXAMPLE 8

[0067] A $Ce_{0.65}Zr_{0.35}O_2$ catalyst support is prepared substantially identically to that of Example 1 above, except that it is calcined at 400° C., rather than at 450° C. One gram of the support, committed to a 50-200 mesh size, is heated in 5 mL of ethanol solution containing 0.1 g/mL of citric acid at 50° C. for 2 hours. The support is then rinsed with ethanol until the pH is greater than (>) 4. After that rinse, the support is submerged or immersed in 3.8 g of tetraamineplatinum nitrate solution for 2 hours at room temperature. The tetraamineplatinum nitrate solution contains 1.01 wt % Pt, 1 wt % ammonia hydroxide, and 15 wt % 2-propanol. The support is then filtered through a 10 μm Teflon® membrane filter and vacuum dried overnight (about 16 hours) at 70° C. The loaded support is then calcined at 450° C., a temperature somewhat greater than that for calcining the support material itself, for about 4 hours with a heating rate of about 2° C./min. ICP analysis has determined the platinum loading to be 2.4 wt %, and the surface area to be 170-180 m^2/g.

[0068] A $Ce_{0.65}Zr_{0.35}O_2$ sample made similarly to Example 8 was seen to have a surface area of 186 m^2/g, an average pore size of 6.82 nm, crystallite size of 3.5 nm, and pore volume of 0.32 cm^3/g. This sample was loaded with 1.8 wt % of Pt, dried, calcined, reduced, and passivated. It was seen to be a very active water gas shift catalyst. A microtomed section of this catalyst was examined by high resolution transmission electron microscopy (TEM), and revealed a nanocrystalline, porous microstructure of randomly oriented grains. The TEM observations corroborated the crystallite size and average pore size data, determined by x-ray diffraction and BET techniques respectively. No regions identifiable as crystalline Pt were identified in either bright field or dark field TEM images or in electron diffraction patterns. After Fourier transform image processing was used to remove the $Ce_{0.65}Zr_{0.35}O_2$ {111} and {200} lattice fringes from the image, a few regions about 2 nm in size were evident, which had a lattice fringe spacing consistent with Pt {111}. The scarcity of such images, when compared to the known Pt content of this material suggested that the majority of Pt crystallites had to be less than 2.5 nm, and typically less than about 1.5-2.0 nm in size.

COMPARATIVE EXAMPLE 9

[0069] The following is an example of Pt loading without surface treatment. 5.59 g of CeO_2 support (calcined at 400° C., with 50-200 mesh size) is submerged in 21.6 mL of tetraamineplatinum nitrate solution for more than 48 hours at room temperature. A vacuum is applied when the support is first added to the solution. The solution is stirred for the first 5-10 minutes, and is then stirred occasionally during the course of submergence. The tetraamineplatinum nitrate solution contains 1.04 wt % Pt, 1 wt % ammonia hydroxide, and 15 wt % 2-propanol. The support is filtered through a 10 μm Teflon membrane filter and vacuum dried at 70° C. overnight. The loaded support is then calcined at 450° C. for about 4 hours with a heating rate of 2° C./min. The platinum loading was analyzed and seen to be only 0.56 wt %, thus showing that the platinum loading is very low without surface treatment.

EXAMPLE 10

[0070] A $Ce_{0.625}Zr_{0.325}Pr_{0.05}O_2$ catalyst support is prepared as was described above in Example 4, except that it is calcined at 400° C. instead of 500° C. 1 g of that $Ce_{0.625}Zr_{0.325}Pr_{0.05}O_2$ support (calcined at 400° C., with 50-200 mesh size) is heated in 5 mL of ethanol solution containing 0.05 g/mL of citric acid at 50° C. for 3 hours. The support is then rinsed with ethanol until the pH is greater than (>) 4. After that rinse, the support is submerged or immersed in 3.8 g of tetraamineplatinum nitrate solution for 2 hours at room temperature, with occasional stirring. The tetraamineplatinum nitrate solution contains 1.01 wt % Pt, 1 wt % ammonia hydroxide, and 15 wt % 2-propanol. The support is then filtered through a 10 μm Teflon® membrane filter and vacuum dried overnight (about 16 hours) at 70° C. The loaded support is then calcined at 450° C., a temperature somewhat greater than that for calcining the support material itself, for about 4 hours with a heating rate of about 2° C./min. The platinum loading was determined to be 2.46 wt %, and the catalyst surface area is 193 m^2/g. The oxide crystallite size was determined by x-ray diffraction to be 3 nm. High platinum dispersion is indicated by x-ray diffraction failing to detect any Pt or PtO because of its small crystallite size.

COMPARATIVE EXAMPLE 11

[0071] The following is another example of Pt loading without surface treatment. 5.8 g of $Ce_{0.625}Zr_{0.325}Pr_{0.05}O_2$ catalyst support, prepared substantially identically to Example 4 above except that it was calcined at 400° C. rather than 500° C., is submerged in 22.1 g of tetraamineplatinum nitrate solution for more than 48 hours at room temperature, with occasional stirring. The tetraamineplatinum nitrate solution contains 1.07 wt % Pt, 1 wt % ammonia hydroxide, and 15 wt % 2-propanol. The support is then filtered through a 10 μm Teflon® membrane filter and vacuum dried overnight (about 16 hours) at 700° C. The loaded support is then calcined at 450° C., a temperature somewhat greater than that for calcining the support material itself, for about 4 hours with a heating rate of about 2° C./min. Platinum loading was determined to be 1.5 wt %. This example again indicates that without the surface treatment, Pt loading continues to be low, even when the concentration of the Pt loading solution is increased and the loading time is increased from 2 hours to more than 48 hours.

EXAMPLE 12

[0072] Four (4.0 g of $Ce_{0.625}Zr_{0.325}Pr_{0.05}O_2$ support (calcined at 400° C., with 50-200 mesh size) is heated in 20 mL ethanol solution of 0.07 g/mL malic acid at 50° C. for 3 h. The support is then rinsed with ethanol until pH>4. After rinse, the support was submerged in 10.27 g of tetraamineplatinum nitrate solution for 2 h at room temperature. The solution was stirred occasionally during the course of 2 hours. The tetraamineplatinum nitrate solution contained 1.03 wt % Pt, 1 wt % ammonia hydroxide and 15 wt % 2-propanol. The support was filtered through a 10 μm teflon membrane filter and vacuum dried at 70° C. overnight. It was then calcined at 450° C. for 4 h with a heating rate of 2° C./min. Platinum loading is 2.35 wt %. High platinum dispersion is indicated by no Pt or PtO being observed by X-ray diffraction due to its small crystallite size.

[0073] As discussed previously, the noble-metal loaded, mixed-metal oxide supported catalyst of the invention is particularly suited for use in water gas shift reactions in hydrocarbon fuel processing systems. In that regard, Table 3 below serves to illustrate the effectiveness, or activity, of a platinum-loaded, ceria-zirconia oxide supported catalyst, formulated and/or made in accordance with the invention, in converting CO and H_2O to CO_2 and H_2. The Table 3 conveys the level of that effectiveness or activity, by tracking, as a function of temperature and time, the quantity (%) of CO entering the catalytic reactor (nominally a constant in the tests) vs. the quantity (%) of CO leaving the reactor. The difference is a measure of the conversion activity, either absolutely or as a percentage, in converting CO (and H_2O) to CO_2 and H_2 in the water gas shift reaction. Catalyst activity is given as (Micromoles of CO per second) per gram of catalyst.

[0074] Describing the activity test material, method and apparatus in greater detail, a mixed ceria zirconia oxide was prepared according to this invention. The extrudate was dried and calcined at 400° C. The resulting solid contained 65 atomic % Ce and 35 atomic % Zr on a metals only basis. The solid had a surface area measured by the BET method of 187 m^2/g, with a pore volume of 0.29 cm3/g. Thus its average pore diameter was 6.13 nm. Its average crystallite size was 3.4 nm by PXRD. Using a skeletal density of 6.6 g/cm^3, its surface area per cm^3 skeletal volume was 425 m^2/cm^3, and its ratio of pore volume, V_P, to skeletal volume, V_S, i.e., V_P/V_S, is 1.93. The extrudate was crushed and sieved to yield a porous granular solid that passed through an 80 mesh sieve and was retained on a 120 mesh sieve. This material was heated in an ethanolic solution of malic acid of 0.07 g/ml, to 50° C. for 3 hours, cooled, rinsed with ethanol until the pH was >4. After rinsing, the solid was immersed in a 1% platinum(II)tetraammine nitrate solution of 1% ammonium hydroxide and 15% 2-propanol for 2 hrs. The solid was recovered, dried under vacuum at 70° C. overnight. It was then calcined at 450° C. for 4 hours. The platinum uptake from the (II)tetraammine nitrate solution is consistent with a platinum loading of 2.34 wt %. 0.50 cm^3, 0.5704 grams of the 80-120 mesh catalyst loaded with Pt, was uniformly blended with 5.00 cm^3, 9.4395 grams +40 mesh Strem Chemical alpha alumina granules and charged into a 0.50" O.D. 316L Stainless Steel reactor tube with 0.049" walls with a 0.402" I.D. equipped with a 0.125" O.D. Axial Thermowell. The net cross sectional area of the reactor was 0.74 cm^2. The catalyst charge was separated from the bottom frit by a 5.25" length of 10 mesh alundum granules and a thin wad of borosilicate glass wool. The catalyst and 40 mesh alumina diluent bed was 3.0" long, and topped with a thin wad of borosilicate glass, above which was loaded about 5" more of 10 mesh alundum granules. As this was a down flow reactor, this 5" top section served to preheat the reaction gas mixture to reaction temperature before it contacted the dilute catalyst. This was confirmed during the initial heating and reduction by the internal, 0.0625" K type thermocouple in the internal, axial thermowell. The 0.5" O.D. reactor tube was inside a tight fitting aluminum block to minimize axial temperature gradients, and none were found at 320° C. under 20% hydrogen, 80% nitrogen flowing at 2.58 standard liters per minute (2.58 SLM). The catalyst after loading into the reactor tube and the reactor tube secured into the reaction system, was first freed of any adsorbed moisture by heating to 150° C. under high purity nitrogen flowing at 1.46 SLM, then the flow rate was further increase to about 2.15 SLM with the addition of 8% very high purity hydrogen. After 1 minute under 8% hydrogen the temperature was increased step wise to 240° C. and held for 5 minutes, then increased to 290° C. and held for 5 minutes, then increased to 330° C. and held for 5 minutes. Then the hydrogen concentration increased to 15%, the flow to 2.2 SLM, and after a 10 minute hold the H_2 was increased further to 30% and the flow to 2.5 SLM. After 10 minutes at 30% H_2, 330° C., the hydrogen concentration was increased to 40% and these conditions were held for 15 minutes. Then the temperature was adjusted to 320° C., the flow to 2.58 SLM and the gas composition to 33% H_2O, 33% H_2, 5% CO_2 and the balance N_2. These prerun conditions were held for 10 minutes before the carbon monoxide was introduced. The gas mixture was adjusted to about 4.9% CO, 33% H_2O, 30.4% H_2, 10.4% CO_2 and the balance N_2. The feed gas composition was sampled every 20 minutes for about 60 minutes by means of a gas chromatograph. The resultant N_2, CO_2 and CO values were then compared to the values obtained at varying temperatures during a 320° C. to 200° C. stepwise down ramp, during which the aluminum block temperature was held constant (within +/−2° C.) while product gas sampling was conducted at each temperature. When the feed gas composition was changed, as in the interval between 24 hours and 66 hours when the quantity of CO in the feed was changed from 4.9% to 1.5% and back, the feed gas was sampled again to insure that conversion calculations and rate calculations were accurate. In Table 2 below, "Effect T" refers to the effective catalyst temperature calculated as Effect T={[(2×Maximum Catalyst Bed Temperature, ° C.)+Catalyst Exit Temperature, ° C.]/3} as measured by the internal thermocouple. The catalyst exit temperature in all cases was approximately the catalyst inlet temperature and the aluminum block temperature. The "Feed" and "Exit" values for only CO are depicted in Table 3 for conciseness. The Time in hours is calculated from when the catalyst bed heater and initial N_2 flow was started. Only very slight deactivation is seen after about the first 24 hours.

TABLE 3

Hours	Effct T C	Feed % CO	Exit CO %	Rate/Sec MicroMole gram
6.86	329	4.9	0.57	101.6
8.00	318	4.9	0.51	103.1
9.18	307	4.9	0.44	104.7
10.33	296	4.9	0.49	103.6
11.49	285	4.9	0.69	98.9

TABLE 3-continued

Hours	Effct T C	Feed % CO	Exit CO %	Rate/Sec MicroMole gram
12.65	274	4.9	1.30	84.4
13.86	264	4.9	2.06	66.9
15.05	253	4.9	2.69	52.1
16.33	242	4.9	3.30	37.9
17.57	232	4.9	3.75	27.3
18.80	222	4.9	4.11	18.7
20.03	212	4.9	4.36	12.9
21.27	202	4.9	4.54	8.8
24.02	307	4.9	0.46	104.2
33.77	252	1.5	0.05	33.8
35.64	243	1.5	0.08	33.1
36.85	232	1.5	0.24	29.5
38.07	223	1.5	0.46	24.2
39.33	213	1.5	0.73	17.9
40.58	203	1.5	0.95	12.8
66.15	233	4.9	3.96	22.4
67.63	306	4.9	0.54	102.3
82.78	306	4.9	0.55	102.3
109.89306	4.9	0.60	100.9	
112.00274	4.9	1.76	74.0	
141.99305	4.9	0.62	100.4	
143.32273	4.9	2.02	67.7	
161.03287	4.9	0.54	102.3	
162.25304	4.9	0.65	99.7	
164.37273	4.9	2.03	67.4	
165.52231	4.9	4.02	21.0	

[0075] It will be noted from Table 3 that the catalyst is relatively more active at the higher temperatures over the practical range of operating temperatures between about 200° C. and 320° C., as would be anticipated. Moreover, for a feed of 1.5% CO, a relatively greater proportion (%) of the CO is removed at lower temperatures than for the 4.9% feed. Importantly also, a significant degree of catalyst stability is indicated by the fact that its activity at 230° C. at 165 hours is at least 90% of its activity at that temperature at 60 hours.

[0076] Although the invention has been described and illustrated with respect to the exemplary embodiments thereof, it should be understood by those skilled in the art that the foregoing and various other changes, omissions and additions may be made without departing from the spirit and scope of the invention.

What is claimed is:

1. A homogeneous, nanocrystalline, mixed metal oxide of cerium and at least one other metal constituent from the group consisting of Zr, Hf, Nb, Ta, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Mo, W, Re, Rh, Sb, Bi, Ti, V, Mn, Co, Cu, Ga, Ca, Sr and Ba, said mixed metal oxide having a surface area of at least about 150 m^2/g, an average crystallite size less than 4 nm and agglomerated to form a skeletal structure with pores, average pore diameters being greater than 4 nm and normally being greater than the average crystallite size, and wherein the surface area of the skeletal structure per volume of the material of the structure is greater than about 320 m^2/cm^3.

2. The mixed metal oxide according to claim 1 wherein the skeletal structure with pores has a pore volume per unit mass,V_P, and a structural volume per unit mass, V_S, and wherein the ratio of V_P to V_S, (V_P/V_S), is less than about 2.5.

3. The mixed metal oxide according to claim 1 wherein, based on metals-only atomic percent, the sum of Ce and one or more optional constituents selected from the group consisting of La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Mo, W, Re, Rh, Sb, Bi, V, Mn, Co, Cu, Mo, Ca, Sr, Ba, and Ga is at least 60 percent and the sum of constituents selected from the group consisting of Zr, Hf, Nb, Ta, and Ti is 40 percent or less.

4. The mixed metal oxide according to claim 3 wherein, within the group of constituents consisting of Zr, Hf, Nb, Ta, and Ti, a sub-group consisting of Zr and Hf comprises 30% or greater and a sub-group consisting of Nb, Ta, and Ti comprises 10% or less.

5. The mixed metal oxide according to claim 1 wherein the at least one other metal constituent comprises up to 20 atomic percent, on a metals basis, of Bi.

6. The mixed metal oxide according to claim 1 wherein the at least one other ingredient is zirconium.

7. The mixed metal oxide according to claim 1 wherein the at least one other ingredient is hafnium.

8. The mixed metal oxide according to claim 1 wherein the surface area of the oxide is at least about 180 m^2/g, the average crystallite size is equal to or less than 3.6 nm, and the average pore diameters are at least about 4.5 nm.

9. The mixed metal oxide according to claim 8 wherein the at least one other metal constituent is selected from the group consisting of Zr, Hf, Nb, Ta, Mo, W, Re, Rh, Ti, V, Mn, and Co, the average crystallite size is less than 3.5 nm, and the average pore diameters are at least about 5.0 nm.

10. The mixed metal oxide according to claim 9 wherein, by metals-only atomic percent, at least 10 percent is from the group consisting of Zr and Hf.

11. A process for the preparation of the mixed metal oxide as defined in claim 1, including:

a. dissolving urea and salts of the Ce and the at least one other constituent in water to form a dilute metal salt solution;

b. heating the solution to near boiling and coprecipitating homogeneously an oxide of the Ce and the at least one other constituent as a nanocrystalline coprecipitate;

c. replacing water existing in the coprecipitate with a water miscible, low surface-tension solvent that displaces water;

d. drying the coprecipitate to remove substantially all of any remaining water and the solvent; and

e. calcining the dried coprecipitate at a moderate temperature for an interval sufficient to remove adsorbed impurities.

12. The process according to claim 11 including, following step b, the further step of maturing the coprecipitate in accordance with a thermal schedule.

13. The process according to claim 11 wherein the step d of drying the coprecipitate includes the step of refluxing the coprecipitate in a dry solvent in the presence of heat.

14. The process according to claim 11 wherein the water miscible, low surface tension solvent of step c is selected from the group consisting of an alcohol, a ketone, and an ester, each with 4 carbons or less.

15. The process according to claim 14 wherein the water miscible, low surface tension solvent is selected from the group consisting of dried 2-propanol, acetone, methyl ethyl ketone, and 1-propanol.

16. The process according to claim 15 wherein the water miscible, low surface tension solvent is dried 2-propanol.

17. The process according to claim 11 including, following the step of coprecipitating the coprecipitate, the further step of isolating the coprecipitate from the solution.

18. The process according to claim 11 wherein the metal concentration in the dilute metal salt solution is less than about 0.16 mol/L.

19. The process according to claim 18 wherein the metal concentration in the dilute metal salt solution is less than about 0.02 mol/L.

20. The process according to claim 19 wherein the metal concentration in the dilute metal salt solution is less than about 0.016 mol/L.

21. The process according to claim 11 wherein the concentration of urea in the dilute metal salt solution is relatively high, being greater than 0.5 mol/L.

22. The process according to claim 21 wherein the concentration of urea in the dilute metal salt solution is at least about 2.0 mol/L.

23. The process according to claim 12 wherein the maturing of the coprecipitated solution includes boiling the solution for a first interval and allowing the solution to cool to ambient during a second interval, the sum of the first and second intervals being less than about 72 hours.

24. The process according to claim 23 wherein the sum of the first and the second intervals is less than about 24 hours.

25. The process according to claim 24 wherein the first interval is in the range of six to ten hours and the second interval is less than about sixteen hours, and including the step of stirring the solution throughout both the heating/coprecipitating step and the maturing step.

26. The process according to claim 12 wherein, following the step of maturing the coprecipitate, the coprecipitate is isolated from the solution and washed with water, and water remaining in the water-washed coprecipitate is replaced by washing the coprecipitate with the water miscible, low surface-tension solvent.

27. The process according to claim 26 wherein the water miscible, low surface tension solvent is selected from the group consisting of an alcohol, a ketone, and an ester, each with 4 carbons or less.

28. The process according to claim 27 wherein the water miscible, low surface tension solvent is selected from the group consisting of dried 2-propanol, acetone, methyl ethyl ketone, and 1-propanol.

29. The process according to claim 28 wherein the water miscible, low surface tension solvent is dried 2-propanol.

30. The process according to claim 26 wherein the step of washing the coprecipitate with the water miscible, low surface tension solvent comprises one or more washings initially at room temperature and the subsequent drying step includes refluxing the coprecipitate in a dry solvent in the presence of heat for an interval of less than about one hour.

31. The process according to claim 11 wherein the step of calcining the dried coprecipitate comprises heating the dried coprecipitate to a calcining temperature in the range of about 250°-60° C. over a period of one to about six hours.

32. The process according to claim 31 wherein the dried coprecipitate is heated to a calcining temperature in the range of about 350°-500° C. over a period of about two to about four hours.

33. A process for the preparation of a mixed metal oxide of cerium, Ce, and at least one other metal constituent, comprising:

a. dissolving urea and salts of the Ce and the at least one other constituent in water to form a dilute metal salt solution;

b. heating the solution to near boiling and coprecipitating homogeneously an oxide of the Ce and the at least one other constituent as a nanocrystalline coprecipitate;

c. replacing water existing in the coprecipitate with a water miscible, low surface-tension solvent that displaces water;

d. drying the coprecipitate to remove substantially all of any remaining water and the solvent; and

e. calcining the dried coprecipitate at a moderate temperature for an interval sufficient to remove adsorbed impurities.

34. The process according to claim 33 wherein the step of calcining the dried coprecipitate comprises heating the dried coprecipitate to a calcining temperature in the range of about 350°-500° C. over a period of about two to four hours.

35. In a water gas shift reaction, a catalyst containing a noble metal on a mixed metal oxide in accordance with claim 1.

36. The catalyst of claim 35 wherein the noble metal is platinum.

37. For use in a water gas shift reaction, a catalyst containing a noble metal on a support prepared in accordance with claim 11.

38. The catalyst of claim 37 wherein the noble metal is platinum.

39. A catalyst on a mixed metal oxide in accordance with claim 1, the catalyst consisting of a highly dispersed metal, including at least a noble metal, loaded on the mixed metal oxide and having a concentration in the range of about 0.1 to about 5 percent by weight.

40. The catalyst of claim 39 wherein the noble metal has crystallites that are predominantly less than 2.5 nm.

41. The catalyst of claim 40 wherein the noble metal is platinum.

42. A process for the preparation of the catalyst defined in accordance with claim 39, comprising the steps of:

a) contacting the mixed metal oxide with a solution containing an acid from the group consisting of amino acids, hydroxy dicarboxylic acids, hydroxy polycarboxylic acids, and keto polycarboxcylic acids to treat the surface of the mixed metal oxide; and

b) loading the surface-treated, mixed metal oxide with the noble metal by contacting the surface-treated mixed metal oxide with a solution containing the noble metal.

43. The process according to claim 42 wherein the acid selected for surface treating the mixed metal oxide is selected from the group consisting of malic acid and citric acid.

44. The process according to claim 42 wherein the noble metal is platinum and the solution is tetraamineplatinum nitrate.

45. The process according to claim 42 wherein the step a) of surface treating the mixed metal oxide comprises:

i. heating the mixed metal oxide in an acid-containing solution of ethanol and the acid at a mild temperature of about 50° C. for about 2 hour, and

ii. rinsing the mixed metal oxide with ethanol until the pH is greater than 4; the step b) of loading the noble metal on the surface-treated mixed metal oxide comprises:

i. submerging the mixed metal oxide in a solution of tetraamineplatinum nitrate having about 1 weight percent platinum, 1 weight percent ammonia hydroxide and 15 weight percent 2-propanol for about 2 hour at room temperature to metal load the mixed metal oxide and

ii. filtering and drying the metal loaded mixed metal oxide; and including the further step of:

c) calcining the metal loaded mixed metal oxide for up to about four hours at a heating rate of about 2° C./hr to a calcining temperature in the range of about 250°-600° C.

46. The process according to claim 45 wherein the calcining temperature to which the metal-loaded mixed metal oxide is heated is in the range of about 400°-500° C.

47. A catalyst comprising a metal-loaded, ceria-based mixed metal oxide containing at least one other metal constituent, the catalyst made according to the process of:

a. dissolving urea and salts of the Ce and the at least one other constituent in water to form a dilute metal salt solution;

b. heating the solution to near boiling and coprecipitating homogeneously an oxide of the Ce and the at least one other constituent as a nanocrystalline coprecipitate;

c. replacing water existing in the coprecipitate with a water miscible, low surface-tension solvent that displaces water;

d. drying the coprecipitate to remove substantially all of any remaining water and the solvent;

e. calcining the dried coprecipitate at a moderate temperature for an interval sufficient to remove adsorbed impurities to provide the mixed metal oxide;

f. contacting the mixed metal oxide with a solution containing an acid from the group consisting of amino acids, hydroxy dicarboxylic acids, hydroxy polycarboxylic acids, and keto polycarboxcylic acids to treat the surface of the mixed metal oxide; and

g. loading the surface-treated, mixed metal oxide with noble metal by contacting the surface-treated mixed metal oxide with a solution containing the noble metal.

48. The process according to claim 47 wherein the step f) of surface treating the mixed metal oxide comprises:

i. heating the mixed metal oxide in an acid-containing solution of ethanol and the acid at a mild temperature of about 50° C. for about 2 hour, and

ii. rinsing the mixed metal oxide with ethanol until the pH is greater than 4; the step g) of loading the noble metal on the surface-treated mixed metal oxide comprises:

i. submerging the mixed metal oxide in a solution of tetraamineplatinum nitrate having about 1 weight percent platinum, 1 weight percent ammonia hydroxide and 15 weight percent 2-propanol for about 2 hour at room temperature to metal load the mixed metal oxide; and including the further step of:

h) calcining the metal loaded mixed metal oxide for up to about four hours at a heating rate of about 2° C./hr to a calcining temperature in the range of about 250°-60 ° C.

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