The invention described herein involves a novel approach to the production of oxidation/reduction catalytic systems. The present invention serves to stabilize the tin oxide reducible metal-oxide coating by co-incorporating at least another metal-oxide species, such as zirconium. In one embodiment, a third metal-oxide species is incorporated, selected from the group consisting of cerium, lanthanum, hafnium, and rutherfordium. The incorporation of the additional metal-oxide components serves to stabilize the active tin-oxide layer in the catalytic process during high-temperature operation in a reducing environment (e.g., automobile exhaust). Moreover, the additional metal oxides are active components due to their oxygen-retention capabilities. Together, these features provide a mechanism to extend the range of operation of the tin-oxide-based catalyst system for automotive applications, while maintaining the existing advantages.
products. In addition, these changes have had a negative impact on automobile fuel efficiency. The outcome of these changes has been ever increasing costs for catalytic converter hardware, including catalytic converters, air pumps, and hoses are not required for catalytic converter operation. Finally, their catalytic formulation is a unique combination of precious metal and promoter chemistries that render it 25-40% less expensive in material cost per gram and less dependent on expensive materials like platinum, palladium, or rhodium than current technologies.

The successful transition of the low-temperature oxidation catalyst technology for internal combustion engine emission applications is dependent on achieving efficient destruction of primary exhaust pollutants: volatile organic compounds, including hydrocarbons (HC), carbon monoxide (CO), and nitrogen oxides (NOx) over extended operational periods. For example, the catalyst must serve to oxidize HC and CO to water and carbon dioxide, and reduce the NOx species to molecular nitrogen. The EPA and California Air Research Bureau (CARB) certification of automotive catalytic converter systems require a catalyst technology to meet minimum performance requirements for a period commensurate with its final application. Gasoline-powered automobile after market catalysts, for example, must currently eliminate 70% of emitted carbon monoxide (CO), 70% hydrocarbons (HC), and 50% nitrogen oxides (NOx) for a period of 25,000 miles operation (Original Equipment (OE) market>100,000 miles). Product durability is evaluated through approved rapid aging tests (RAT) that involve subjecting the catalyst to the emissions stream of a full-scale automobile engine operating under elevated inlet temperatures (e.g., 850° C.) and varying fuel-to-air ratios ranging from rich to lean relative to stoichiometric (i.e., ideal) operational conditions. Catalytic converter performance is characterized by the efficiency of the conversion process and product durability in maintaining mandated pollutant destruction levels. These tests involve subjecting the catalyst to an automobile exhaust emission stream under various operating conditions (e.g., drive cycles) and elevated inlet temperatures.

Despite their improvement over existing catalysts, the improved, low-temperature tin-oxide catalysts failed to maintain the minimum pollutant destruction levels following 5,000 and 10,000 mile simulated operation. Investigations reveal evidence of thermally induced reorganization that resulted in the reduced performance. Thus, despite the significant advancement of the improved catalysts over the current technology, these catalysts require greater thermal stability to extend durability.

SUMMARY OF THE INVENTION

The purpose of the invention described herein is to significantly enhance the thermal stability of the existing low-temperature, oxidation/reduction catalyst, originally developed for use in internal combustion engine emission applications, described generally in U.S. Pat. Nos. 4,829,035; 4,839,330; 4,855,274; 4,912,082; 4,991,181; 5,585,083; 5,948,965; and 6,132,694. The present invention serves to stabilize the tin oxide reducible metal-oxide coating by co-incorporating at least another metal-oxide species, such as zirconium. In at least one embodiment, a third metal-oxide species is incorporated, selected from the group consisting of cerium, lanthanum, hafnium, and ruthenium. The incorporation of the additional metal oxide components serves to stabilize the active tin-oxide layer in the catalytic process during high-temperature operation in a reducing environment (e.g., automobile exhaust). Moreover, the additional metal oxides are active components due to their oxygen-retention capabilities. Together, these features provide a mechanism to extend the range of operation of the tin-oxide-based catalyst system for automotive applications, while maintaining the existing...
advantages (e.g., better cold start performance and lower cost due to lower precious metal loading and thinner coatings.)

DETAILED DESCRIPTION OF THE INVENTION

The catalyst composite can be created by mixing metal-oxide precursor solutions, either neat or in a compatible solvent, and applying the solution to a substrate. In one embodiment, the metal-oxide precursor solution is tin, cerium, zirconium-(II) ethyl hexanoate and the compatible solvent is methyl ethyl ketone [MEK]. In this embodiment, the mass ratio for the tin:cerium:zirconium is 1:0.5:0.5. For automotive applications, the substrate can, for example, be a honeycomb-structured ceramic or metal and the coating application can be performed by a single dip-deaerate-dip sequence. Following the application, the catalyst coating can be thermally treated through various programs to eliminate solvent and convert the mixed-metal precursor solution to a mixed-metal oxide coating. In at least one embodiment, promoter metal species, selected from the group consisting of oxides of the metals of the transition series of the periodic table of elements (e.g., iron, cobalt, nickel) are then applied by dipping in aqueous metal nitrate solutions followed by an additional thermal treatment. Noble metal species, selected from the group consisting of platinum, palladium, gold, silver, and rhodium, are then applied from aqueous solutions directly to the coating channels quantitatively. This can be done by using a Pasteur pipette followed by a final thermal treatment. In at least one embodiment, the noble metal comprises from about 1 to about 50 weight percent, based on the total weight of the catalyst and the metal oxides comprise from about 50 to about 99 weight percent, based on the total weight of the catalyst. The promoter may be present in an amount sufficient to provide from about 1 to about 12 atom percent of promoter metal to tin metal.

In the conventional mode of catalyst preparation, multiple layers of the inactive support (e.g., alumina) are applied to a substrate material (e.g., cordierite, silica gel) by successive wash coating of a slurry of particles dispersed in a solvent (e.g., alcohol). The mechanism for adherence is simple absorption of material, relying heavily on the predilection of smaller particles to penetrate and absorb to the porous regions of the substrate to form an anchor for subsequent layers. In contrast, the mixed metal (e.g., Sn, Ce, Zr) precursor solutions can readily penetrate the porous cracks and fissures in the substrate material, chemically bonding to the surface through a condensation mechanism with surface hydroxyl groups. The result of this approach is significant improvement in catalyst adherence, catalytic efficiency/surface area, and durability (temperature stability). In at least one embodiment, the reducible metal oxide active layer is produced by applying a homogeneous solution of tin ethylhexanoate (SnEH), cerium (II) ethylhexanoate (CeEH), and zirconium (II) ethylhexanoate (ZrEH) to the substrate and oxidizing the absorbed and adsorbed SnEH/CeEH/ZrEH to a tin oxide (SnO2)/ceria/zirconia composite by heating the precursor solution and dispersing a noble metal selected from the group consisting of platinum, palladium, gold, silver, and rhodium, on the surface of the mixed-metal oxide active layer.

The invention claimed is:
1. A method for preparing a stabilized oxidation and reduction catalyst comprising the steps of:
   a. preparing a mixed-metal oxide precursor solution, the mixed-metal oxide precursor solution comprising a solution of tin ethylhexanoate (SnEH), cerium (II) ethylhexanoate (CeEH) and zirconium (II) ethylhexanoate (ZrEH);
   b. applying the mixed-metal oxide precursor solution to a substrate, wherein the substrate does not include an aluminum compound;
   c. treating the precursor solution to convert the mixed-metal oxide precursor solution to a mixed-metal oxide active layer, the step of treating the precursor solution to convert the mixed-metal oxide precursor solution to a mixed-metal oxide active layer further comprising the step of oxidizing absorbed and adsorbed SnEH, CeEH and ZrEH to a tin oxide (SnO2)/ceria/zirconia composite by heating the precursor solution; and
   d. dispersing a noble metal selected from the group consisting of platinum, palladium, gold, silver, and rhodium, on the surface of the mixed-metal oxide active layer.

2. The method according to claim 1, further comprising the step of adding at least one promoter metal selected from the group consisting of oxides of the metals of the transition series of the periodic table of elements, prior to the dispersing step.

3. The method according to claim 2, wherein said step of adding at least one promoter metal comprises the steps of: dip coating the substrate in at least one aqueous metal nitrate solution; and thermally treating the substrate.

4. The method according to claim 3, wherein said step of preparing a mixed-metal oxide precursor solution comprises one of the following:
   a. mixing metal oxide precursor solutions; or
   b. mixing metal oxide precursor solutions in a solvent.

5. The method according to claim 4 wherein said step of preparing a mixed-metal oxide precursor solution comprises one of the following:
   a. mixing metal oxide precursor solutions; or
   b. mixing metal oxide precursor solutions in a solvent.

6. The method according to claim 5 wherein said step of dispersing a noble metal selected from the group consisting of platinum, palladium, gold, silver, and rhodium, on the surface of the mixed-metal oxide active layer comprises the steps of: quantitatively applying the noble metal from an aqueous solution directly to the mixed metal oxide coating; and thermally treating the catalyst.

7. The method according to claim 6 wherein the noble metal is about 1 to about 50 weight percent, based on the total weight of the mixed-metal oxide active layer and the promoter is present in an amount sufficient to provide from about 1 to 12 atom percent of promoter metal to tin metal.

8. The method according to claim 1 wherein said step of preparing a mixed-metal oxide precursor solution comprises one of the following:
   a. mixing metal oxide precursor solutions; or
   b. mixing metal oxide precursor solutions in a solvent.
9. The method according to claim 8, wherein the mixed-metal oxide precursor solution further comprises the solvent methyl ethyl ketone (MEK).

10. The method according to claim 8, wherein:
   the mixed-metal oxide precursor solution comprises a homogeneous solution; and
   said step of oxidizing absorbed and adsorbed SnEH, CeEH and ZrEH to a tin oxide (SnO₂)/ceria/zirconia composite by heating the precursor solution comprising heating the substrate to 550-800 centigrade.

11. The method according to claim 8, wherein the mass ratio for the tin:cerium:zirconium is 1.0:0.5:0.5.

12. The method according to claim 1, wherein said step of applying the mixed-metal oxide precursor solution to a substrate comprises the step of applying the mixed-metal oxide precursor solution to a honeycomb-structured substrate by performing a single dip-deaerate-dip sequence.

13. A method for preparing a stabilized oxidation and reduction catalyst comprising the steps of:
   preparing a mixed-metal oxide precursor solution comprising precursors for a first metal oxide which possesses more than one stable oxidation state including at least tin oxide and a second metal oxide including at least zirconium oxide;
   applying the mixed-metal oxide precursor solution to a substrate, wherein the substrate does not include an aluminum compound;
   treating the precursor solution to convert the mixed-metal oxide precursor solution to a mixed-metal oxide active layer;
   dispersing a noble metal selected from the group consisting of platinum, palladium, gold, silver, and rhodium, on the surface of the mixed-metal oxide active layer, wherein the mixed-metal oxide precursor solution comprises precursors for a third metal oxide selected from the group consisting of cerium oxide, lanthanum oxide, hafnium oxide, and ruthenium oxide; wherein said step of preparing a mixed-metal oxide precursor solution comprises one of the following:
   mixing metal oxide precursor solutions; and
   mixing metal oxide precursor solutions in a solvent; and wherein the mixed-metal oxide precursor solution comprises tin, cerium, zirconium-(II) ethyl hexanoate and the solvent methyl ethyl ketone (MEK).

14. A method for preparing a stabilized oxidation and reduction catalyst comprising the steps of:
   preparing a mixed-metal oxide precursor solution comprising precursors for a first metal oxide which possesses more than one stable oxidation state including at least tin oxide and a second metal oxide including at least zirconium oxide;
   applying the mixed-metal oxide precursor solution to a substrate, wherein the substrate does not include an aluminum compound;
   treating the precursor solution to convert the mixed-metal oxide precursor solution to a mixed-metal oxide active layer;
   dispersing a noble metal selected from the group consisting of platinum, palladium, gold, silver, and rhodium, on the surface of the mixed-metal oxide active layer, wherein said step of preparing a mixed-metal oxide precursor solution comprises one of the following:
   mixing metal oxide precursor solutions; and
   mixing metal oxide precursor solutions in a solvent; and wherein the mixed-metal oxide precursor solution comprises a homogeneous solution of tin ethylhexanoate (SnEH), cerium (II) ethylhexanoate (CeEH) and zirconium (II) ethylhexanoate (ZrEH); and
   said step treating the catalyst to convert the mixed-metal oxide precursor solution to a mixed-metal oxide active layer comprises oxidizing absorbed and adsorbed SnEH, CeEH and ZrEH to a tin oxide (SnO₂)/ceria/zirconia composite by heating the catalyst at a high temperature.
17. A method for preparing a stabilized oxidation and reduction catalyst comprising the steps of:

preparing a mixed-metal oxide precursor solution comprising precursors for a first metal oxide which possesses more than one stable oxidation state including at least tin oxide and a second metal oxide including at least zirconium oxide;

applying the mixed-metal oxide precursor solution to a substrate, wherein the substrate does not include an aluminum compound;

treating the precursor solution to convert the mixed-metal oxide precursor solution to a mixed-metal oxide active layer:

dispersing a noble metal selected from the group consisting of platinum, palladium, gold, silver, and rhodium, on the surface of the mixed-metal oxide active layer, the step of dispersing a noble metal on the surface of the mixed-metal oxide active layer comprising the steps of:

quantitatively applying the noble metal from an aqueous solution directly to the mixed-metal oxide active layer;

and

thermally treating the catalyst;

adding at least one promoter metal selected from the group consisting of oxides of the metals of the transition series of the periodic table of elements, prior to the dispersing step; and

wherein the noble metal is about 1 to about 50 weight percent, based on the total weight of the mixed-metal oxide active layer, and the first and second metal oxide together comprise about 50 to 99 weight percent, based on the total weight of the mixed-metal oxide active layer, and the promoter is present in an amount sufficient to provide from about 1 to 12 atom percent of promoter metal to tin metal.

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