TREATMENT SYSTEMS AND METHODS FOR INTERNAL COMBUSTION ENGINE EXHAUST STREAMS

Inventor: Sanath V. Kumar, North Brunswick, NJ (US)

Publication Classification

Int. Cl.
F01N 3/20 (2006.01)
F01N 3/10 (2006.01)

U.S. Cl. 60/299, 422/222, 60/274

ABSTRACT

Emissions treatment systems and methods are disclosed, which reduce the carbon monoxide, unburned hydrocarbons, and nitrogen oxides content in the exhaust stream of an internal combustion engine adjusted to a rich combustion ratio. One embodiment of a system comprises an ammonia oxidation catalyst, a supplemental air supply for providing a lean combustion ratio, and at least one three-way catalyst. Another embodiment further comprises a second three-way catalyst located in the exhaust stream.
FIG. 1B

FIG. 1C
TREATMENT SYSTEMS AND METHODS FOR INTERNAL COMBUSTION ENGINE EXHAUST STREAMS

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims priority to U.S. Provisional Application No. 60/826,487, filed Sep. 21, 2006, which is hereby incorporated by reference in its entirety.

FIELD OF INVENTION

[0002] Embodiments of the present invention are generally related to processes and systems for reduction of atmospheric pollutants present in internal combustion engine exhaust streams. More particularly, embodiments of the present invention are directed to methods of undesirable complex engine management systems.

BACKGROUND

[0003] Internal combustion engines have evolved into the backbone of the world’s individual transportation system. In most highly developed countries, this individual transportation system is dominated by automobiles having digital processor-based engine control systems that continually adjust combustion parameters such as fuel supply, intake air temperature, spark timing and duration, and the like. These complex systems minimize output of potential atmospheric pollutants such as carbon monoxide, unburned hydrocarbons and oxides of nitrogen. The pollutant content of the exhaust stream is further reduced by exhaust gas recirculation, secondary air injection, and catalysts in the exhaust system. Even a simple example of one of these engine management systems including microprocessor controllers, sensors, catalysts and the like can easily add hundreds of dollars to the cost of the automobile.

[0004] In developing countries, individual transportation is making a transition from bicycles to internal combustion engine-powered scooters, motorcycles, and small cars. The small displacement two-stroke or four-stroke engines powering these transports are necessarily simple and low-cost, and as a result do not have complex engine management systems. These engines are typically open-loop-carbureted or fuel-injected. Additionally, the small inexpensive vehicles often do not receive much maintenance. In many of these developing countries, atmospheric pollution has become a problem. These small displacement engines are substantial sources of the pollution.

[0005] Internal combustion engines used in automobiles typically include relatively complex engine management systems for reducing pollutants from an engine exhaust stream. Representative early work on complex engine emission management systems is described in U.S. Pat. No. 3,943,709. This patent discloses an exhaust treatment system that includes an air duct with a choke valve, means for controlling the choke valve, a first stage catalytic converter, a secondary air supply, an air pump, means for controlling the secondary air supply and a secondary catalytic converter. More recently, U.S. Pat. No. 6,634,169 discloses a catalyst system that includes a programmable engine management system, a plurality of sensors communicative with the engine management system, a secondary air supply system communicative with the engine management system, a fuel injection system and at least two catalytic converters. Both of these patents suggest a complex and costly addition to the vehicle’s basic cost.

[0006] In simple low displacement engines such as those used in scooters, motorcycles and simple, small cars, the addition of a complex engine management system could easily raise the cost of such vehicles to the point where they would not be accessible to those desiring them. Such engines can be adjusted to maintain a “rich”, i.e., from about 8 to about 14.7 parts air to 1 part fuel, combustion ratio. An approach for reducing emissions in a scooter or motorcycle is disclosed in U.S. Patent Application Pub. No. 2006/0101813, which discloses a muffler device divided into three chambers by partition boards, the muffler device includes a front reduction catalyst within a front exhaust pipe, a rear exhaust pipe with a secondary air inlet behind the reduction catalyst for introducing secondary air into the exhaust stream so as to raise the combustion ratio above the stoichiometric ratio to greater than 14.7 (lean) before passing the exhaust stream into an oxidation catalyst. However, this combination may result in ammonia being produced in the reducing catalyst and subsequently being oxidized to NO₃ in the oxidation catalyst, resulting in a net increase in NO₂ emissions.

[0007] There is a need to provide simple and effective systems for reducing potential pollutants in the exhaust of low cost vehicles that do not possess sensors and digital controls. In addition, there is a continuing need to provide improved systems and methods for the treatment of exhaust gas streams from internal combustion engines.

SUMMARY

[0008] In an embodiment of the invention, an emissions treatment system for engines that do not possess complex engine management systems is provided. According to one or more embodiments, an emissions treatment system for reducing the carbon monoxide, unburned hydrocarbons, and nitrogen oxides content in the exhaust gas stream of an internal combustion engine adjusted to a rich stoichiometric ratio includes at least one three-way catalyst, a supplemental air supply, and an ammonia oxidation catalyst. The supplemental air source supplies supplemental air upstream of the ammonia oxidation catalyst. A first three-way catalyst is located to receive and pass the exhaust gas from the engine through the first three-way catalyst.

[0009] In one embodiment, the first three-way catalyst is located downstream of the supplemental air source. In another embodiment, the first three-way catalyst is located downstream from the ammonia oxidation catalyst, and the supplemental air source is upstream of the ammonia oxidation catalyst. In a further embodiment, a second three-way catalyst is located downstream from the ammonia oxidation catalyst.

[0010] In an embodiment, the first three-way catalyst comprises a precious metal component and a rare earth oxide deposited on a substrate. In one or more embodiments, the first three-way catalyst comprises a precious metal component selected from the group consisting of palladium, platinum, rhodium, and combinations thereof; and a rare earth oxide selected from the group consisting of ceria, zirconia, lanthana, praseodynia, neodymia, and combinations thereof. A detailed embodiment provides a two-layered three-way catalyst deposited on a substrate, wherein a first catalytic layer comprises a platinum component in an
amount in the range of about 12.5 to about 100 g/ft³, an alumina support in an amount in the range of about 0.2 to about 2.0 g/in³, a ceria-zirconia composite in an amount in the range of about 0.2 to about 1.0 g/in³, a zirconia component in an amount in the range of about 0.03 to about 0.15 g/in³, and a barium component in an amount in the range of about 0.03 to about 0.15 g/in³. A second layer deposited on the first layer comprises a rhodium component in an amount in the range of about 12.5 to about 100 g/ft³; an alumina support in an amount in the range of about 0.2 to about 2.0 g/in³; a ceria-zirconia composite in an amount in the range of about 0.2 to about 1.0 g/in³; and a zirconia component in an amount in the range of about 0.03 to about 0.15 g/in³.

[0011] In one or more embodiments, the ammonia oxidation catalyst comprises a precious metal component; a zeolite component containing a base metal oxide selected from the group consisting of oxides of chromium, manganese, iron, cobalt, nickel, copper, vanadium, titanium, zinc, and combinations thereof; and a silica component deposited on a substrate. A detailed embodiment provides that the ammonia oxidation catalyst comprises a layer deposited on a substrate, comprising a platinum component in an amount in the range of about 1 to about 25 g/ft³, a zeolite component in an amount in the range of about 0.5 to about 2.5 g/ft³, wherein the zeolite component contains iron, and a silica component in an amount in the range of about 0.1 to about 0.5 g/ft³. In another detailed embodiment, the zeolite component further comprises a copper-oxide copper-nitrate composite in an amount in the range of about 0.1 to about 0.5 g/ft³, and a silica component in an amount in the range of about 0.1 to about 1.5 g/ft³.

[0012] In one or more embodiments, the second three-way catalyst comprises a precious metal component and a rare earth oxide deposited on a substrate. In a detailed embodiment, the second three-way catalyst comprises a precious metal component selected from the group consisting of platinum, palladium, rhodium, and combinations thereof; and a rare earth oxide selected from the group consisting of ceria, lanthana, praseodymia, neodymia, and combinations thereof.

[0013] One embodiment provides that a monolithic substrate comprises a first discrete portion including a coating of the ammonia oxidation catalyst, and a second discrete portion including a coating of the second three-way catalyst. A detailed embodiment provides that the monolithic substrate is selected from the group consisting of a ceramic material with a multiplicity of passageways therethrough, a metallic material being in the form of an expanded matrix, and a metallic material being in the form of a flat or corrugated metal foil configured in a multiplicity of layers.

[0014] In certain embodiments, the ammonia oxidation catalyst is effective to selectively oxidize at least about 99% of ammonia formed in the first three-way catalyst to nitrogen and water, and to selectively reduce the nitrogen oxides to nitrogen; and the first three-way catalyst is effective to selectively oxidize at least about 99% of the unburned hydrocarbon to carbon dioxide and water, oxidize at least about 99% of the carbon monoxide to carbon dioxide.

[0015] Another aspect provides methods for reducing carbon monoxide, unburned hydrocarbons, and nitrogen oxides in an exhaust stream of an internal combustion engine. The methods comprise providing the internal combustion engine adjusted to a rich combustion ratio; passing the exhaust stream through a first three-way catalyst; adding sufficient air to the exhaust stream, upstream of an ammonia oxidation catalyst, to provide a lean combustion ratio; and passing the exhaust stream through the ammonia oxidation catalyst.

[0016] In one embodiment, passing the exhaust stream through the ammonia oxidation catalyst occurs after passing the exhaust stream through the first three-way catalyst. The method can further comprise passing the exhaust stream exiting the ammonia oxidation catalyst through a second three-way catalyst.

[0017] In a detailed embodiment, the method further comprises providing a sufficient amount of the first three-way catalyst to oxidize at least about 50% of the carbon monoxide to carbon dioxide, and to oxidize at least about 50% of the unburned hydrocarbons to carbon dioxide and water, and providing an ammonia oxidation catalyst to oxidize at least about 99% of ammonia formed in the first three-way catalyst selectively to nitrogen and water.

[0018] In another detailed embodiment, the method further comprises providing a sufficient amount of the first three-way catalyst to oxidize at least about 99% of the unburned hydrocarbons entering the second three-way catalyst to carbon dioxide and water, and about 99% of the carbon monoxide entering the second three-way catalyst to carbon dioxide.

[0019] Other aspects include providing exhaust systems having an exhaust conduit, a first three-way catalyst deposited on a metallic foil substrate; an air source having an inlet to the exhaust downstream from the first three-way catalyst for introducing sufficient air into the exhaust stream to provide a lean combustion ratio; an ammonia oxidation catalyst downstream from the air source deposited on a metallic foil substrate; and a second three-way catalyst downstream from the ammonia oxidation catalyst deposited on a metallic foil substrate.

[0020] In one or more embodiments, the three-way catalysts are three-layered, having an undercoat layer below the first layer. Other embodiments provide that one or more of the first three-way catalyst, the second three-way catalyst, the air inlet, and the ammonia oxidation catalyst are contained in a housing comprising a muffler.

BRIEF DESCRIPTION OF THE DRAWINGS

[0021] FIG. 1A is a schematic representation of an embodiment of exhaust system;
[0022] FIG. 1B is a block diagram of an embodiment of an exhaust treatment system;
[0023] FIG. 1C is a block diagram of another embodiment of an exhaust treatment system;
[0024] FIGS. 2A, 2B, 2C and 2D are schematic representations of several embodiments of substrates useful in exhaust systems;
[0025] FIG. 3 is a cut-away schematic representation of a catalyst useful in an embodiment of the invention;
[0026] FIG. 4 is a graphical representation of concentrations of a model exhaust stream passing through an exhaust treatment system without an ammonia oxidation catalyst; and
[0027] FIG. 5 is a graphical representation of concentrations of a model exhaust stream, substantially identical to
that represented in FIG. 3 passing through a specific embodiment of the exhaust treatment system of the invention.

DETAILED DESCRIPTION

[0028] Before describing several exemplary embodiments of the invention, it is to be understood that the invention is not limited to the details of construction or process steps set forth in the following description. The invention is capable of other embodiments and of being practiced or being carried out in various ways.

[0029] Embodiments of the exhaust system and method of the present invention are particularly well-suited for open loop low displacement engines that do not have sophisticated engine management systems. In a simple low displacement engine, the addition of a complex engine management system could easily raise the cost of a simple low-cost vehicle using the engine to the point where it would not be accessible to those desiring such a vehicle. Such an engine can be adjusted to maintain a “rich” combustion ratio. Such systems and methods are disclosed hereinbelow.

[0030] In this disclosure, the term NOx is used. The term refers to oxides of nitrogen, primarily NO and NO2, but also refers to other nitrogen oxides which may be formed as combustion products of internal combustion engines fueled by hydrocarbon fuels.

[0031] Reference is also made to internal combustion engines being adjusted to a “rich combustion ratio” in this disclosure. In this disclosure, the term “rich” is intended to include a combustion ratio that is less than 14.7 parts of air to one part of fuel to about 8 parts of air to about one part of fuel. Such a “rich” mixture generally includes the normal hydrocarbon combustion products of carbon dioxide and water as well as unburned hydrocarbons, carbon monoxide and various oxides of nitrogen. Generally, this stoichiometric, or ideal combustion ratio of 14.7 applies to hydrocarbon fuels referred to in the United States as “gasoline”. Other fuels, such as two-cycle blends including lubricants and the like, may have a stoichiometric ratio different than 14.7. Fuels that are oxygenated, i.e., that have oxygen containing components generally will have a stoichiometric ratio of less than 14.7. For particular applications, a stoichiometric ratio may differ and is considered to be within the scope of this disclosure. Thus, the term rich as used herein should not be limited to a particular type of fuel or stoichiometric ratio.

[0032] Referring to FIG. 1A, an embodiment of the exhaust system 10 of the present invention is provided that is useful for reducing the carbon monoxide, unburned hydrocarbons, and nitrogen oxides content in the exhaust stream of an internal combustion engine 12 adjusted to a rich combustion ratio and, optionally, the sound produced by the engine. Exhaust system 10 includes an exhaust manifold or conduit 14 that is situated to receive substantially all the exhaust gas from engine 12.

[0033] System 10 has a first three-way catalyst 16 located to receive and pass the exhaust gas from engine 12 there-through. According to one or more embodiments, the first three-way catalyst 16 generally includes sufficient amounts of a precious metal component, one or more base metal oxides, and a rare earth oxide deposited on a surface 17A of a substrate 18 to oxidize at least about 50% of the unburned hydrocarbon to CO2 and H2O, oxidize at least about 50% of the carbon monoxide to CO2, and reduce about 90% of the nitrogen oxides to NH3, N2 and H2O. The precious metal components can include platinum, palladium, rhodium, ruthenium, and iridium. The base metal oxides include, but are not limited to, base metal oxides such as oxides of chromium, manganese, iron, cobalt, nickel, barium, copper, vanadium, titanium and zinc. The rare earth oxides may include cerium, lanthanum, neodymium, praseodymium, etc., and combinations thereof. Suitable supports include activated compounds selected from the group consisting of alumina, silica, silica-alumina, alumino-silicates, alumina-zirconia, alumina-chromia, and alumina-ceria. Useful three-way catalysts are disclosed in U.S. Pat. Nos. 5,254,519 and 5,597,771, the entire contents of which are incorporated herein by reference.

[0034] Still referring to FIG. 1A, system 10 further includes a source 20 for supplying supplemental air into the exhaust stream downstream from the first three-way catalyst 16. Suitable sources for supplying supplemental air include, but are not limited to, an electrically- or an engine-powered air pump capable of supplying air into the system, or in another embodiment, a reed valve opening and closing in synchronization with the engine exhaust pulses that alternately opens and closes to admit atmospheric air into the system. Source 20 includes an inlet 21 that allows the supplemental air to be admitted into the system at a selected location. The addition of the supplemental air serves to provide a lean combustion ratio by raising the air to fuel ratio above the stoichiometric value. As discussed above, depending upon the fuel being used, the stoichiometric value may differ from 14.7.

[0035] System 10 then includes an ammonia oxidation catalyst 22 located to receive and pass the exhaust gas from, i.e., downstream from, the first three-way catalyst 16 there-through. In one or more embodiments, the ammonia oxidation catalyst 22 includes a sufficient amount of a catalytic material on a surface 17B of suitable substrate 18B) to oxidize at least about 90% of the ammonia formed in first three-way catalyst to N2 and H2O. According to one or more embodiments, the ammonia oxidation catalyst is designed to achieve selectivity in converting ammonia to nitrogen in the exhaust gas stream of an internal combustion engine adjusted to a rich combustion ratio. Thus, as used herein, the phrase “ammonia oxidation catalyst” refers to a catalyst that effectively and selectively converts ammonia to nitrogen (N2) and H2O with minimal NOx formation. For example, according to one embodiment, an ammonia oxidation catalyst selectively converts ammonia to at least about 40% nitrogen, specifically, to at least about 50% nitrogen, and more specifically to at least about 60% nitrogen. In a further embodiment, the ammonia oxidation catalyst converts ammonia to at least about 85% nitrogen, for example, greater than about 90%. A useful, non-limiting example of an ammonia oxidation catalyst includes a zeolite component selected from the group including ZSM-5, beta- and y-zeolites, and the like that includes a base metal oxide selected from the group including, but not limited to, oxides of chromium, manganese, iron, cobalt, nickel, copper, vanadium, titanium, and zinc. Said ammonia oxidation catalyst further comprising a platinum group metal component (i.e., platinum, palladium, rhodium, and iridium components, and combinations thereof) dispersed on a refractory metal oxide, for example, alumina, and, optionally, further including a cerium component such as ceria. An example of such an ammonia oxidation catalyst is disclosed in U.S. Pat. No. 5,462,907, the entire content of which is incorporated herein by reference.
In the system shown in FIG. 1A, a second three-way catalyst 30 is located to receive and pass the exhaust gas from, i.e., downstream from, ammonia oxidation catalyst 22 threethrough. In one or more embodiments, the second three-way catalyst 30 includes sufficient amounts of a precious metal, a base metal oxide, and a rare earth oxide deposited on a surface 17C of suitable substrate 18C to oxidize at least about 80% of the remaining unburned hydrocarbon to CO₂ and H₂O, oxidize at least about 99% of the remaining carbon monoxide to CO₂. Suitable materials useful in the second three-way catalyst 30 include, but are not limited to, the group consisting of platinum, palladium, rhodium, and combinations thereof; oxides of chromium, manganese, iron, cobalt, nickel, copper, vanadium, titanium, zinc and the like; oxides of aluminum, oxides of cerium; and compatible combinations thereof. Useful three-way catalysts are disclosed in U.S. Pat. Nos. 5,254,519 and 5,597,771, the entire contents of which are incorporated herein by reference.

Optionally, system 10 includes a muffler 40 for reducing the sound produced by engine 12. In one embodiment, the components of system 10 are substantially contained in a housing 60 that is formed from a metallic material. Suitable materials include mild steel or mild steel having a corrosion-resistant metallic plating, such as a chromium plating. In another embodiment, housing 60 may be formed from stainless steel.

It will be appreciated that the system 10 shown in FIG. 1A is exemplary only. According to one or more embodiments, the system may be modified. For example, as shown in FIG. 1B, system 103 comprises an air source 20 and an inlet 21 upstream of an ammonia oxidation catalyst 22 and a three-way catalyst 16, all being downstream from engine 12. In another embodiment shown in FIG. 1C, the system 10C has the three-way catalyst 16 placed upstream of the air source 20 and inlet 21 so that the air source 20 is situated between the three-way catalyst and the ammonia oxidation catalyst 22, all of which are located downstream from engine 12. This embodiment can further be modified to provide a second three-way catalyst located downstream from the ammonia oxidation catalyst similar to the embodiment shown in FIG. 1A.

Referring to Figs. 2A, 2B, 2C and 2D, suitable materials for forming substrates 18A, B and C include, but are not limited to, materials resistant to thermal shock and that are mechanically strong. In one embodiment, each of catalysts 16, 22, and 30 is deposited on individual discrete portions of a substrate. For particular applications, the substrate materials may be the same or different. Examples of suitable materials include, but are not limited to, ceramic materials having different physical forms, i.e., a monolithic cylinder 70 having a multiplicity of small passageways 72 threethrough (as shown in FIG. 2A), a multiplicity of beads 80 (as shown in FIG. 2B), either formed from a suitable ceramic or metal material and the like, or a metal matrix 90 (as shown in FIG. 2C). FIG. 2D shows an embodiment in which a suitable metal matrix is formed from a multiplicity of thin layers 94 of a flat or corrugated foil 92 formed from a stainless steel alloy including chromium and aluminum. One suitable alloy is produced by Sanvik Materials Technology, Benton Harbor, Mich. The layer is formed into sheets having a thickness from about 50 to 60 micrometers. In one embodiment, these sheets are assembled into a form suitable for use as a catalyst substrate by Emitec, Auburn Hills, Mich. The surface of the substrate typically has coatings of the selected catalytic material applied thereto in one or more layers. Generally speaking, the coatings include one or more catalytic materials on support materials in amounts ranging from about 0.0001% to about 1000 grams per cubic foot of catalyst, more commonly from about 0.20 to about 80 grams per cubic foot. Various aluminas are suitable as support materials. However, for particular applications greater or lesser amounts may be selected.

Suitable catalytic materials for three-way catalysts include, but are not limited to, precious metals such as platinum, palladium, rhodium, and the like, either singly or in combinations. Other materials useful in these type catalysts include rare earth metal oxides/zirconia composites, one suitable material being a ceria-zirconia composite; and base metal oxides such as oxides of chromium, manganese, iron, cobalt, nickel, copper, vanadium, titanium, zinc and the like. Other materials include, but are not limited to, zirconium components, barium components, and nickel components.

The catalytic materials may be mixed into aqueous slurry, also known as a washcoat, with one or more refractory oxides of aluminum, titanium, silica or zirconium as nitrate or acetate salts. The slurry is then applied to the substrate material, dried, and then calcined, generally by heating in a controlled atmosphere. The calcination step forms a porous, substantially permanent coating having the catalytic material therein on the substrate. In the embodiments of the present invention, as shown in FIG. 3, there generally is more than one coating layer applied sequentially to the substrate.

Generally, the catalytic layers also contain at least a portion of a material known as an oxygen storage component. The oxygen storage component may be selected from any known material in the art, but generally is an oxide of a rare earth element such as cerium, praseodymium, lanthanum, neodymium, and combinations thereof or one or more of these elements combined with zirconia. Cerium oxide is generally preferred. Additionally, for particular applications, one or more of catalysts 16, 22, and 30 may be deposited on different zones on a monolithic substrate or contained in separate portions of housing 60 as separate catalysts 16, 22, and 30.

In one embodiment of the present invention, a method for reducing the amount of CO, NOₓ, and HC in the exhaust stream of an internal combustion engine adjusted to a stoichiometric ratio of includes passing the exhaust stream from internal combustion engine 12 adjusted to a rich combustion ratio, i.e., generally from about 8 to about 14.7 parts of air to about one part of fuel, containing unburned hydrocarbons, nitrogen oxides and carbon monoxide through a first three-way catalyst 16. The method according to an embodiment of the invention then includes adding sufficient air to the exhaust stream from first three-way catalyst at inlet 21 to provide a lean combustion ratio by raising the air fuel ratio above about 14.7 and passing the exhaust stream from the first three-way catalyst 16 through the ammonia oxidation catalyst 30 located downstream from air inlet 21. An optional further step in the method according to this embodiment of the invention includes passing the exhaust gas from ammonia oxidation catalyst 30 through second three-way catalyst 30. For particular applications, the method may also include passing the exhaust stream through muffler 40 or silencer to substantially reduce the sound produced by the engine. In other embodiments, the method
may first include passing the exhaust stream through a three-way catalyst prior to addition of the air.

[0044] In one embodiment, there is provided a sufficient amount of first three-way catalyst 16 to oxidize at least about 50% of the carbon monoxide to CO₂, reduce about 90% of the nitrogen oxides to NH₃, N₂ and H₂O and oxidize at least about 50% of the unburned hydrocarbon to CO₂ and H₂O. Additionally, the method further includes providing a sufficient amount of ammonia oxidation catalyst 22 to selectively oxidize at least about 99% of the ammonia formed in the first three-way catalyst to N₂ and H₂O; and providing a sufficient amount of second three-way catalyst 30 to oxidize at least about 99% of the remaining unburned hydrocarbon to CO₂ and H₂O and about 99% of the remaining CO to CO₂.

[0045] In one embodiment, as seen in FIG. 3, three-way catalyst 16 is in the form of one or more porous layers 17 of catalytic materials 18 applied to surface of multi-layer metallic foil substrate 94. An exemplary first layer includes, but is not limited to, a platinum component in an amount in the range of about 12.5 to about 100 g/ft³, or 25 g/ft³ in one embodiment; an alumina support in an amount in the range of about 0.2 to about 2.0 g/in³, or 1.0 g/in³ in a specific embodiment; a rare earth metal oxide-zirconia composite in an amount in the range of about 0.3 to about 0.15 g/in³, or in a specific embodiment, a ceria-zirconia composite in an amount in the range of about 0.2 to about 1.0 g/in³, or in a specific example, 0.5 g/in³; a zirconium component in an amount in the range of about 0.2 to about 0.15 g/in³, or in a specific embodiment, 0.08 g/in³; and a barium component in an amount in the range of about 0.05 to about 0.15 g/in³, or in a specific embodiment, 0.1 g/in³.

[0046] An exemplary second catalytic layer deposited on the first catalytic layer includes, but is not limited to, a rhodium component in an amount of about 12.5 to about 100 g/ft³, or in a specific embodiment, 25 g/ft³; an alumina support in an amount in the range of about 0.2 to about 2.0 g/in³, or 1.0 g/in³ in a specific embodiment; a rare earth metal oxide-zirconia composite in an amount in the range of about 0.2 to about 1.0 g/in³, or in a specific embodiment, 0.7 g/in³ of a ceria-zirconia composite, which functions as an oxygen storage component; and a zirconium component in an amount in the range of about 0.2 to about 2.0 g/in³; or specifically 0.03 to about 0.15 g/in³; or even 0.08 g/in³.

[0047] The second three-way catalyst 30 may have the same or different washcoat slurries as the first three-way catalyst 16. In a specific embodiment, catalyst 16 and catalyst 30 are formed from substantially the same materials in the same concentrations.

[0048] An additional embodiment of either or both three-way catalysts 16 and 30 for particular applications may include an undercoat layer 19 applied to surface 17a of substrate 92 prior to the application of the first and second coating layers described above. In one embodiment, the undercoat 19 layer includes, but is not limited to, an undercoat alumina support in an amount in the range of about 0.5 to about 1.5 g/in³, or 0.9 g/in³ in a specific embodiment; an undercoat zirconium component in an amount in the range of about 0.05 to about 0.15 g/in³, or in a specific embodiment, 0.10 g/in³.

[0049] In an embodiment of the invention, ammonia oxidation catalyst 22 is formed from one or more porous layers applied to the surface of a substrate formed from a multi-layer metallic foil substrate. The layer includes, but is not limited to, a platinum component in an amount in the range of about 1 to about 25 g/ft³, or in a specific embodiment, about 5.0 g/ft³; a beta-zelite component in an amount in the range of about 0.5 to about 2.5 g/in³, wherein the beta-zelite component contains iron, or in a specific embodiment about 1.5 g/in³; and a silica component in an amount in the range of about 0.1 to about 1.5 g/in³, or in a specific embodiment, 0.6 g/in³. Optionally, the zeolite component also includes a copper-nitrate copper-oxide composite in an amount in the range of about 0.1 to about 0.5 g/in³, or in a specific embodiment, about 0.16 g/in³.

Specific Embodiments of Catalysts

[0050] A specific embodiment of a three-way catalyst useful in the system of the invention includes a first catalytic layer deposited on the substrate comprising about 25 g/ft³ of a platinum component; about 1 g/in³ of an alumina support; about 0.3 g/in³ of a rare earth metal oxide-zirconia component; about 0.08 g/in³ of a zirconium component; and about 0.1 g/in³ of a barium component. The specific embodiment of a three-way catalyst also includes a second catalytic layer deposited on the first catalytic layer comprising about 25 g/ft³ of a rhodium component; about 1.0 g/in³ of an alumina support; about 0.7 g/in³ of a rare earth metal oxide-zirconia composite, preferably a ceria-zirconia composite; and about 0.08 g/in³ of a second zirconium component. In the system of the invention, the first three-way catalyst and the second three-way catalyst may have the same or different composition, in this specific embodiment, both the first and the second three-way catalysts have the same composition as given above. A specific embodiment of an ammonia oxidation catalyst useful in the system of the invention includes about 5 g/ft³ of a platinum component; about 1.5 g/in³ of a zeolite component containing iron; about 0.16 g/in³ of a base metal oxide composite, preferably copper nitrate; and about 0.6 g/in³ of a silica.

[0051] In a further specific embodiment, the three-way catalysts of the invention may utilize an additional undercoat catalytic layer deposited directly on the substrate surface beneath the first catalytic layer. The undercoat layer includes about 0.9 g/in³ of an undercoat alumina support; about 0.1 g/in³ of an undercoat zirconium component.

[0052] Referring to FIGS. 4 and 5, the graphical representations show a model exhaust stream including hydrocarbons, about 1500 ppm, (THC), nitrogen oxides, about 2500 ppm, (NOx) and carbon monoxide, about 1600 ppm, (CO), about 10,000 ppm water vapor with the balance being nitrogen. In FIG. 4, a model exhaust system that includes two three-way (TWC) catalysts made in accordance with the specific embodiments referred to above, a first three-way catalyst and a second three-way catalyst, and a blank chamber is illustrated. At the first position, represented by (FG), the initial concentrations of the model exhaust stream are seen. At the mid-bed (MB) location the concentration of the several components of the model stream are shown after passage through the first three-way catalyst. At the tail-pipe (TP) position, the concentrations of the several components of the model exhaust stream are seen after passage through the second three-way catalyst. A person skilled in the art of exhaust stream catalysis will recognize that the concentration of the NOx component is increased by passage through the second three-way catalyst in this embodiment.

[0053] Referring now to FIG. 5, a model exhaust stream similar to that of FIG. 4 is passed through an embodiment of the system of the present invention which includes the first
three-way catalyst made in accordance with the specific embodiment discussed above, a supplemental air supply, an ammonia oxidation catalyst made in accordance with the specific embodiment discussed above and the second three-way catalyst made in accordance with the specific embodiment described above. At the TP position, one skilled in the art of exhaust stream catalysis will recognize that by incorporation of the ammonia oxidation catalyst of the invention, substantially all of the ammonia produced by passing the model exhaust stream through the first three-way catalyst is converted in the ammonia oxidation catalyst to nitrogen and water. Thus, there are very little residual nitrogen compounds that are re-oxidized to nitrogen oxides in the second three-way catalyst, thereby substantially reducing the NOx concentration in the TP position when compared to the TP position of FIG. 4 without the ammonia oxidation catalyst.

It will be apparent to those skilled in the art that various modifications and variations can be made to the present invention without departing from the spirit or scope of the invention. Thus, it is intended that the present invention cover modifications and variations of this invention provided they come within the scope of the appended claims and their equivalents.

What is claimed is:

1. An emissions treatment system for reducing carbon monoxide, unburned hydrocarbons, and nitrogen oxides content in an exhaust gas stream of an internal combustion engine adjusted to a rich combustion ratio comprising: an ammonia oxidation catalyst; a supplemental air source for supplying supplemental air upstream of the ammonia oxidation catalyst; and a first three-way catalyst located to receive and pass the exhaust gas from the engine through the first three-way catalyst, wherein the internal combustion engine is adjusted to the rich combustion ratio.

2. The emissions treatment system of claim 1, wherein the first three-way catalyst is located upstream of the supplemental air source.

3. The emissions treatment system of claim 1, wherein the first three-way catalyst is located downstream from the ammonia oxidation catalyst, and the supplemental air source is upstream of the ammonia oxidation catalyst.

4. The emissions treatment system of claim 2 further comprising a second three-way catalyst located downstream from the ammonia oxidation catalyst.

5. The emissions treatment system of claim 4 wherein: the first three-way catalyst comprises a precious metal component and a rare earth oxide deposited on a substrate; the ammonia oxide catalyst comprises a precious metal component; a zeolite component containing a base metal oxide selected from the group consisting of oxides of chromium, manganese, iron, cobalt, nickel, copper, vanadium, titanium, zinc, and combinations thereof; and a silica component; deposited on a substrate; and the second three-way catalyst comprises a precious metal component and a rare earth oxide deposited on a substrate.

6. The emissions treatment system of claim 1 wherein the first three-way catalyst comprises a precious metal component selected from the group consisting of platinum, palladium, rhodium, and combinations thereof; and a rare earth oxide selected from the group consisting of ceria, lanthanum, praseodymium, neodymium, and combinations thereof.

7. The emissions treatment system of claim 1 wherein the first three-way catalyst comprises: a first catalytic layer deposited on a substrate comprising a platinum component in an amount in the range of about 1.25 to about 2.5 g/ft², an alumina support in an amount in the range of about 0.2 to about 2.0 g/ft², a ceria-zirconia composite in an amount in the range of about 0.2 to about 1.0 g/ft², a zirconium component in an amount in the range of about 0.03 to about 0.15 g/ft², and a boron component in an amount in the range of about 0.03 to about 0.15 g/ft²; and a second catalytic layer deposited on the first catalytic layer comprising a rhodium component in an amount of about 12.5 to about 100 g/ft², an alumina support in an amount in the range of about 0.2 to about 2.0 g/ft², a ceria-zirconia composite in an amount in the range of about 0.2 to about 1.0 g/ft², and a zirconium component in an amount in the range of about 0.03 to about 0.15 g/ft².

8. The emissions treatment system of claim 1 wherein the ammonia oxidation catalyst comprises a layer deposited on a substrate comprising a platinum component in an amount in the range of about 1 to about 25 g/ft², a zeolite component in an amount in the range of about 0.5 to about 2.5 g/ft², wherein the zeolite component contains iron, and a silica component in an amount in the range of about 0.1 to about 1.5 g/ft².

9. The emissions treatment system of claim 4 wherein the second three-way catalyst comprises a precious metal component selected from the group consisting of platinum, palladium, rhodium, and combinations thereof; and a rare earth oxide selected from the group consisting of ceria, lanthanum, praseodymium, neodymium, and combinations thereof.

10. The emissions treatment system of claim 4 wherein a monolithic substrate comprises a first discrete portion including a coating of the ammonia oxidation catalyst, and a second discrete portion including a coating of the second three-way catalyst.

11. The emissions treatment system of claim 10 wherein the monolithic substrate selected from the group consisting of a ceramic material with a multiplicity of passageways therethrough, a metallic material being in the form of an expanded matrix, and a metallic material being in the form of a flat or corrugated metal foil configured in a multiplicity of layers.

12. The emissions treatment system of claim 3 wherein: the ammonia oxidation catalyst comprises a platinum component in an amount in the range of about 1 to about 25 g/ft², and is effective to selectively oxidize at least about 99% of ammonia formed in the first three-way catalyst to nitrogen and water, and to selectively reduce the nitrogen oxides to nitrogen; and the first three-way catalyst comprises a precious metal component, a base metal oxide selected from the group consisting of oxides of chromium, manganese, iron, cobalt, nickel, copper, vanadium, titanium, zinc, and combinations thereof; and a rare earth oxide deposited on a substrate, and is effective to oxidize at least about 99% of the unburned hydrocarbon to carbon dioxide and water, oxidize at least about 99% of the carbon monoxide to carbon dioxide.
13. The emissions treatment system of claim 12 wherein the ammonia oxidation catalyst comprises a zeolite component in an amount in the range of about 0.5 to about 2.5 g/in³, wherein the zeolite of contains iron or a copper-oxide copper-nitrate composite in an amount in the range of about 0.1 to about 0.5 g/in³ and a silica component in an amount in the range of about 0.1 to about 1.5 g/in³.

14. The emissions treatment system of claim 12 wherein the first three-way catalyst comprises a first catalytic layer deposited on the substrate comprising a platinum component in an amount in the range of about 12.5 to about 100 g/ft³, an alumina support in an amount in the range of about 0.2 to about 2.0 g/in³, a ceria-zirconia composite in an amount in the range of about 0.2 to about 1.0 g/in³, a zirconium component in the range of about 0.03 to about 0.15 g/in³, and a barium component in an amount in the range of about 0.03 to about 0.15 g/in³; and

a second catalytic layer deposited on the first catalytic layer, the second catalytic layer comprising a rhodium component in the range of about 12.5 to about 100 g/ft³, an alumina support in an amount in the range of about 0.2 to about 2.0 g/in³, a ceria-zirconia composite in the range of about 0.2 to about 1.0 g/in³, and a zirconium component in the range of about 0.03 to about 0.15 g/in³.

15. A method for reducing carbon monoxide, unburned hydrocarbons, and nitrogen oxides in an exhaust stream of an internal combustion engine comprising:

providing the internal combustion engine adjusted to a rich combustion ratio;

passing the exhaust stream through a first three-way catalyst;

adding sufficient air to the exhaust stream, upstream of an ammonia oxidation catalyst, to provide a lean combustion ratio; and

passing the exhaust stream through the ammonia oxidation catalyst.

16. The method of claim 15, wherein passing the exhaust stream through the ammonia oxidation catalyst occurs after passing the exhaust stream through the first three-way catalyst.

17. The method of claim 16, further comprising passing the exhaust stream exiting the ammonia oxidation catalyst through a second three-way catalyst.

18. The method of claim 15 further comprising providing a sufficient amount of the first three-way catalyst to oxidize at least about 50% of the carbon monoxide to carbon dioxide, and to oxidize at least about 50% of the unburned hydrocarbons to carbon dioxide and water, and providing a sufficient amount of the ammonia oxidation catalyst to selectively oxidize at least about 99% of ammonia formed in the first three-way catalyst to nitrogen and water.

19. The method of claim 17 further comprising providing a sufficient amount of the second three-way catalyst to oxidize at least about 99% of the unburned hydrocarbons entering the second three-way catalyst to carbon dioxide and water, and about 99% of the carbon monoxide entering the second three-way catalyst to carbon dioxide.

20. An exhaust system for reducing the carbon monoxide, unburned hydrocarbons, and nitrogen oxides content in an exhaust stream of an internal combustion engine adjusted to a rich stoichiometric ratio comprising:

an exhaust conduit located to receive exhaust from the engine; a first three-way catalyst located to receive and pass the exhaust gas through the first three-way catalyst, the first three-way catalyst comprising a first catalytic layer deposited on a first substrate comprising a platinum component in an amount in the range of about 12.5 to about 100 g/ft³, an alumina support in an amount in the range of about 0.2 to about 2.0 g/in³, a ceria-zirconia composite in an amount in the range of about 0.2 to about 1.0 g/in³, a zirconium component in the range of about 0.03 to about 0.15 g/in³, and a barium component in an amount in the range of about 0.03 to about 0.15 g/in³; and

a second catalytic layer deposited on the first catalytic layer, the second catalytic layer comprising a rhodium component in the range of about 12.5 to about 100 g/ft³, an alumina support in an amount in the range of about 0.2 to about 2.0 g/in³, a ceria-zirconia composite in the range of about 0.2 to about 1.0 g/in³, and a zirconium component in the range of about 0.03 to about 0.15 g/in³, wherein the first substrate comprises a metallic foil substrate comprising a multiplicity of layers, each having the first three-way catalyst deposited thereon;

an air source having an inlet to the exhaust downstream from the first three-way catalyst for introducing sufficient air into the exhaust stream to provide a lean combustion ratio;

an ammonia oxidation catalyst downstream from the air source comprising a layer deposited on a second substrate comprising a platinum component in an amount in the range of about 1 to about 25 g/ft³, a zeolite component in an amount in the range of about 0.5 to about 2.5 g/in³, wherein the zeolite of contains iron or a copper-oxide copper-nitrate composite in an amount in the range of about 0.1 to about 0.5 g/in³ and a silica component in an amount in the range of about 0.1 to about 1.5 g/in³, wherein the second substrate comprises a metallic foil substrate comprising a multiplicity of layers, each having the ammonia oxidation catalyst deposited thereon; and

a second three-way catalyst downstream from the ammonia oxidation catalyst comprising a comprising a first catalytic layer deposited on a third substrate comprising a platinum component in an amount in the range of about 12.5 to about 100 g/ft³, an alumina support in an amount in the range of about 0.2 to about 2.0 g/in³, a ceria-zirconia composite in an amount in the range of about 0.2 to about 1.0 g/in³, a zirconium component in an amount in the range of about 0.03 to about 0.15 g/in³, and a barium component in an amount in the range of about 0.03 to about 0.15 g/in³; and

a second catalytic layer deposited on the first catalytic layer comprising a rhodium component in the range of about 12.5 to about 100 g/ft³, an alumina support in an amount in the range of about 0.2 to about 2.0 g/in³, a ceria-zirconia composite in the range of about 0.2 to about 1.0 g/in³, and a zirconium component in the range of about 0.03 to about 0.15 g/in³, wherein the first substrate comprises a metallic foil substrate comprising a multiplicity of layers, each having the ammonia oxidation catalyst deposited thereon.