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(54) **ZPGM DIESEL OXIDATION CATALYSTS AND METHODS OF MAKING AND USING SAME**

(71) Applicant: **Clean Diesel Technologies, Inc.**, Oxnard, CA (US)

(72) Inventors: **Zahra Nazarpoor**, Camarillo, CA (US); **Stephen J. Golden**, Santa Barbara, CA (US)

(73) Assignee: **Clean Diesel Technologies, Inc. (CDTI)**, Oxnard, CA (US)

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(58) **Field of Classification Search**

None

See application file for complete search history.

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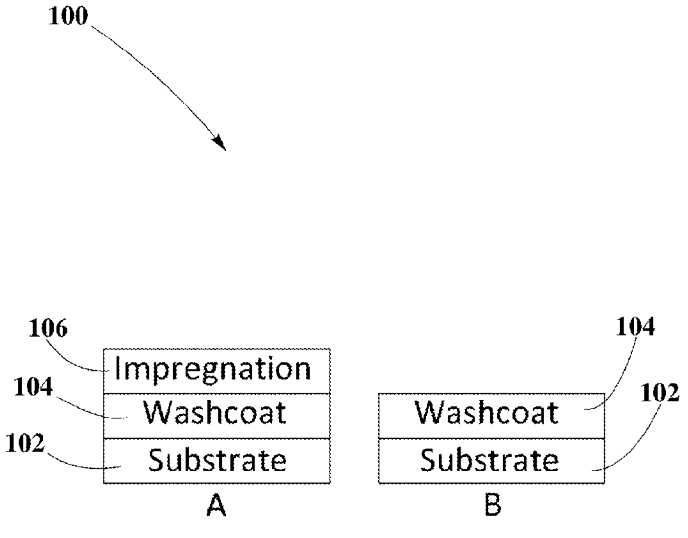
Primary Examiner — Walter D Griffin
Assistant Examiner — Jelitza Perez
(74) *Attorney, Agent, or Firm* — Alston & Bird LLP

(57) **ABSTRACT**

Diesel oxidation ZPGM catalyst systems are disclosed. ZPGM catalyst systems may oxidize toxic gases, such as carbon monoxide, hydrocarbons and nitrogen oxides that may be included in exhaust gases. ZPGM catalyst systems may include: a substrate, a washcoat, and an impregnation layer. The washcoat may include at least one carrier material oxides. The impregnation layer may include at least one ZPGM catalyst, carrier material oxides and OSMs. Suitable known in the art chemical techniques, deposition methods and treatment systems may be employed in order to form the disclosed ZPGM catalyst systems.

16 Claims, 8 Drawing Sheets



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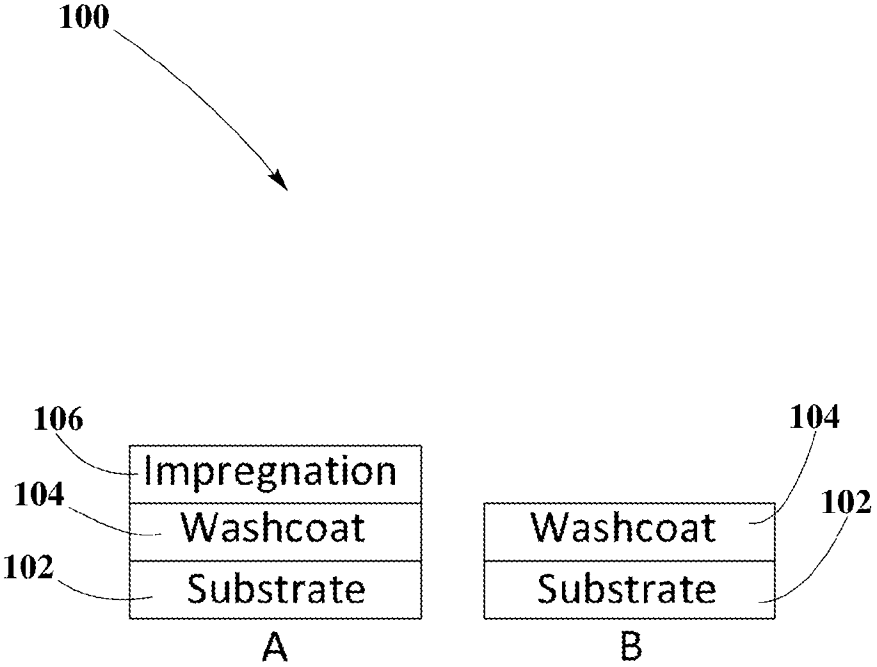
100
106
Impregnation
104
Washcoat
102
Substrate
A
104
Washcoat
102
Substrate
B

FIG. 1

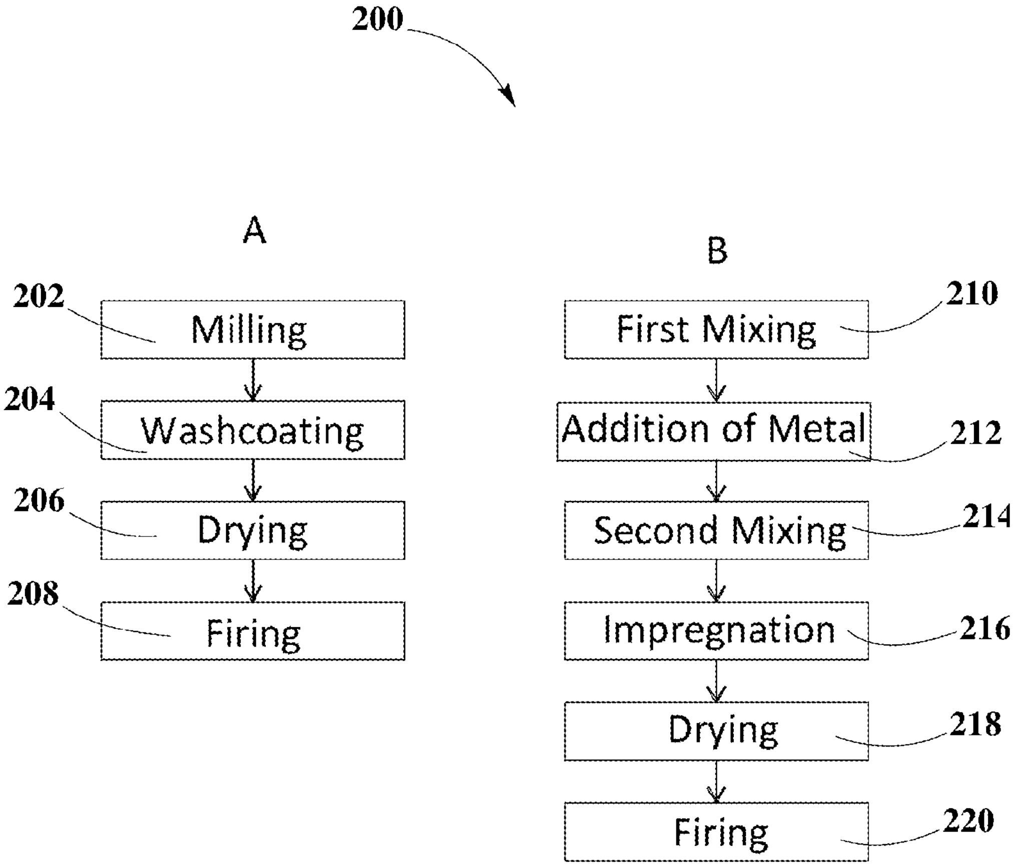
200
A
202
Milling
204
Washcoating
206
Drying
208
Firing
B
First Mixing
210
Addition of Metal
212
Second Mixing
214
Impregnation
216
Drying
218
Firing
220

FIG. 2

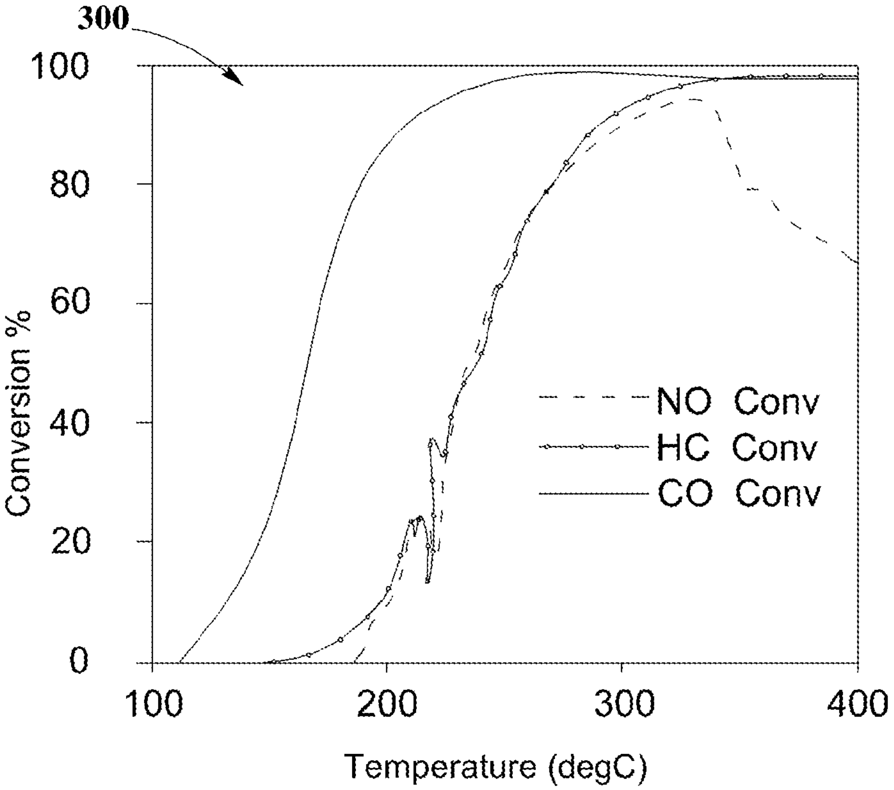
300
Conversion %
100
80
60
40
20
0
100
200
300
400
Temperature (degC)
NO Conv
HC Conv
CO Conv

FIG. 3

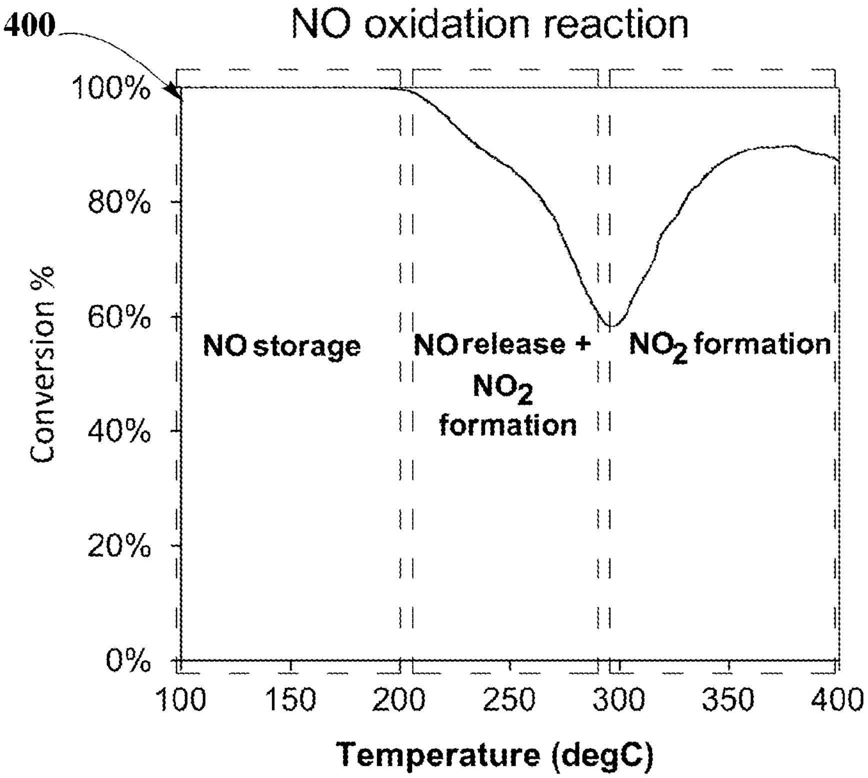
400
NO oxidation reaction
100%
80%
60%
40%
20%
0%
Conversion %
NO storage
NO release +
NO_2
formation
NO_2 formation
100
150
200
250
300
350
400
Temperature (degC)

FIG. 4

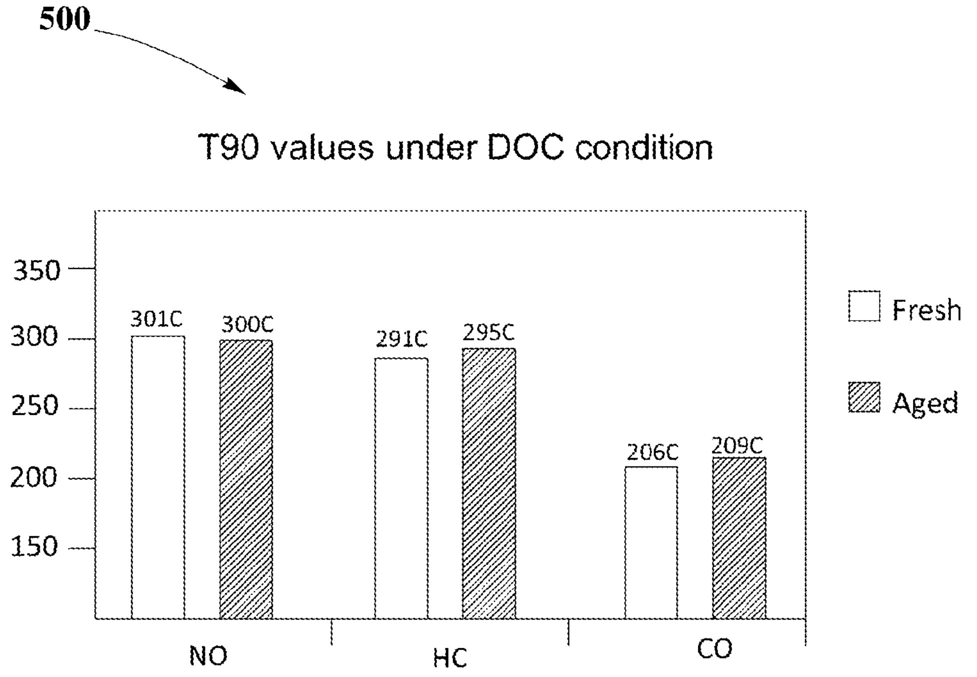
500
T90 values under DOC condition
350
300
250
200
150
301C
300C
291C
295C
206C
209C
NO
HC
CO
Fresh
Aged

FIG. 5

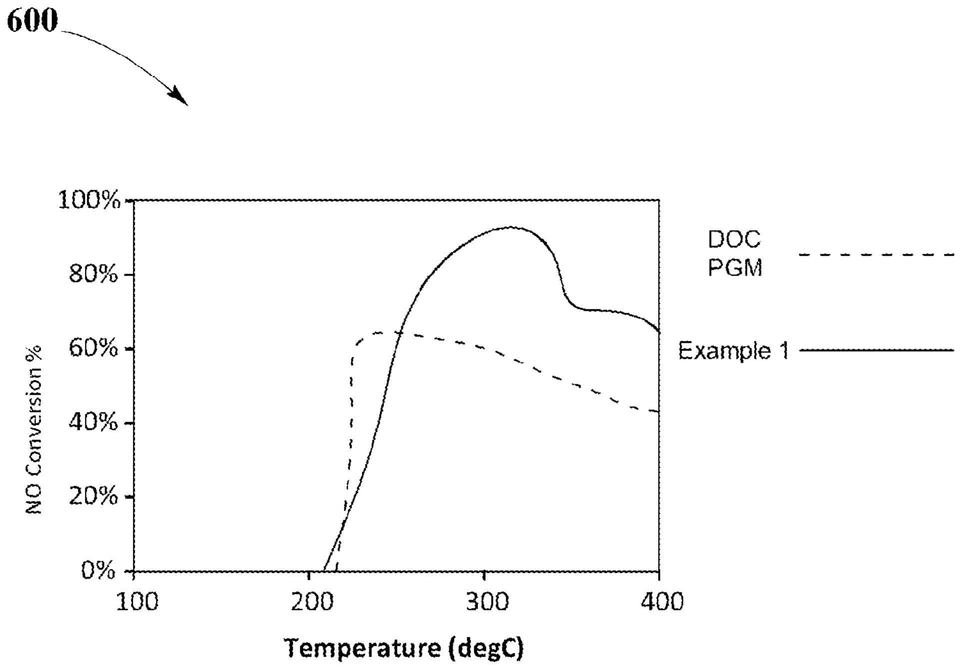
600
100%
80%
60%
40%
20%
0%
NO Conversion %
100
200
300
400
Temperature (degC)
DOC
PGM
Example 1

FIG. 6

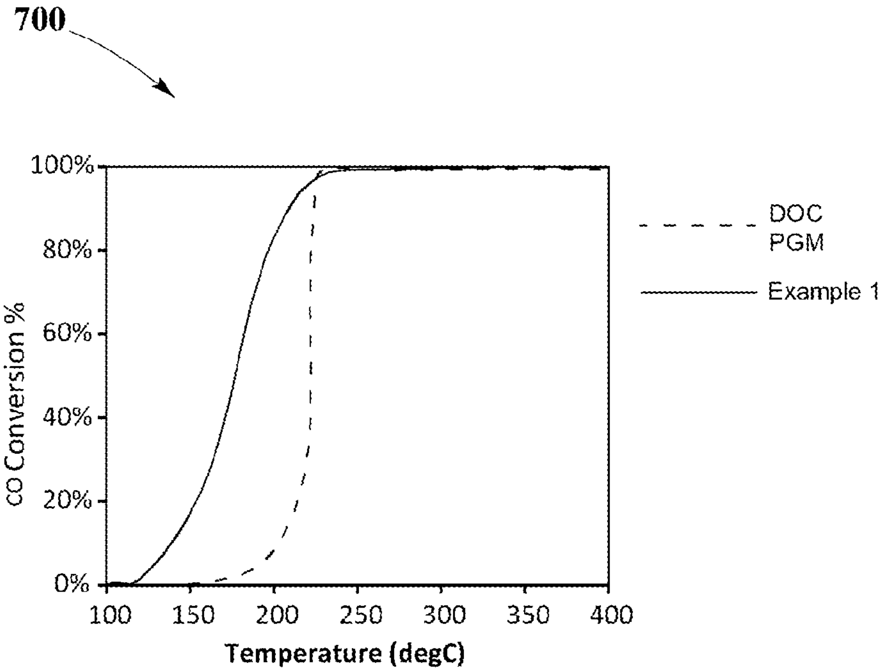
700
100%
80%
60%
40%
20%
0%
CO Conversion %
100
150
200
250
300
350
400
Temperature (degC)
DOC PGM
Example 1

FIG. 7

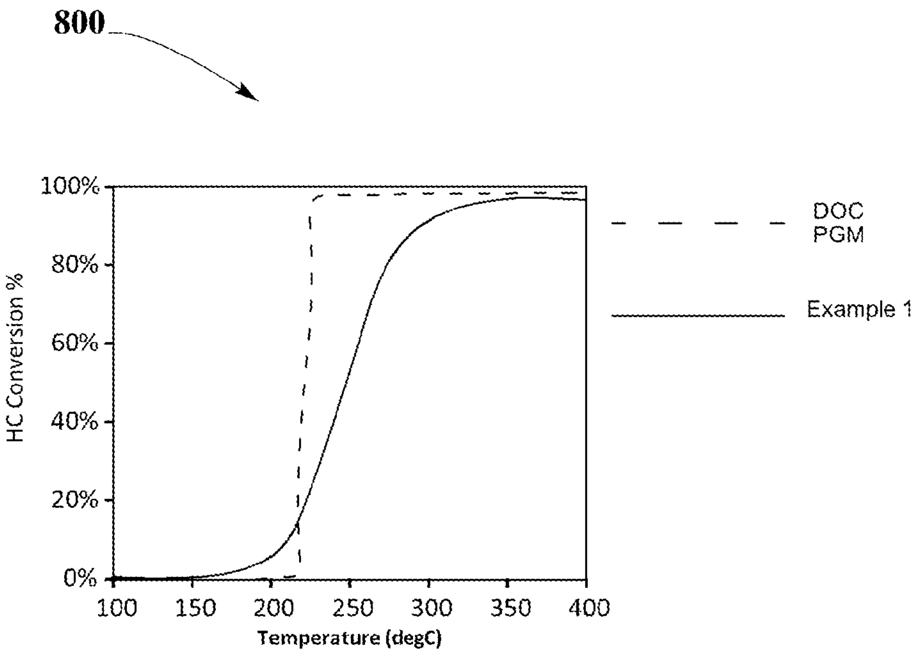
800
100%
80%
60%
40%
20%
0%
HC Conversion %
100
150
200
250
300
350
400
Temperature (degC)
DOC PGM
Example 1

FIG. 8

ZPGM DIESEL OXIDATION CATALYSTS AND METHODS OF MAKING AND USING SAME

CROSS-REFERENCE TO RELATED APPLICATIONS

N/A

BACKGROUND

Technical Field

The present disclosure relates generally to catalytic converters, more particularly, to zero platinum group metals Diesel Oxidation Catalysts.

Background Information

Emission standards for unburned contaminants, such as hydrocarbons, carbon monoxide and nitrogen oxide, continue to become more stringent. In order to meet such standards, Diesel Oxidation Catalysts (DOCs), lean NOx traps (LNTs) and Continuously Regenerating Traps (CRTs) are used in the exhaust gas lines of internal combustion engines. These catalysts promote the oxidation of unburned hydrocarbons and carbon monoxide as well as the oxidation of nitrogen oxides in the exhaust gas stream to reduce engine generated pollutants. Oxidation of NO to NO_2 may be used for the removal of carbon soot in CRTs. One of the major limitations of current catalysts is that the Platinum Group Metals (PGM) used in their fabrication have very high demand and increasing prices.

Therefore, there is a continuing need to provide cost effective catalyst systems that provide sufficient conversion so that HC, NOx, and CO emission standards can be satisfied, minimizing the amount of PGM catalysts required.

SUMMARY

Diesel Oxidation ZPGM catalyst systems are disclosed. ZPGM catalyst systems may oxidize toxic gases, such as carbon monoxide, hydrocarbons and nitrogen oxides that may be included in exhaust gases.

In one embodiment, the disclosed ZPGM catalyst systems may be used in DOCs, upstream of Diesel Particulate Filters (DPFs), to oxidize carbon monoxide, hydrocarbons and nitrogen oxides present in the exhaust stream of diesel engines.

In one embodiment, ZPGM catalyst systems may oxidize NO to NO_2 which may be used in Continuously Regenerating Traps (CRTs) for the oxidation of carbon soot.

The disclosed ZPGM catalyst systems may store NO at low temperatures, and may be included in Lean NOx Trap (LNT) systems.

ZPGM catalyst converters may include: a substrate, a washcoat, an overcoat and an impregnation layer. Washcoats and overcoats may include at least carrier metal oxides and may include ZPGM catalysts. Suitable known in the art chemical techniques, deposition methods and treatment systems may be employed in order to form the disclosed ZPGM catalyst converters.

Materials suitable for use as catalysts include Yttrium, (Y), Silver (Ag), Manganese (Mn) and combinations thereof. The disclosed ZPGM DOC systems may include perovskite structures with the characteristic formulation ABO_3 or related structures.

Suitable materials for use as substrates may include cordierite, metallic alloys, foams, microporous materials, zeolites or combinations.

Support materials of use in catalysts including one or more of the aforementioned combinations may also include ZrO_2, doped ZrO_2 with Lanthanum group metals, Nb_2O_5, Nb_2O_5—ZrO_2, alumina and doped alumina, TiO_2 and doped TiO_2 or mixtures thereof.

Suitable known in the art chemical techniques, deposition methods and treatment systems may be employed to form the disclosed ZPGM catalyst systems.

According to some embodiments, ZPGM catalyst systems may include substrate and washcoat and may be formed in one step processing. In this embodiment, washcoat includes carrier metal oxides and ZPGM catalysts with perovskite structure.

According to yet another embodiment, ZPGM catalyst systems may include washcoat and impregnation layers deposited over a substrate and may be formed in two steps processing. In this embodiment, the washcoat layer may include only metal oxide supports and the impregnation layer may include ZPGM catalyst with perovskite structure.

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

BRIEF DESCRIPTION OF THE DRAWINGS

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 prior art, the figures represent aspects of the present disclosure.

FIG. **1** shows ZPGM catalyst system structures, according to an embodiment.

FIG. **2** is a flowchart of a method of preparation of a ZPGM catalyst, according to an embodiment.

FIG. **3** shows light-off test results of a ZPGM catalyst system, according to an embodiment.

FIG. **4** shows the NO oxidation reaction of a ZPGM catalyst system, according to an embodiment.

FIG. **5** shows T50s and T90s of a ZPGM catalyst system, according to an embodiment.

FIG. **6** shows light-off test results of a ZPGM catalyst system, according to an embodiment.

FIG. **7** shows light-off test results of a ZPGM catalyst system, according to an embodiment.

FIG. **8** shows light-off test results of a ZPGM catalyst system, according to an embodiment.

DETAILED DESCRIPTION

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

As used here, the following terms have the following definitions:

"Exhaust" refers to the discharge of gases, vapor, and fumes including hydrocarbons, nitrogen oxide, and/or carbon monoxide.

"Impregnation" refers to the process of totally saturating a solid layer with a liquid compound.

"Wash-coat" refers to at least one coating including at least one oxide solid that may be deposited on a substrate.

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

"T50" refers to the temperature at which 50% of a material is converted.

"T90" refers to the temperature at which 90% of a material is converted.

"Oxidation Catalyst" refers to a catalyst suitable for use in oxidizing at least hydrocarbons and carbon monoxide.

"Zero Platinum Group (ZPGM) Catalyst" refers to a catalyst completely or substantially free of platinum group metals.

"Platinum Group Metals (PGMs)" refers to platinum, palladium, ruthenium, iridium, osmium, and rhodium.

Description

Various example embodiments of the present disclosure are described more fully with reference to the accompanying drawings in which some example embodiments of the present disclosure are shown. Illustrative embodiments of the present disclosure are disclosed herein. However, specific structural and functional details disclosed herein are merely representative for purposes of describing example embodiments of the present disclosure. This disclosure however, may be embodied in many alternate forms and should not be construed as limited to only the embodiments set forth herein.

System Configuration and Composition

FIG. **1** depicts ZPGM catalyst system **100** configurations, according to various embodiments. As shown in FIG. **1** A, ZPGM catalyst system **100** may include a substrate **102**, a washcoat **104**, and an impregnation layer **106**, where washcoat **104** or impregnation layer **106**, or both, may contain active oxidation ZPGM catalyst components. FIG. **1** B shows an embodiment of ZPGM catalyst system **100** that includes a substrate **102** and a washcoat **104**, where washcoat **104** includes active oxidation ZPGM catalyst components.

According to an embodiment, ZPGM catalyst system **100** may include a perovskite structure having the general formula ABO_3 or related structures resulting from the partial substitution of the A site. Partial substitution of the A site with M element will yield the general formula $A_{1-x}M_xBO_3$. "A" may include yttrium, lanthanum, strontium, or mixtures thereof. "B" may include a single transition metal, including manganese, cobalt, chromium, or mixture thereof. M may include silver, iron, Cerium, niobium or mixtures thereof; and "x" may take values between 0 and 1. The perovskite or related structure may be present in about 1% to about 30% by weight.

ZPGM catalyst systems **100** may also include carrier material oxides in washcoat. Suitable carrier material oxides may include ZrO_2, doped ZrO_2 with Lanthanide group metals, Nb_2O_5, Nb_2O_5—ZrO_2, alumina and doped alumina, TiO_2 and doped TiO_2 or mixtures thereof.

Methods of Preparation of Washcoat and Impregnation Layers

FIG. **2** illustrates method for preparation **200** of ZPGM catalyst system **100**, according to an embodiment.

In one embodiment, method for preparation **200** may be a two-step process. FIG. **2** A is a washcoat **104** preparation process. In this process, components of washcoat **104** may undergo a milling **202** process in which washcoat **104** materials may be broken down into smaller particle sizes; the mixture may include water, a suitable binder material and a carrier material oxide or OSM, or both. After milling **202** process, an aqueous slurry may be obtained. Milling **202** process may take from about 10 minutes to about 10 hours, depending on the batch size, kind of material and particle size desired. In one embodiment of the present disclosure, suitable average particle size (APSs) of the slurry may be of about 4 microns to about 10 microns, in order to get uniform distribution of washcoat **104** particles. Finer particles may have more coat ability and better adhesion to substrate **102** and enhanced cohesion between washcoat **104** and impregnation layers **106**. Milling **202** process may be achieved by employing any suitable mill such as vertical or horizontal mills. In order to measure exact particle size desired during milling **202** process, laser light diffraction equipment may be employed.

After milling **202** process the aqueous slurry may be coated onto a suitable substrate **102** in washcoating **204** step. In this step, the aqueous slurry may be placed on substrate **102** in any suitable manner. For example, substrate **102** may be dipped into the slurry, or the slurry may be sprayed on substrate **102**. Other methods of depositing the slurry onto substrate **102** known to those skilled in the art may be used in alternative embodiments. If substrate **102** is a monolithic carrier with parallel flow passages, a washcoat **104** may be formed on the walls of the passages. Followed by a drying **206** step, in which the washcoated substrate **102** may be dried at room temperature. Afterwards, the washcoated substrate **102** may undergo a firing **208** stage, in which the washcoated substrate **102** may be fired at a temperature ranging from 400° C. to 700° C., for approximately 2 hours to 6 hours. In an embodiment, 550° C. for 4 hours.

FIG. **2** B is a flowchart of impregnation layer **106** preparation method. The process may start with first mixing **210** step, where an yttrium nitrate solution may be added to a manganese nitrate solution and the solutions may be mixed for a suitable amount of time at room temperature. In some embodiments first mixing **210** process may last from 1 hour to 5 hours. Afterwards, during addition of metal **212** step, a silver nitrate solution or other suitable metal solutions may be added to the mixture of yttrium nitrate and manganese nitrate; then the solution may be mixed at room temperature for about 1 hour to 5 hours, during second mixing **214**. When the mixture is ready, it may undergo impregnation **216** process, where the mixture may be impregnated onto a previously washcoated substrate **102**. Subsequently, impregnated substrate **102** may be subjected to a drying **218** process and a firing **220** process. Firing **220** process may last between 3 hours and 6 hours, and may be performed and a temperature between 600° C. and 800. According to some embodiments, 4 hours for about 750° C.

Various amounts of washcoats **104** and impregnation layers **106** may be coupled with a substrate **102**, preferably an amount that covers most of, or all of, the surface area of a substrate **102**. In an embodiment, about 60 g/L to about 250 g/L of a washcoat **104** may be coupled with a substrate **102**.

Other components such as acid or base solutions or various salts or organic compounds may be added to the aqueous slurry to adjust the rheology of the slurry and enhance binding of the washcoat **104** and impregnation layer **106** to the substrate **102**.

EXAMPLES

In example 1, a ZPGM catalyst system **100** including a ZPGM perovskite catalyst having a cordierite substrate **102**, a washcoat **104** and an impregnation layer **106** is prepared. Where washcoat **104** includes at least a carrier material oxide, such as zirconia, but free of OSM material. The washcoat **102** may include a binder or small amount rheology adjustment additives. Rheology adjustment additives may include acids, among other suitable substances. The loading may be about 80 g/L to about 180 g/L, preferably 120 g/L. The impregnation layer **106** includes at least yttrium, silver and manganese. This catalyst system is free of any oxygen storage material. The yttrium in impregnation layer **106** is present in about 1% to about 10%, by weight. The silver in impregnation layer **106** is present in about 1% to about 10%, by weight. The manganese in impregnation layer **106** is present in about 1% to about 10%, by weight. To prepare the ZPGM catalyst system **100** of example 1, carrier material oxide (zirconia) is milled. The milled slurry is deposited on the cordierite substrate **102** in the form of a washcoat **104** and then heat treated. This treatment may be performed at about 400° C. to about 700° C. In some embodiments this treatment may be performed at about 550° C. The heat treatment may last from about 2 to about 6 hours. In an embodiment the treatment may last about 4 hour. Then the impregnation **216** components may be mixed together following the process described in FIG. **2** B. After impregnation **216** the ZPGM catalyst system **100** may be dried and heat treated. This treatment may be performed at about 400° C. to about 800° C. In some embodiments this treatment may be performed at about 750° C. The heat treatment may last from about 2 to about 6 hours. In an embodiment the treatment may last about 4 hour. The resulting ZPGM catalyst system **100** has a perovskite structure $Y_{1-x}Ag_xMnO_3$.

FIG. **3** shows the light-off test results **300** for the ZPGM catalyst system **100** of example 1 for fresh sample. The light-off test is performed under simulated DOC condition. Feed stream includes of 150 ppm NO, 1500 ppm of CO, 430 ppm of C_3H_6 as hydrocarbon, 4% CO_2, 4% of H_2O and 14% of oxygen. The test is performed by increasing the temperature from about 100° C. to 400° C. at a constant rate of 20° C./min. The light-off test results **300** show that the ZPGM catalyst system **100** of example 1 has very high NOx conversion and hydrocarbons conversion. The T50 for CO of 166° C., a T50 for HC of 237° C. and a T50 for NO of 235° C. are obtained.

FIG. **4** shows the NO oxidation reaction **400** of the ZPGM catalyst system **100** of example 1. The feed stream includes 150 ppm of NO and 14% of oxygen. The ZPGM catalyst system **100** of example 1 shows 100% conversion of NO at very beginning of NO oxidation reaction **400**, this behavior is related to the adsorption of NO by the ZPGM catalyst system **100** of example 1 at temperatures below 200° C. The ZPGM catalyst system **100** of example 1 may function as a NOx trap, storing NO present in the exhaust stream at temperatures as low as 100° C. As shown in FIG. **4**, between 200° C. and approximately 300° C., the NO conversion of the ZPGM catalyst system **100** of example 1 may decrease, this may be caused by the releasing the stored NO. However, NO_2 production may also start within this temperature range, characterize by a large desorption (release) of NO. At temperatures higher than about 300° C., the increasing the conversion of NO in the ZPGM catalyst system **100** of example 1 may be caused by the oxidization of the NO present in the exhaust stream and the formation of NO_2.

FIG. **5** shows bar graph **500**, which compares the T90s for conversion of HC, NO and CO of fresh and aged samples of the ZPGM catalyst systems **100** of example 1, under simulated DOC condition. The gas in the feed stream includes 150 ppm of NO, 1500 ppm of CO, 430 ppm of C3H6 as hydrocarbon, 4% of CO_2, 4% of H_2O and 14% of oxygen. The tests are performed by increasing the temperature from about 100° C. to about 400° C. at a constant rate of 20° C./min. The aged samples were hydrothermally aged at 750° C. during 5 hours with 10% steam present. As shown in bar graph **500** there is no significant difference between the behavior of fresh and aged samples, which shows that the ZPGM catalyst systems **100** of example 1 are highly stable under aging conditions.

FIG. **6** shows light-off test results **600**. FIG. **6** compares the NO conversion of a reference platinum group metal (PGM) catalyst and the ZPGM catalyst system **100** of example 1 under simulated DOC conditions. The gas in the feed stream includes 150 ppm of NO, 1500 ppm of CO, 430 ppm of C_3H_6 as hydrocarbon, 4% of CO_2, 4% of H_2O and 14% of oxygen. The test is performed by increasing the temperature from about 100° C. to 400° C. at a constant rate of 20° C./min. Both catalysts are hydrothermally aged at 750° C. for 5 hours with 10% steam present. The PGM catalyst used as reference contains Pt (about 18 g/ft^3) and Pd (about 1 g/ft^3). As shown in FIG. **6**, the ZPGM catalyst system **100** of example 1 is capable of oxidizing higher percentages of the NO present in an exhaust stream. The NO conversion is related to the oxidation of NO to NO_2. Reference PGM catalyst, after aging, shows a T50 for NO of 228° C., while T90 for NO is not available. ZPGM catalyst system **100** of example 1, after aging, shows a T50 for NO of 247° C. and T90 for NO of 303° C. The oxidation of NO to NO_2 is important in diesel emission control systems in which NO_2 may be used in CRTs for oxidation of carbon soot.

FIG. **7** shows light-off test results **700**. FIG. **7** compares the CO conversion of a reference platinum group metal (PGM) catalyst and the ZPGM catalyst system **100** of example 1 under simulated DOC conditions. Gas in the feed stream includes 150 ppm of NO, 1500 ppm of CO, 430 ppm of C_3H_6 as hydrocarbon, 4% of CO_2, 4% of H_2O and 14% of oxygen. The test is performed by increasing the temperature from about 100° C. to 400° C. at a constant rate of 20° C./min. Both catalysts are hydrothermally aged at 750° C. for 5 hours with 10% steam present. The PGM catalyst used as reference includes Pt (18 g/ft^3) and Pd (1 g/ft^3). As shown in FIG. **7**, the ZPGM catalyst system **100** of example 1 is capable of oxidizing higher percentages of CO present in an exhaust stream at lower temperatures than the reference PGM catalyst system. Reference PGM catalyst, after aging, shows a T50 and T90 for CO of 219° C. and 223° C., respectively. ZPGM catalyst system **100** of example 1, after aging, shows a T50 and T90 for CO of 178° C. and 209° C., respectively.

FIG. **8** shows light-off test results **800**. FIG. **8** compares the HC conversion of a reference PGM catalyst and the ZPGM catalyst system **100** of example 1, under simulated DOC condition. Gas in the feed stream includes 150 ppm of NO, 1500 ppm of CO, 430 ppm of C_3H_6 as hydrocarbon, 4% of CO_2, 4% of H_2O and 14% of oxygen. The test is performed by increasing the temperature from about 100° C. to about 400° C. at a constant rate of 20° C./min. Both catalysts are hydrothermally aged at 750° C. for 5 hours with 10% steam present. The PGM catalyst is used as reference includes Pt (about 18 g/ft^3) and Pd (about 1 g/ft^3). The reference PGM catalyst, after aging, shows a T50 and T90 for HC of 220° C. and 224° C., respectively. ZPGM catalyst system **100** of example 1, after aging, shows a T50 and T90 for HC of 248° C. and 295° C., respectively.

In example 2, a ZPGM catalyst system **100** including a ZPGM perovskite catalyst having a cordierite substrate **102**, a washcoat **104** and an impregnation layer **106** is prepared. Where washcoat **104** includes at least carrier material oxide such as zirconia. The ZPGM catalyst system **100** of example 2 is free OSM material. The washcoat may include binder or small amount of acid for rheology adjustment. The loading is about 80 g/L to 180 g/L, preferably 120 g/L. The impregnation layer **106** includes at least yttrium and manganese. The yttrium in impregnation layer **106** is present in about 1% to about 10%, by weight and the manganese in impregnation layer **106** is present in about 1% to about 10%, by weight. To prepare the ZPGM catalyst system **100** of example 2, the carrier material oxide (zirconia) is milled. The milled slurry is deposited on the cordierite substrate **102** in the form of a washcoat **104** and then heat treated. This treatment may be performed at about 400° C. to about 700° C. In some embodiments this treatment may be performed at about 550° C. The heat treatment may last from about 2 to about 6 hours. In an embodiment the treatment may last about 4 hour. Then the impregnation components may be mixed together following the process described in FIG. **2** B. After impregnation **216** the ZPGM catalyst system **100** may be dried and heat treated. This treatment may be performed at about 400° C. to about 800° C. In some embodiments this treatment may be performed at about 750° C. The heat treatment may last from about 2 to about 6 hours. In an embodiment the treatment may last about 4 hour. The resulting ZPGM catalyst system **100** has a perovskite structure $YMnO_3$. The behavior of the ZPGM catalyst system **100** of example 2 may be similar to the behavior of the ZPGM catalyst system **100** of example 1.

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

We claim:

1. A zero platinum group metal (ZPGM) catalyst system, comprising:

a substrate; and

a washcoat suitable for deposition on the substrate, comprising at least one carrier metal oxide, and at least one ZPGM catalyst; and

wherein at least one of the ZPGM catalyst comprises at least one perovskite structured compound having the formula ABO_3, wherein each of A and B is selected from the group consisting of at least one of yttrium, silver, manganese, and combinations thereof;

wherein yttrium is present in about 1% to about 5% by weight of the at least one ZPGM catalyst, silver is present in about 1% to about 5% by weight of the at least one ZPGM catalyst, and wherein manganese is present in about 1% to about 5% by weight of the at least one ZPGM catalyst.

2. The ZPGM catalyst system of claim **1**, further comprising at least one impregnation layer, wherein the impregnation layer includes at least one ZPGM catalyst.

3. The ZPGM catalyst system of claim **2**, wherein yttrium is present in about 1% to about 10% by weight of the at least one ZPGM catalyst in the at least one impregnation layer.

4. The ZPGM catalyst system of claim **2**, wherein silver is present in about 1% to about 10% by weight of the at least one ZPGM catalyst in the at least one impregnation layer.

5. The ZPGM catalyst system of claim **2**, wherein manganese manganese is present in about 1% to about 10% by weight of the at least one ZPGM catalyst in the at least one impregnation layer.

6. The ZPGM catalyst system of claim **1**, wherein the substrate is selected from the group consisting of cordierite, metallic alloys, foams, microporous materials, zeolites, and combinations thereof.

7. The ZPGM catalyst system of claim **1**, wherein the ZPGM catalyst comprises at least one perovskite structured compound having the formula $Y_{1-x}Ag_xMnO_3$ or $YMnO_3$, wherein x is from 0 to 1.

8. The ZPGM catalyst system of claim **1**, wherein the at least one perovskite structured compound comprises about 1% to about 30% of the at least one of the ZPGM catalyst by weight.

9. The ZPGM catalyst system of claim **1**, wherein the at least one oxide solid is selected from the group consisting of ZrO_2, doped ZrO_2 with lanthanide group metals, Nb_2O_5, Nb_2O_5—ZrO_2, alumina and doped alumina, TiO_2 and doped TiO_2.

10. The ZPGM catalyst system of claim **1**, wherein the at least one catalyst oxidizes one selected from the group consisting of CO, hydrocarbons, nitrogen oxides, and combinations thereof.

11. An apparatus for reducing emissions from an engine having associated therewith an exhaust system, comprising:

a substrate;

a washcoat suitable for deposition on the substrate, comprising at least one oxide solid further comprising at least one carrier metal oxide; and

at least one impregnation layer, wherein the impregnation layer includes at least one ZPGM catalyst;

wherein the at least one ZPGM catalyst comprises at least one perovskite structured compound having the formula ABO_3, wherein each of A and B is selected from the group consisting at least one of yttrium, silver, manganese, and combinations thereof;

wherein yttrium is present in about 1% to about 5% by weight of the at least one ZPGM catalyst, silver is present in about 1% to about 5% by weight of the at least one ZPGM catalyst, and wherein manganese is present in about 1% to about 5% by weight of the at least one ZPGM catalyst.

12. The apparatus of claim **11**, wherein the washcoat and at least one impregnation layer are applied in two different application steps.

13. The apparatus of claim **12**, further comprising at least one continuously regenerating trap associated with the exhaust system wherein NO or NO_2 is oxidized and at least partially removes carbon soot from the exhaust system.

14. The apparatus of claim **13**, wherein the at least one continuously regenerating trap comprises zeolite.

15. The apparatus of claim **12**, further comprising at least one lean NOx trap associated with the exhaust system.

16. A zero platinum group metal (ZPGM) catalyst system, comprising:

a substrate;

an overcoat suitable for deposition on the substrate, comprising at least one overcoat oxide solid selected from the group consisting at least one of a carrier metal oxide, and a ZPGM catalyst; and

a washcoat suitable for deposition on the substrate, comprising at least one oxide solid selected from the group consisting of at least one carrier metal oxide, and at least one ZPGM catalyst; and

wherein at least one of the ZPGM catalyst comprises at least one perovskite structured compound having the formula ABO_3, wherein each of A and B is selected from the group consisting at least one of yttrium, silver, manganese, and combinations thereof;

wherein at least one of the washcoat and overcoat comprises a carrier metal oxide and the at least one ZPGM catalyst, and wherein the yttrium is present in about 1% to about 5% by weight of the at least one ZPGM catalyst, silver is present in about 1% to about 5% by weight of the at least one ZPGM catalyst, and wherein manganese is present in about 1% to about 5% by weight of the at least one ZPGM catalyst.

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