Title: SYNERGIZED PGM CATALYST SYSTEMS FOR DIESEL OXIDATION CATALYST APPLICATIONS

Abstract: Synergized platinum group metals (SPGM) oxidation catalyst systems are disclosed. Disclosed SPGM oxidation catalyst systems may include a washcoat with a Cu-Mn spinel structure and an overcoat including PGM, such as palladium (Pd), platinum (Pt), rhodium (Rh), or combinations thereof, supported on carrier material oxides. SPGM systems show significant improvement in abatement of unburned hydrocarbons (HC) and carbon monoxide (CO), and the oxidation of NO to NO2, which allows reduction of fuel consumption. Disclosed SPGM oxidation catalyst systems exhibit enhanced catalytic activity compared to PGM oxidation systems, showing that there is a synergistic effect between PGM and Cu-Mn spinel composition within the disclosed SPGM oxidation catalyst systems. Disclosed SPGM oxidation catalyst systems may be available for a plurality of DOC applications.
Synergized PGM Catalyst Systems for Diesel Oxidation Catalyst

Applications

CROSS-REFERENCE TO RELATED APPLICATIONS


BACKGROUND

Technical Field

[0002] The present disclosure relates generally to low loading of PGM catalyst systems, and, more particularly, to synergized PGM catalyst systems having at least two layers of material composites and for use in diesel oxidation catalyst (DOC) applications, with improved light-off performance and catalytic activity.

Background Information

[0003] Diesel engine exhaust emissions are a heterogeneous mixture including not only carbon monoxide (CO), unburned hydrocarbons (HC) and nitrogen oxides (NOx), but also condensed phase materials in liquid and solid form known as particulate matter (PM).

[0004] Typically, DOCs provided in diesel engine exhaust systems include platinum group metals (PGM) dispersed on a metal oxide support to convert some or all of these exhaust components into less harmful components. Additional to the conversions of HC, CO and PM, DOCs including PGM
promote the oxidation of NO\textsubscript{x} to NO\textsubscript{2}. PGMs are used alone or in combination with other noble metals as active components in oxidation catalysts, but noble metals catalyze different oxidation reactions in the catalyst system with different effectiveness.

[0005] Early diesel oxidation catalysts were composed of platinum on a high surface area support and were generally operated at temperatures up to 500 °C to 600 °C. More recently, diesel oxidation catalysts have been required to operate at higher temperatures to regenerate the particulate filter that is conventionally located downstream of the oxidation catalyst.

[0006] It is known that mixed platinum (Pt) and palladium (Pd) catalysts offer improved thermal stability as compared with platinum alone and hence the catalyst industry has moved to manufacture Pt/Pd-based diesel oxidation catalysts. However, currently available Pt/Pd-based oxidation catalysts suffer from the problems of poor alloying between the platinum and palladium and a tendency for the size of the metal particles to grow both as the platinum concentration is increased and during use. Both of these factors limit the performance of the catalyst and the possibility for further enhancements in thermal stability. Despite the lower cost of Pd compared to Pt, Pd-based catalyst composites typically show higher light-off temperatures for oxidation of CO and HC, potentially causing a delay in HC and/or CO light-off. Additionally, Pd-based catalyst composites may poison the activity of Pt to convert hydrocarbons and/or oxidize NO\textsubscript{x}, and may also make the catalyst composite more susceptible to sulfur poisoning when used in diesel engine exhaust systems.

[0007] Rhodium (Rh) is used in catalyst systems for the reduction of NO\textsubscript{x} by CO in the presence of excess oxygen. As Rh is a byproduct of the mining of Pt, Rh in any catalyst system must be used effectively during the catalyst system's operational life. Additionally, as Rh interacts strongly under oxidizing conditions at elevated temperatures, it may diffuse and dissolve so that Rh is only partly recovered when reducing conditions are once again established over the catalyst system. Thus, exposure of a catalyst system including Rh to high temperature conditions may result in the loss of Rh as an effective catalyst material over the life of the catalyst system.
[0008] Therefore, as emissions regulations become more stringent, there is significant interest in developing diesel oxidation catalysts with improved properties for effective utilization and particularly with improved initial activity, improved thermal stability, controlled and stable metal particle size and reduced aging. The continuing goal is to develop DOC including catalyst composites that provide improved light-off performance and removal of residual hydrocarbons, carbon monoxide and NOX. Additionally, as NO emission standards tighten and PGMs become scarce with small market circulation volume, constant fluctuations in price, and constant risk to stable supply, amongst others, there is an increasing need for new compositions for DOC applications including combined catalyst systems with low amounts of PGM catalysts, which may exhibit a synergistic behavior in yielding enhanced catalyst activity under diesel oxidation condition, and which may be cost-effectively manufactured.

SUMMARY

[0009] The present disclosure provides synergized platinum group metals (SPGM) oxidation catalyst systems which may exhibit high catalytic activity under DOC light-off condition, and thus improved light-off performance and oxidation of hydrocarbons, carbon monoxide and nitrogen oxide, when compared to PGM systems.

[0010] According to various embodiment, SPGM oxidation catalysts in present disclosure may include at least a substrate, a washcoat, and an overcoat, where substrate may include a plurality of material, such as ceramic material, washcoat may include a Cu-Mn spinel structure supported on plurality of support metal oxides, such as doped ZrO₂, and overcoat may include a specific PGM material, such as palladium (Pd), or a combination of different PGM materials, such as a bimetallic composite of platinum (Pt) and rhodium (Rh), supported on carrier material oxides, such as alumina.

[0011] In order to compare performance and determine the synergistic influence of Cu-Mn spinel structure with PGM layer, a PGM oxidation catalyst without Cu-Mn spinel structure may be prepared
as control sample. The PGM oxidation system may include a ceramic substrate, a washcoat that may include doped ZrO₂, and an overcoat which may include PGM material, such as Pd or a bimetallic composite of Pt and Rh, supported on carrier material oxides, such as alumina.

[0012] Disclosed SPGM oxidation catalyst and PGM control systems may be prepared using suitable synthesis method, as known in the art, such as co-milling process, and co-precipitation process, amongst others.

[0013] According to one aspect of the present disclosure, to determine the influence on oxidation activity that PGM loadings and Cu-Mn spinel structure may have in the catalytic behavior of both synergized and non-synergized PGM oxidation systems, fresh samples of disclosed SPGM systems and fresh samples of PGM control systems, not including the Cu-Mn spinel structure, may be prepared using different loadings of Pd and Pt/Rh material. In present disclosure, total PGM loading may be as low as 1.0 g/ft³.

[0014] According to another aspect of the present disclosure, a DOC standard light-off test may be performed for fresh SPGM and PGM control samples employed in present disclosure. Standard light-off test may be performed under steady state condition for catalytic activity in NO, CO, and HC conversions. Analyses of catalytic activity may be developed for fresh SPGM sample and PGM control samples, including HC and CO light-off temperatures, T₅₀, resulting from light-off test procedure employed to verify influence on catalyst activity that may derive from synergistic effect of Cu-Mn spinel and to measure NO to NO₂ conversion.

[0015] SPGM diesel oxidation catalyst of the present disclosure may provide significant improvements in NO conversion under lean operating conditions which is a result of the synergistic effect of the Cu-Mn spinel structure included in both Pd-based and Pt/Rh-based PGM DOCs. Furthermore, disclosed SPGM catalyst systems including Cu-Mn spinel structures may enable catalytic converters employing low amounts of PGM materials.
According to the foregoing, catalytically active ZPGM material compositions used in present disclosure in the form of Cu-Mn spinel structure as synergizing material may allow high dispersion systems for SPGM oxidation catalyst, which may be manufactured cost-effectively to make them readily available for a plurality of DOC applications, because of the effect on performance provided by ZPGM compositions improving the catalytic layers in diesel oxidation catalysis.

Numerous other aspects, features and benefits of the present disclosure may be made apparent from the following detailed description taken together with the drawing figures.

BRIEF DESCRIPTION OF THE DRAWINGS

Non-limiting embodiments of the present disclosure are described by way of example with reference to the accompanying figures which are schematic and are not intended to be drawn to scale. Unless indicated as representing the background art, the figures represent aspects of the disclosure.

FIG. 1 corresponds to an SPGM oxidation catalyst configuration with overcoat of palladium on alumina and washcoat with Cu-Mn spinel on doped Zirconia, referred as SPGM oxidation catalyst system Type 1, according to an embodiment.

FIG. 2 illustrates a PGM control system configuration with overcoat of palladium on alumina and washcoat of doped Zirconia, referred as PGM system Type 2, according to an embodiment.

FIG. 3 depicts an SPGM oxidation catalyst configuration with overcoat of platinum and rhodium on alumina and washcoat with Cu-Mn spinel on doped Zirconia, referred as SPGM oxidation catalyst system Type 3, according to an embodiment.

FIG. 4 shows a PGM control system configuration with overcoat of platinum and rhodium on alumina and washcoat of doped Zirconia, referred as PGM system Type 4, according to an embodiment.
[0023] FIG. 5 represents CO and HC conversion comparisons for fresh samples of SPGM oxidation catalyst system Type 1, and PGM control system Type 2, within a temperature range from about 150 °C to about 500 °C and space velocity (SV) of about 54,000 h⁻¹, and PGM loading of about 1.0 g/ft³, according to an embodiment. FIG. 5A shows the CO conversion comparison chart and FIG. 5B depicts the HC conversion comparison chart for fresh samples of SPGM oxidation catalyst system Type 1 and PGM control system Type 2.

[0024] FIG. 6 depicts NO conversion and NO₂ production comparisons for fresh samples of SPGM oxidation catalyst system Type 1 and PGM control system Type 2 within a temperature range from about 150 °C to about 500 °C and space velocity (SV) of about 54,000 h⁻¹, PGM loading of about 1.0 g/ft³. FIG. 6A represents the NO conversion comparison chart and FIG. 6B depicts NO₂ production comparison chart for fresh samples of SPGM oxidation catalyst system Type 1 and PGM control system Type 2.

[0025] FIG. 7 illustrates CO and HC conversion comparisons for fresh samples of SPGM oxidation catalyst system Type 3, and PGM control system Type 4, within a temperature range from about 150 °C to about 500 °C and space velocity (SV) of about 54,000 h⁻¹, and Pt loading of about 0.5 g/ft³ and Rh loading of about 0.5 g/ft³, according to an embodiment. FIG. 7A shows the CO conversion comparison chart and FIG. 7B depicts the HC conversion comparison chart for fresh samples of SPGM oxidation catalyst system Type 3 and PGM control system Type 4.

[0026] FIG. 8 shows NO conversion and NO₂ production comparisons for fresh samples of SPGM DOC systems Type 3 and PGM control system Type 4, within a temperature range from about 150 °C to about 500 °C and space velocity (SV) of about 54,000 h⁻¹, Pt loading of about 0.5 g/ft³ and Rh loading of about 0.5 g/ft³. FIG. 8A represents the NO conversion comparison chart and FIG. 8B depicts NO₂ production comparison chart for fresh samples of SPGM DOC system Type 3 and PGM control system Type 4.
DETAILED DESCRIPTION

[0027] In the following detailed description, reference is made to the accompanying drawings, which form a part hereof. In the drawings, which are not to scale or to proportion, similar symbols typically identify similar components, unless context dictates otherwise. The illustrative embodiments described in the detailed description, drawings and claims, are not meant to be limiting. Other embodiments may be used and/or and other changes may be made without departing from the spirit or scope of the present disclosure.

Definitions

[0028] As used here, the following terms may have the following definitions:

[0029] “Catalyst system” refers to a system of at least two layers including at least one substrate, a washcoat, and/or an overcoat.

[0030] “Substrate” refers to any material of any shape or configuration that yields a sufficient surface area for depositing a washcoat and/or overcoat.

[0031] “Washcoat” refers to at least one coating including at least one oxide solid that may be deposited on a substrate.

[0032] “Overcoat” refers to at least one coating that may be deposited on at least one washcoat layer.

[0033] “Catalyst” refers to one or more materials that may be of use in the conversion of one or more other materials.

[0034] “Milling” refers to the operation of breaking a solid material into a desired grain or particle size.
[0035] "Co-precipitation" refers to the carrying down by a precipitate of substances normally soluble under the conditions employed.

[0036] "Calcination" refers to a thermal treatment process applied to solid materials, in presence of air, to bring about a thermal decomposition, phase transition, or removal of a volatile fraction at temperatures below the melting point of the solid materials.

[0037] "Platinum group metals (PGM)" refers to platinum, palladium, ruthenium, iridium, osmium, and rhodium.

[0038] "Zero platinum group (ZPGM) catalyst" refers to a catalyst completely or substantially free of platinum group metals.

[0039] "Synergized platinum group metal (SPGM) catalyst" refers to a PGM catalyst system which is synergized by a non-PGM group metal compound under different configuration.

[0040] "Treating," "treated," or "treatment" refers to drying, firing, heating, evaporating, calcining, or mixtures thereof.

[0041] "Diesel oxidation catalyst" refers to a device which utilizes a chemical process in order to break down pollutants from a diesel engine or lean burn gasoline engine in the exhaust stream, turning them into less harmful components.

[0042] "Conversion" refers to the chemical alteration of at least one material into one or more other materials.

[0043] "Spinel" refers to any of various mineral oxides of magnesium, iron, zinc, or manganese in combination with aluminum, chromium, copper or iron with AB₂O₄ structure.

[0044] "Tₚ₀" refers to the temperature at which 50% of a material is converted.
Description of the Drawings

[0045] The present disclosure may provide material compositions including catalyst layer of stoichiometric Cu-Mn spinel at selected base metal loadings on support oxide and their influence on light-off performance of diesel oxidation catalyst (DOC) systems in order to enable suitable catalytic layers, which may ensure high chemical reactivity. Aspects that may be treated in present disclosure may show improvements in the process for overall catalytic conversion capacity for a plurality of synergized PGM (SPGM) oxidation catalyst systems which may be suitable for a plurality of DOC applications and have enhanced catalytic performance when compared with PGM systems.

[0046] Embodiments of the present disclosure incorporate more active components into phase materials possessing DOC properties and provide catalyst performance comparison of disclosed SPGM systems and PGM control systems that may include different palladium (Pd) loadings, or platinum (Pt)/rhodium (Rh) loadings within the overcoat layer.

[0047] According to embodiments in the present disclosure, an SPGM oxidation catalyst may be configured with a washcoat including stoichiometric Cu-Mn spinel with doped Zirconia support oxide, an overcoat including a PGM catalyst, such as Pd with alumina-based support, or Pt/Rh material composite with alumina-based support, and suitable ceramic substrate, here referred as SPGM oxidation catalyst system Type 1 and SPGM oxidation catalyst system Type 3, respectively. According to other embodiments in the present disclosure, PGM control systems may be configured with washcoat layer including doped Zirconia support oxide, an overcoat including PGM catalyst, such as such as Pd with alumina-based support, or Pt/Rh material composite with alumina-based support, and suitable ceramic substrate, here referred as PGM control system Type 2 and PGM control system Type 4, respectively.

[0048] SPGM oxidation catalyst and PGM control catalyst configurations
[0049] FIG. 1 shows oxidation catalyst configuration 100, here referred as SPGM oxidation catalyst system Type 1, according to an embodiment.

[0050] As shown in FIG. 1, SPGM oxidation catalyst system Type 1 may include at least substrate 102, washcoat 104, and overcoat 106, where washcoat 104 may include a Cu-Mn spinel structure supported on doped Zirconia and overcoat 106 may include PGM catalyst material supported on carrier material oxides.

[0051] According to embodiments in present disclosure, substrate 102 materials for SPGM catalyst system Type 1 may include a refractive material, a ceramic material, a honeycomb structure, a metallic material, a ceramic foam, a metallic foam, a reticulated foam, or suitable combinations, where substrate 102 may have a plurality of channels with suitable porosity. Porosity may vary according to the particular properties of substrate 102 materials. Additionally, the number of channels may vary depending upon substrate 102 and its type and shape may be apparent to one of ordinary skill in the art. According to the present disclosure, preferred substrate 102 may be a ceramic substrate.

[0052] Washcoat 104 for SPGM oxidation catalyst system Type 1 may include a Cu-Mn stoichiometric spinel, $\text{Cu}_{1.9}\text{Mn}_{0.1}\text{O}_4$, on support oxide of doped Zirconia. According to present disclosure, suitable material for disclosed washcoat 104 may be $\text{Nb}_2\text{O}_5$-$\text{ZrO}_2$.

[0053] Overcoat 106 for SPGM oxidation catalyst system Type 1 may include a PGM catalyst, such as palladium (Pd), Platinum (Pt), Rhodium (Rh), and combinations thereof, which may be supported on carrier material oxides, such as doped aluminum oxide, zirconium oxide, doped Zirconia, titanium oxide, tin oxide, silicon dioxide, zeolite, and mixtures thereof. In present disclosure, disclosed overcoat 106 may include suitable PGM catalyst of Pd supported on alumina.

[0054] FIG. 2 illustrates PGM system configuration 200, here referred as PGM control system Type 2, according to an embodiment.
[0055] As shown in FIG. 2, PGM control system Type 2 may include at least substrate 102, washcoat 202, and an overcoat 106, where washcoat 202 may include doped Zirconia and overcoat 206 may include PGM catalyst material supported on carrier material oxides.

[0056] According to embodiments in present disclosure, substrate 102 materials for PGM control system Type 2 may include a refractive material, a ceramic material, a honeycomb structure, a metallic material, a ceramic foam, a metallic foam, a reticulated foam, or suitable combinations. According to the present disclosure, preferred substrate 102 may be a ceramic substrate.

[0057] Washcoat 202 for PGM control system Type 2 may include support oxides such as zirconium oxide or doped Zirconia. According to the present disclosure, suitable material for disclosed washcoat 202 may be Nb₂O₃-ZrO₂.

[0058] Overcoat 106 for PGM control system Type 2 may include a PGM catalyst, such as palladium (Pd), Platinum (Pt), Rhodium (Rh), and combinations thereof, which may be supported on carrier material oxides, such as doped aluminum oxide, zirconium oxide, doped Zirconia, titanium oxide, tin oxide, silicon dioxide, zeolite, and mixtures thereof. In present disclosure, disclosed overcoat 106 may include suitable PGM catalyst of Pd supported on alumina.

[0059] FIG. 3 depicts oxidation catalyst configuration 300, here referred as SPGM oxidation catalyst system Type 3, according to an embodiment.

[0060] As shown in FIG. 3, SPGM oxidation catalyst system Type 3 may include at least substrate 102, washcoat 104, and overcoat 302, where washcoat 104 may include a Cu-Mn spinel structure supported on doped Zirconia and overcoat 302 may include PGM catalyst material supported on carrier material oxides.

[0061] According to embodiments in present disclosure, substrate 102 materials for SPGM catalyst system Type 3 may include a refractive material, a ceramic material, a honeycomb structure, a metallic
material, a ceramic foam, a metallic foam, a reticulated foam, or suitable combinations, where
substrate 102 may have a plurality of channels with suitable porosity. Porosity may vary according to
the particular properties of substrate 102 materials. Additionally, the number of channels may vary
depending upon substrate 102 and its type and shape may be apparent to one of ordinary skill in the
art. According to the present disclosure, preferred substrate 102 may be a ceramic substrate.

[0062] Washcoat 104 for SPGM oxidation catalyst system Type 3 may include a Cu-Mn stoichiometric
spinel, Cu1.0Mn2.0O4, on support oxide of doped Zirconia. According to present disclosure, suitable
material for disclosed washcoat 104 may be Nb2O5-ZrO2.

[0063] Overcoat 302 for SPGM oxidation catalyst system Type 3 may include a PGM catalyst, such as
palladium (Pd), Platinum (Pt), Rhodium (Rh), and combinations thereof, which may be supported on
carrier material oxides, such as doped aluminum oxide, zirconium oxide, doped Zirconia, titanium
oxide, tin oxide, silicon dioxide, zeolite, and mixtures thereof. In present disclosure, disclosed overcoat
302 may include suitable PGM catalyst of Pt/Rh supported on alumina.

[0064] FIG. 4 illustrates PGM system configuration 400, here referred as PGM control system Type 4,
according to an embodiment.

[0065] As shown in FIG. 4, PGM control system Type 4 may include at least substrate 102, washcoat
202, and an overcoat 302, where washcoat 202 may include doped Zirconia and overcoat 302 may
include PGM catalyst material supported on carrier material oxides.

[0066] According to embodiments in present disclosure, substrate 102 materials for PGM control
system Type 4 may include a refractive material, a ceramic material, a honeycomb structure, a metallic
material, a ceramic foam, a metallic foam, a reticulated foam, or suitable combinations. According to
the present disclosure, preferred substrate 102 may be a ceramic substrate.
[0067] Washcoat 202 for PGM control system Type 4 may include support oxides such as zirconium oxide or doped Zirconia. According to the present disclosure, suitable material for disclosed washcoat 202 may be Nb₂O₅-ZrO₂.

[0068] Overcoat 302 for PGM control system Type 4 may include a PGM catalyst, such as palladium (Pd), Platinum (Pt), Rhodium (Rh), and combinations thereof, which may be supported on carrier material oxides, such as doped aluminum oxide, zirconium oxide, doped Zirconia, titanium oxide, tin oxide, silicon dioxide, zeolite, and mixtures thereof. In present disclosure, disclosed overcoat 302 may include suitable PGM catalyst of Pt/Rh supported on alumina.

[0069] The synergistic effect of selected base metal loadings of Cu-Mn stoichiometric spinel, Cu₃₋ₓMnₓO₄, may be verified preparing samples of the disclosed SPGM oxidation catalyst system and PGM control system, which may be tested under light-off conditions.

[0070] DOC standard light-off test procedure

[0071] DOC standard light-off test under steady state condition may be performed employing a flow reactor in which temperature may be increased from about 100 ºC to about 500 ºC at a rate of about 40 ºC/min, feeding a gas composition of about 100 ppm of NOₓ, 1,500 ppm of CO, about 4% of CO₂, about 4% of H₂O, about 14% of O₂, and about 430 ppm of C₅H₁₀, at space velocity (SV) of about 54,000 h⁻¹. During DOC light-off test neither N₂O nor NH₃ may form.

[0072] The following examples are intended to illustrate the scope of the disclosure. It is to be understood that other procedures known to those skilled in the art may alternatively be used. Examples in the present disclosure may be prepared according to the plurality of DOC system configurations previously disclosed.
EXAMPLES

[0073] Example #1 - SPGM oxidation catalyst system Type 1

[0074] Example #1 may illustrate preparation of fresh samples of SPGM oxidation catalyst system Type 1 having oxidation catalyst configuration 100.

[0075] The preparation of washcoat 104 may begin by milling Nb₂O₅-ZrO₂ support oxide to make aqueous slurry. The Nb₂O₅-ZrO₂ support oxide may have Nb₂O₅ loadings of about 15% to about 30% by weight, preferably about 25%, and ZrO₂ loadings of about 70% to about 85% by weight, preferably about 75%.

[0076] The Cu-Mn solution may be prepared by mixing for about 1 to 2 hours, an appropriate amount of Mn nitrate solution (Mn(NO₃)₂) and Cu nitrate solution (CuNO₃). Subsequently, Cu-Mn nitrate solution may be mixed with Nb₂O₅-ZrO₂ support oxide slurry for about 2 to 4 hours, where Cu-Mn nitrate solution may be precipitated on Nb₂O₅-ZrO₂ support oxide aqueous slurry. A suitable base solution, such as sodium hydroxide (NaOH) solution, sodium carbonate (Na₂CO₃) solution, ammonium hydroxide (NH₄OH) solution, and tetraethyl ammonium hydroxide (TEAH) solution, amongst others, may be added to adjust the pH of the slurry to a suitable range. The precipitated Cu-Mn/Nb₂O₅-ZrO₂ slurry may be aged for a period of time of about 12 to 24 hours under continued stirring at room temperature.

[0077] Subsequently, the precipitated slurry may be coated on ceramic substrate 102. The aqueous slurry of Cu-Mn/Nb₂O₅-ZrO₂ may be deposited on the suitable ceramic substrate 102 to form washcoat 104, employing vacuum dosing and coating systems. In the present disclosure, a plurality of capacities of washcoat 104 loadings may be coated on suitable ceramic substrate 102. Subsequently, after deposition on ceramic substrate 102 of the suitable loadings of Cu-Mn/Nb₂O₅-ZrO₂ slurry, washcoat
may be dried overnight at about 120 °C and subsequently calcined at a suitable temperature within a range of about 550 °C to about 650 °C, preferably at about 600 °C for about 5 hours.

[0078] Overcoat 106 may include a combination of Pd on alumina-based support. The preparation of overcoat 106 may begin by milling the alumina-based support oxide separately to make aqueous slurry. Subsequently, a solution of Pd nitrate may be mixed with the aqueous slurry of alumina with a loading within a range from about 0.5 g/ft³ to about 25.0 g/ft³, preferably about 1.0 g/ft³ in present disclosure. After mixing of Pd and alumina slurry, Pd may be locked down with an appropriate amount of one or more base solutions, such as sodium hydroxide (NaOH) solution, sodium carbonate (Na₂CO₃) solution, ammonium hydroxide (NH₄OH) solution, and tetraethyl ammonium hydroxide (TEAH) solution, amongst others. Then, the resulting slurry may be aged from about 12 to 24 hours for subsequent coating as overcoat 106 on washcoat 104, dried and fired at about 550 °C for about 4 hours.

[0079] Example #2 - SGM control system Type 2

[0080] Example #2 may illustrate preparation of fresh samples of PGM control system Type 2 having PGM system configuration 200.

[0081] The preparation of washcoat 202 may begin by milling Nb₂O₅-ZrO₂ support oxide to make aqueous slurry. The Nb₂O₅-ZrO₂ support oxide may have Nb₂O₅ loadings of about 15% to about 30% by weight, preferably about 25% and ZrO₂ loadings of about 70% to about 85% by weight, preferably about 75%. Washcoat 202 particle size (d₅₀) may be adjusted within a range of about 4 μm to about 5 μm.

[0082] Subsequently, washcoat 202 slurry may be coated on substrate 102. Washcoat 202 slurry may be deposited on suitable ceramic substrate 102 to form washcoat 202, employing vacuum dosing and coating systems. In the present disclosure, a plurality of capacities of washcoat 202 loadings may be coated on suitable ceramic substrate 102. Washcoat 202 may be dried overnight at about 120 °C and
subsequently calcined at a suitable temperature within a range of about 550 °C to about 650 °C, preferably at about 550 °C for about 4 hours.

[0083] Overcoat 106 may include a combination of Pd on alumina-based support. The preparation of overcoat 106 may begin by milling the alumina-based support oxide separately to make aqueous slurry. Subsequently, a solution of Pd nitrate may be mixed with the aqueous slurry of alumina with a loading within a range from about 0.5 g/ft³ to about 25.0 g/ft³, preferably about 1.0 g/ft³ in present disclosure. After mixing of Pd and alumina slurry, Pd may be locked down with an appropriate amount of one or more base solutions, such as sodium hydroxide (NaOH) solution, sodium carbonate (Na₂CO₃) solution, ammonium hydroxide (NH₄OH) solution, and tetraethyl ammonium hydroxide (TEAH) solution, amongst others. Then, the resulting slurry may be aged from about 12 hours to about 24 hours for subsequent coating as overcoat 106 on washcoat 104, dried and fired at about 550 °C for about 4 hours.

[0084] DOC Light-off performance for SPGM oxidation catalyst system Type 1 and PGM control system Type 2 may be compared by preparing fresh samples for each of the catalyst formulations and configurations to measure/analyze the synergistic effect of adding Cu-Mn spinel to PGM catalyst materials, which may be used in DOC applications, and to show the resulting improvement in oxidation activity. In order to compare light-off performance and DOC activity of disclosed SPGM DOC system Type 1 and PGM control system Type 2, DOC standard light-off tests may be performed.

[0085] Example #3 - SPGM oxidation catalyst system Type 3

[0086] Example #3 may illustrate preparation of fresh samples of SPGM oxidation catalyst system Type 3 having oxidation catalyst configuration 300.

[0087] The preparation of washcoat 104 may begin by milling Nb₂O₅-ZrO₂ support oxide to make aqueous slurry. The Nb₂O₅-ZrO₂ support oxide may have Nb₂O₅ loadings of about 15% to about 30% by
weight, preferably about 25% and ZrO₂ loadings of about 70% to about 85% by weight, preferably about 75%.

[0088] The Cu-Mn solution may be prepared by mixing for about 1 to 2 hours, an appropriate amount of Mn nitrate solution (Mn(NO₃)₂) and Cu nitrate solution (CuNO₃). Subsequently, Cu-Mn nitrate solution may be mixed with Nb₂O₅-ZrO₂ support oxide slurry for about 2 to 4 hours, where Cu-Mn nitrate solution may be precipitated on Nb₂O₅-ZrO₂ support oxide aqueous slurry. A suitable base solution, such as sodium hydroxide (NaOH) solution, sodium carbonate (Na₂CO₃) solution, ammonium hydroxide (NH₄OH) solution, and tetraethyl ammonium hydroxide (TEAH) solution, amongst others, may be added to adjust the pH of the slurry to a suitable range. The precipitated Cu-Mn/Nb₂O₅-ZrO₂ slurry may be aged for a period of time of about 12 to 24 hours under continued stirring at room temperature.

[0089] Subsequently, the precipitated slurry may be coated on ceramic substrate 102. The aqueous slurry of Cu-Mn/Nb₂O₅-ZrO₂ may be deposited on suitable ceramic substrate 102 to form washcoat 104, employing vacuum dosing and coating systems. In the present disclosure, a plurality of capacities of washcoat 104 loadings may be coated on the suitable ceramic substrate 102. Subsequently, after deposition on ceramic substrate 102 of the suitable loadings of Cu-Mn/Nb₂O₅-ZrO₂ slurry, washcoat 104 may be dried overnight at about 120 °C and subsequently calcined at a suitable temperature within a range of about 550 °C to about 650 °C, preferably at about 600 °C for about 5 hours.

[0090] Overcoat 302 may include a combination of Pt and Rh on alumina-based support. The preparation of overcoat 302 may begin by milling the alumina-based support oxide separately to make aqueous slurry. Subsequently, a solution of Pt and Rh nitrates may be mixed with the aqueous slurry of alumina with a loading within a range from about 0.5 g/ft³ to about 25.0 g/ft³, preferably about 0.5 g/ft³ of Pt and about 0.5 g/ft³ of Rh. After mixing of Pt/Rh and alumina slurry, Pt/Rh may be locked down with an appropriate amount of one or more base solutions, such as sodium hydroxide (NaOH) solution, sodium carbonate (Na₂CO₃) solution, ammonium hydroxide (NH₄OH) solution, and tetraethyl
ammonium hydroxide (TEAH) solution, amongst others. Then, the resulting slurry may be aged from about 12 to 24 hours for subsequent coating as overcoat 106 on washcoat 104, dried and fired at about 550 °C for about 4 hours.

[0091] Example #4 - PGM control system Type 4

[0092] Example #4 may illustrate preparation of fresh samples of PGM control system Type 4 having PGM system configuration 400.

[0093] The preparation of washcoat 202 may begin by milling Nb₂O₅-ZrO₂ support oxide to make aqueous slurry. The Nb₂O₅-ZrO₂ support oxide may have Nb₂O₅ loadings of about 15% to about 30% by weight, preferably about 25% and ZrO₂ loadings of about 70% to about 85% by weight, preferably about 75%. Washcoat 202 particle size (d₅₀) may be adjusted within a range of about 4 μm to about 5 μm.

[0094] Subsequently, washcoat 202 slurry may be coated on substrate 102. Washcoat 202 slurry may be deposited on suitable ceramic substrate 102 to form washcoat 202, employing vacuum dosing and coating systems. In the present disclosure, a plurality of capacities of washcoat 202 loadings may be coated on suitable ceramic substrate 102. Washcoat 202 may be dried overnight at about 120 °C and subsequently calcined at a suitable temperature within a range of about 550 °C to about 650 °C, preferably at about 550 °C for about 4 hours.

[0095] Overcoat 302 may include a combination of Pt and Rh on alumina-based support. The preparation of overcoat 302 may begin by milling the alumina-based support oxide separately to make aqueous slurry. Subsequently, a solution of Pt and Rh nitrates may be mixed with the aqueous slurry of alumina with a loading within a range from about 0.5 g/ft³ to about 25.0 g/ft³, preferably about 0.5 g/ft³ of Pt and about 0.5 g/ft³ of Rh. After mixing of Pt/Rh and alumina slurry, Pt/Rh may be locked down with an appropriate amount of one or more base solutions, such as sodium hydroxide (NaOH) solution, sodium carbonate (Na₂CO₃) solution, ammonium hydroxide (NH₄OH) solution, and tetraethyl
ammonium hydroxide (TEAH) solution, amongst others. Then, the resulting slurry may be aged from about 12 to 24 hours for subsequent coating as overcoat 106 on washcoat 104, dried and fired at about 550 °C for about 4 hours.

[0096] **DOC Light-off performance for SPGM oxidation catalyst system Type 3 and PGM control system Type 4 may be compared by preparing fresh samples for each of the catalyst formulations and configurations to measure/analyze the synergistic effect of adding Cu-Mn spinel to PGM catalyst materials, which may be used in DOC applications, and to show the resulting improvement in oxidation activity. In order to compare light-off performance and DOC activity of disclosed SPGM DOC system Type 3 and PGM control system Type 4, DOC standard light-off tests may be performed.**

[0097] **Analysis of oxidation property for fresh samples of SPGM oxidation catalyst and PGM control systems**

[0098] **FIG. 5** represents CO and HC conversion comparisons 500 for fresh samples of SPGM oxidation catalyst system Type 1, and PGM control system Type 2, respectively, under light-off condition, at a temperature range from about 150 °C to about 500 °C and space velocity (SV) of about 54,000 h⁻¹, according to an embodiment. **FIG. 5A** shows the CO conversion comparison curves 502 and **FIG. 5B** depicts the HC conversion comparison curves 504 for fresh samples of SPGM oxidation catalyst system Type 1 and PGM control system Type 2.

[0099] Accordingly, as can be seen in **FIG. 5A**, conversion curve 506 represents CO conversion for SPGM oxidation catalyst system Type 1 fresh samples and conversion curve 508 depicts CO conversion for PGM control system Type 2 fresh samples, respectively. It may be observed in **FIG. 5A** that CO T₅₀ for fresh samples of SPGM oxidation catalyst system Type 1 is about 235 °C, while CO T₅₀ for fresh samples of PGM control system Type 2 is about 325 °C. CO light off temperature of Synergized PGM samples is lower than that of PGM control samples, showing enhanced CO oxidation performance of SPGM Type 1. Even though PGM samples present desirable oxidation activity in CO conversion,
synergized PGM samples significantly surpass PGM samples in regards to CO conversion, verifying the synergistic effect between Cu-Mn spinel and Pd.

[0100] As can be seen in FIG. 5B, conversion curve 510 represents HC conversion for SPGM oxidation catalyst system Type 1 fresh samples and conversion curve 512 depicts HC conversion for PGM control system Type 2 fresh samples, respectively. It may be observed in FIG. 5B that HC T50, for fresh samples of SPGM oxidation catalyst system Type 1 is about 235 °C, while HC T50, for PGM control system Type 2 is about 350 °C. HC light off temperature of synergized PGM samples is lower than that of PGM control samples showing enhanced HC oxidation activity of SPGM oxidation catalyst system Type 1 verifying the synergistic effect between Cu-Mn spinel and Pd.

[0101] The resulting levels of CO and HC oxidation improvement for SPGM oxidation catalyst system Type 1 may indicate that the synergistic effect between Cu-Mn spinel and Pd may deliver improved oxidation catalyst with ultra low Pd loading of about 1.0 g/ft³ for DOC application.

[0102] FIG. 6 depicts NO conversion and NO2 production comparisons 600 for fresh samples of SPGM oxidation catalyst system Type 1 and PGM control system Type 2 at a temperature range from about 150 °C to about 500 °C and space velocity (SV) of about 54,000 h⁻¹ according to an embodiment. FIG. 6A represents NO conversion comparison 602 and FIG. 6B depicts NO2 production comparison 604 for fresh samples of SPGM oxidation catalyst system Type 1 and PGM control system Type 2.

[0103] Accordingly, as can be seen in FIG. 6A, conversion curve 606 represents NO conversion for SPGM oxidation catalyst system Type 1 fresh samples and conversion curve 608 depicts NO conversion for PGM control system Type 2 fresh samples under DOC light-off condition, respectively.

[0104] As may be seen in FIG. 6B, concentration profile curve 610 represents NO2 production for SPGM oxidation catalyst system Type 1 and concentration profile curve 612 depicts NO2 production for PGM control system Type 2 under DOC light-off condition, respectively.
It may be observed in **FIG. 6A** that NO conversion for SPGM oxidation catalyst system Type 1 reach a maximum of about 34% conversion at about 390 °C, while PGM control system Type 2 fresh samples reach maximum NO conversion of about 18%, at about 465 °C.

SPGM oxidation catalyst system Type 1 present a significantly higher catalytic activity in NO oxidation than PGM control system Type 2. A significantly high improvement of about 83% in NO\textsubscript{x} conversion may indicate that SPGM oxidation catalyst system Type 1 may deliver enhanced oxidation activity verifying synergistic effect of Cu-Mn with pd.

As may be seen in **FIG. 6B**, NO\textsubscript{2} production from concentration profile curve 610 is about 35 ppm at about 390 °C, while NO\textsubscript{2} production from concentration profile curve 612 is about 18 ppm, at about 465 °C. By considering the concentration of NO in feed stream (100 ppm), the comparison of NO\textsubscript{2} concentration from **FIG. 6B** with NO conversion from **FIG. 6A** confirms NO convert to NO\textsubscript{2} and no other products such as NH\textsubscript{3} or N\textsubscript{2}O formed.

As may be noted, SPGM oxidation catalyst system Type 1 may deliver a higher level of NO oxidation to NO\textsubscript{2} production level than that of PGM control system Type 2. The increased NO\textsubscript{2} production and the resulting level of NO conversion for SPGM oxidation catalyst system Type 1 may indicate that the synergistic effect provided by Cu-Mn spinel may also deliver improved NO oxidation activity under diesel oxidation conditions and Pd loading of about 1.0 g/ft\textsuperscript{3}. These results may confirm that improvement is derived due to the synergistic effect between Cu-Mn spinel and Pd, which may also enable synergized PGM diesel oxidation catalyst systems for a plurality of engine applications operating under real conditions. Higher level of NO oxidation may be obtained by using higher loading of Pd in OC layer.

**FIG. 7** illustrates CO and HC conversion comparisons 700 for fresh samples of SPGM oxidation catalyst system Type 3, and PGM control system Type 4, respectively, under DOC light-off condition, at a temperature range from about 150 °C to about 500 °C and space velocity (SV) of about 54,000 h\textsuperscript{-1}. 

21
according to an embodiment. FIG. 7A shows the CO conversion comparison curves 702 and FIG. 7B depicts the HC conversion comparison curves 704 for fresh samples of SPGM oxidation catalyst system Type 3 and PGM control system Type 4, respectively.

[0110] Accordingly, as can be seen in FIG. 7A, conversion curve 706 represents CO conversion for SPGM oxidation catalyst system Type 3 and conversion curve 708 depicts CO conversion for PGM control system Type 4 under DOC light-off condition, respectively. It may be observed in FIG. 7A that CO T<sub>50</sub> for SPGM oxidation catalyst system Type 3 is about 245 °C while CO T<sub>50</sub> for PGM control system Type 4 is about 265 °C. CO light off temperature of synergized PGM samples is lower than that of PGM control samples, showing enhanced CO oxidation performance of SPGM oxidation catalyst system Type 3. Even though PGM samples present a significant oxidation activity in CO conversion, synergized PGM samples surpass PGM samples in regards to CO conversion verifying the synergistic effect between Cu-Mn spinel and Pt/Rh.

[0111] As can be seen in FIG. 7B, conversion curve 710 represents HC conversion for SPGM oxidation catalyst system Type 3 and conversion curve 712 depicts HC conversion for PGM control system Type 4 under DOC light-off condition, respectively. It may be observed in FIG. 7B that HC T<sub>50</sub> for SPGM oxidation catalyst system Type 3 is about 250 °C , while HC T<sub>50</sub> for PGM control system Type 4 is about 285 °C . HC light off temperature of synergized PGM samples is lower than that of PGM control sample showing enhanced HC oxidation performance. Even though PGM sample present significant oxidation activity in HC conversion, synergized PGM samples surpass PGM samples in regards to HC conversion verifying the synergistic effect between Cu-Mn spinel and Pt/Rh.

[0112] The resulting levels of CO and HC oxidation improvement for SPGM oxidation catalyst system Type 3 may indicate that the synergistic effect between Cu-Mn spinel and Pt/Rh may deliver improved oxidation catalyst with ultra low PGM loading of about 1.0 g/ft<sup>3</sup> for DOC application.
FIG. 8 depicts NO conversion and NO2 production comparisons for fresh samples of SPGM oxidation catalyst system Type 3 and PGM control system Type 4, under DOC light-off condition and space velocity (SV) of about 54,000 h⁻¹ according to an embodiment. FIG. 8A represents NO conversion comparison and FIG. 8B depicts NO2 production comparison for fresh samples of SPGM oxidation catalyst Type 3 and PGM control system Type 4.

Accordingly, as can be seen in FIG. 8A, conversion curve represents NO conversion for SPGM oxidation catalyst Type 3 and conversion curve depicts NO conversion for PGM control system Type 4 under DOC light-off condition, respectively.

As may be seen in FIG. 8B, concentration profile curve represents NO₂ production for SPGM oxidation catalyst system Type 3 and concentration profile curve depicts NO₂ production for PGM control system Type 4 under DOC light-off condition, respectively.

It may be observed in FIG. 8A that NO conversion for SPGM oxidation catalyst system Type 3 fresh samples reach a maximum of about 32% conversion at about 385 °C, while PGM control system Type 4 fresh samples reach maximum NOx conversion of about 19%, at about 460 °C.

SPGM oxidation catalyst system Type 3 presents a higher catalytic activity in NO oxidation than PGM control system Type 4 sample. An improvement of about 55% in NOx conversion may indicate that SPGM oxidation catalyst system Type 3 may deliver enhanced activity in NO oxidation.

As may be seen in FIG. 8B, NO₂ production from concentration profile curve is about 35 ppm at about 385 °C, while NO₂ production from concentration profile curve is about 20 ppm, at about 460 °C. These results may verify that catalytic behavior of fresh samples of SPGM oxidation catalyst system Type 3 surpasses the catalytic behavior of samples of PGM control system Type 4. DOC activity for NO₃ production is increased by the presence of Cu-Mn spinel in SPGM oxidation catalyst system Type 3.
As may be noted, SPGM oxidation catalyst system Type 3 may deliver a higher level of NO oxidation to NO\textsubscript{2} production level than that of PGM control system Type 4. The increased NO\textsubscript{2} production and the resulting level of NO conversion for SPGM oxidation catalyst system Type 3 may indicate that the synergistic effect provided by Cu-Mn spinel may also deliver improved NO oxidation activity under diesel oxidation conditions and Pt/Rh loading of about 1.0 g/ft\textsuperscript{3}. These results may confirm that improvement is derived due to the synergistic effect between Cu-Mn spinel and PGM, which may also enable synergized PGM diesel oxidation catalyst systems for a plurality of engine applications operating under real conditions. Higher level of NO oxidation may be obtained by using higher loading of Pt/Rh in OC layer.

The catalytic oxidation of SPGM oxidation catalyst systems Type 1 and Type 3 has been carried out using these catalysts under DOC light-off conditions to show and verify that DOC catalytic performance of the disclosed systems increased when compared with oxidation activity of PGM control system Type 2 and Type 4. Both SPGM systems have shown to be significantly active catalyst for diesel oxidation as determined by their corresponding light-off performance compare to same PGM systems with no Cu-Mn composition. In all disclosed SPGM systems may be observed that the presence of Cu-Mn spinel may be associated with the enhanced oxidation activity not shown by the non-synergized PGM systems. The disclosed SPGM oxidation catalyst systems may provide a basis for a plurality of applications in lean burn engine operations.

While various aspects and embodiments have been disclosed, other aspects and embodiments may be contemplated. The various aspects and embodiments disclosed here are for purposes of illustration and are not intended to be limiting, with the true scope and spirit being indicated by the following claims.
CLAIMS

What is claimed is:

1. A synergized platinum group metal (SPGM) catalyst system, comprising:
   at least one substrate comprising at least one metal;
   at least one washcoat comprising at least one oxygen storage material further comprising Cu-Mn having a niobium-zirconia support oxide; and
   at least one overcoat comprising at least one platinum group metal catalyst;
   wherein the at least one platinum group metal catalyst comprises at least one selected from the group consisting of palladium, a bimetallic composite of platinum and rhodium, and combinations thereof;
   wherein the at least one overcoat is supported on at least one carrier material oxide comprising alumina.

2. The catalyst system of claim 1, wherein the Cu-Mn spinel comprises CuMn$_2$O$_4$.

3. The catalyst system of claim 1, wherein the at least one platinum group metal catalyst is present at about 0.5 g/ft$^3$ to about 25.0 g/ft$^3$.

4. The catalyst system of claim 1, wherein the at least one platinum group metal catalyst is present at about 1.0 g/ft$^3$.

5. The catalyst system of claim 1, wherein the T$_{50}$ for CO is between about 235 °C to about 325 °C.

6. The catalyst system of claim 1, wherein the T$_{50}$ for HC is between about 235 °C to about 325 °C.

7. The catalyst system of claim 1, wherein the conversion of NO is about 34% at 390 °C.

8. The catalyst system of claim 1, wherein the conversion of NO is about 18% at 465 °C.
9. The catalyst system of claim 1, wherein the conversion of NO\textsubscript{x} is about 19% at 460 °C.

10. The catalyst system of claim 1, wherein the Cu-Mn is in spinel form.

11. The catalyst system of claim 1, wherein the niobium-zirconia support oxide comprises Nb\textsubscript{2}O\textsubscript{5}–ZrO\textsubscript{2}.

12. The catalyst system of claim 1, further comprising at least one impregnation layer.

13. The catalyst of claim 1, wherein the at least one substrate comprises a ceramic.

14. The catalyst of claim 1, wherein the at least one platinum group metal catalyst is prepared by co-milling.

15. The catalyst of claim 1, wherein the at least one platinum group metal catalyst is prepared by co-precipitation.
FIG. 1

Palladium/Alumina

Cu$_{1.0}$Mn$_{2.0}$O$_4$/Doped ZrO$_2$

Ceramic Substrate
FIG. 2
FIG. 3
FIG. 4
FIG. 5A

FIG. 5B

SUBSTITUTE SHEET (RULE 26)
A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - B01J 21/00 (2015.01)
CPC - C10G 35/0995; B01J 29/068; B01J 29/061
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
CPC - C10G 35/0995; B01J 29/068; B01J 29/061
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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
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PatBase, Google Scholar (NPL), Google Patents; search terms: platinum group metal catalyst system, syngas, substrate, washcoat, oxygen storage, Cu-Mn, niobium-zirconia support oxide, overcoat, palladium, rhodium, carrier material oxide, alumina, CuMn2O4, lightoff, NO, NOx, HC, CO, spinel, Nb2O5-ZrO2, impregnate, ceramic, milling, precipitate

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<tbody>
<tr>
<td>Y</td>
<td>US 2010/0233045 A1 (KIM et al.) 16 September 2010 (16.10.2010) para [0029], Fig. 11</td>
<td>7, 8, 9</td>
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