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Wan et al.(10) **Pub. No.: US 2010/0251700 A1**(43) **Pub. Date: Oct. 7, 2010**(54) **HC-SCR SYSTEM FOR LEAN BURN ENGINES**

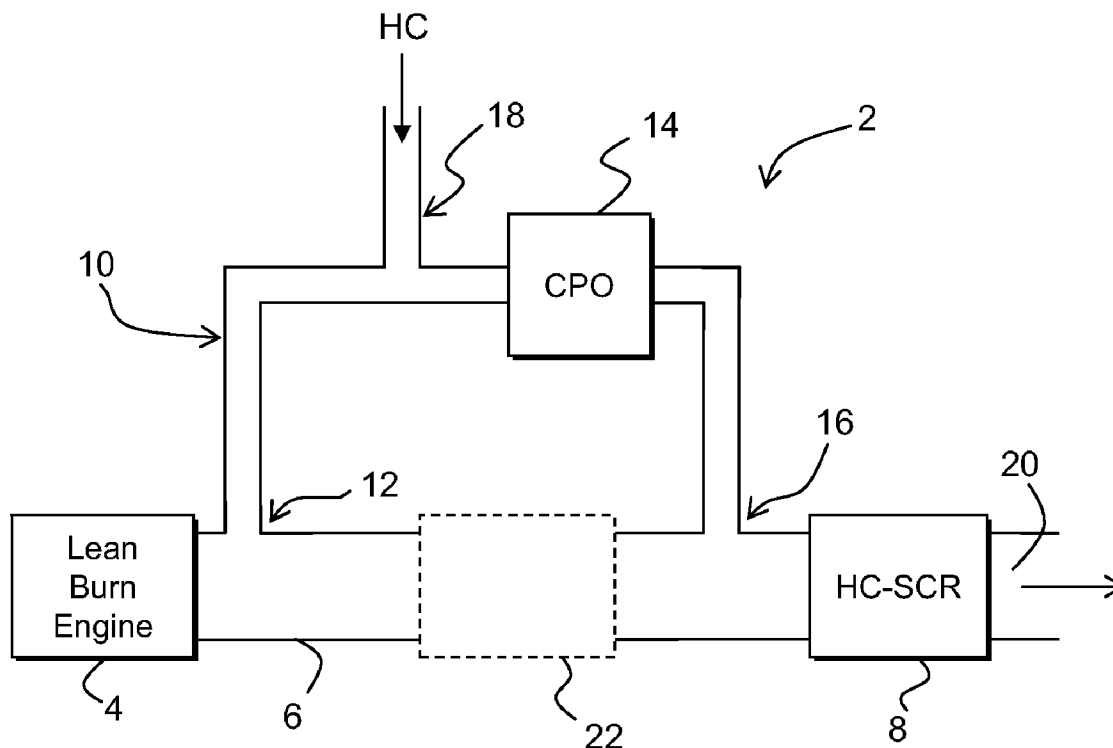
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(57) **ABSTRACT**

Systems and methods for abating NO_x emission in an exhaust stream are provided. Systems comprising hydrocarbon conversion over a partial oxidation catalyst in a slip stream and a hydrocarbon selective catalytic reduction catalyst are described. The emissions treatment system is advantageously used for the treatment of exhaust streams from lean burn engines including diesel engines, lean burn gasoline engines and locomotive engines.



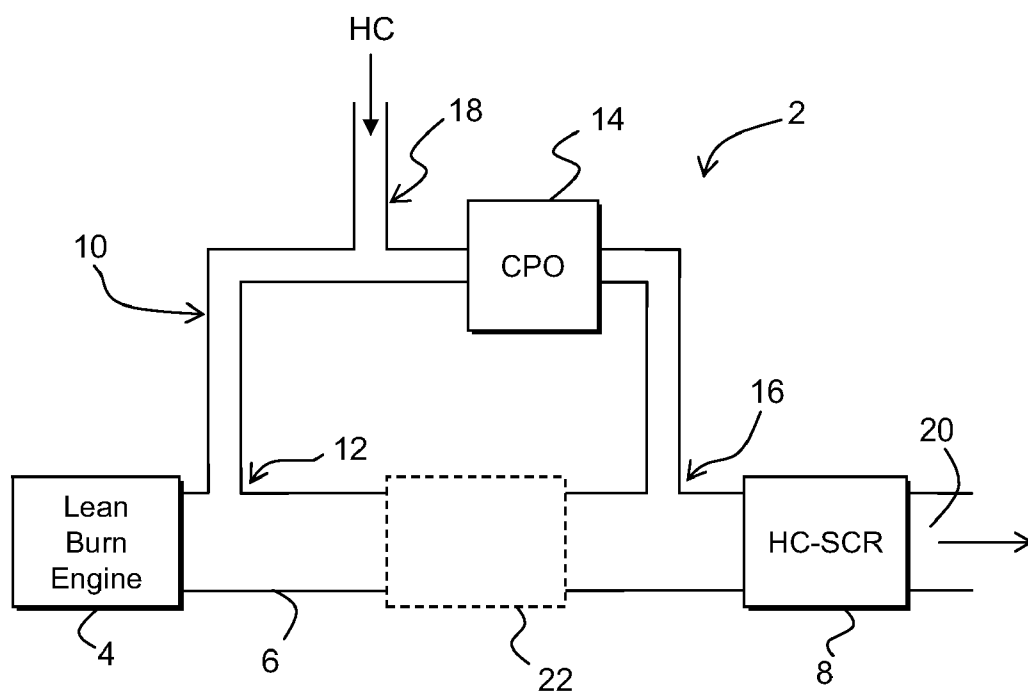


FIG. 1

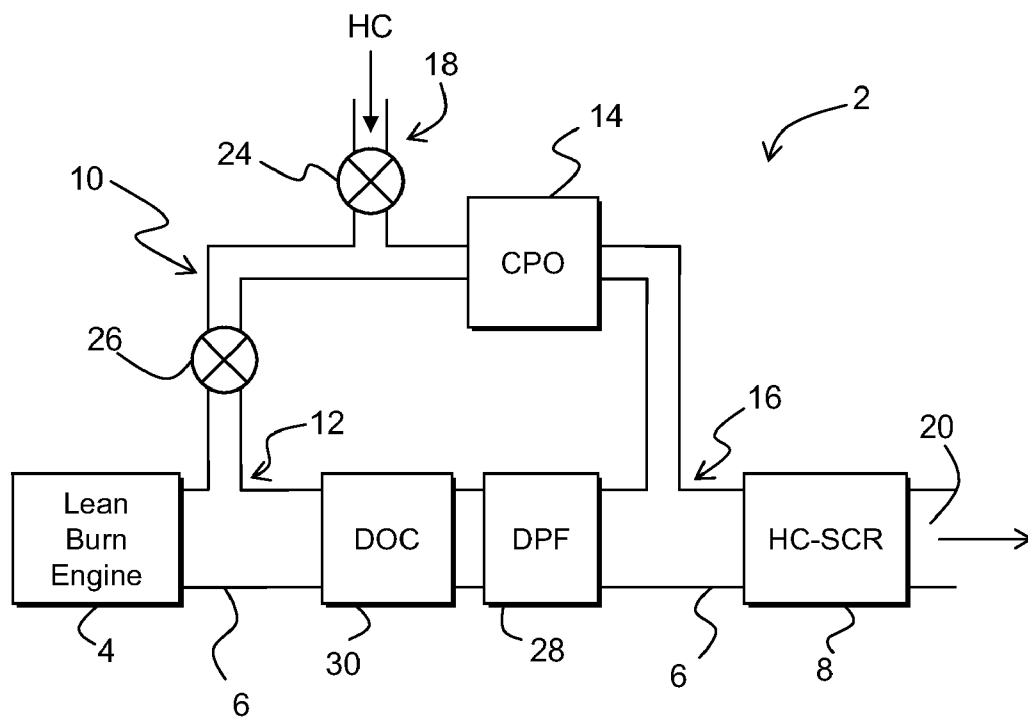


FIG. 2

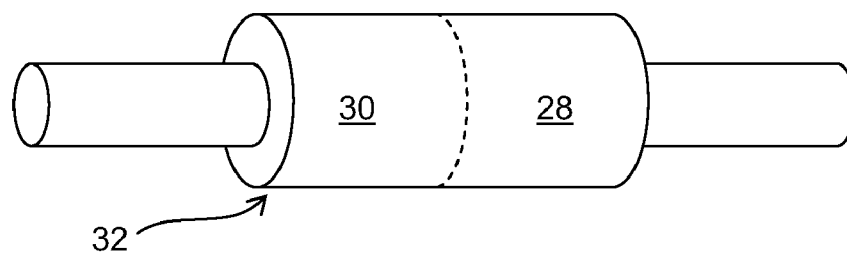


FIG. 3

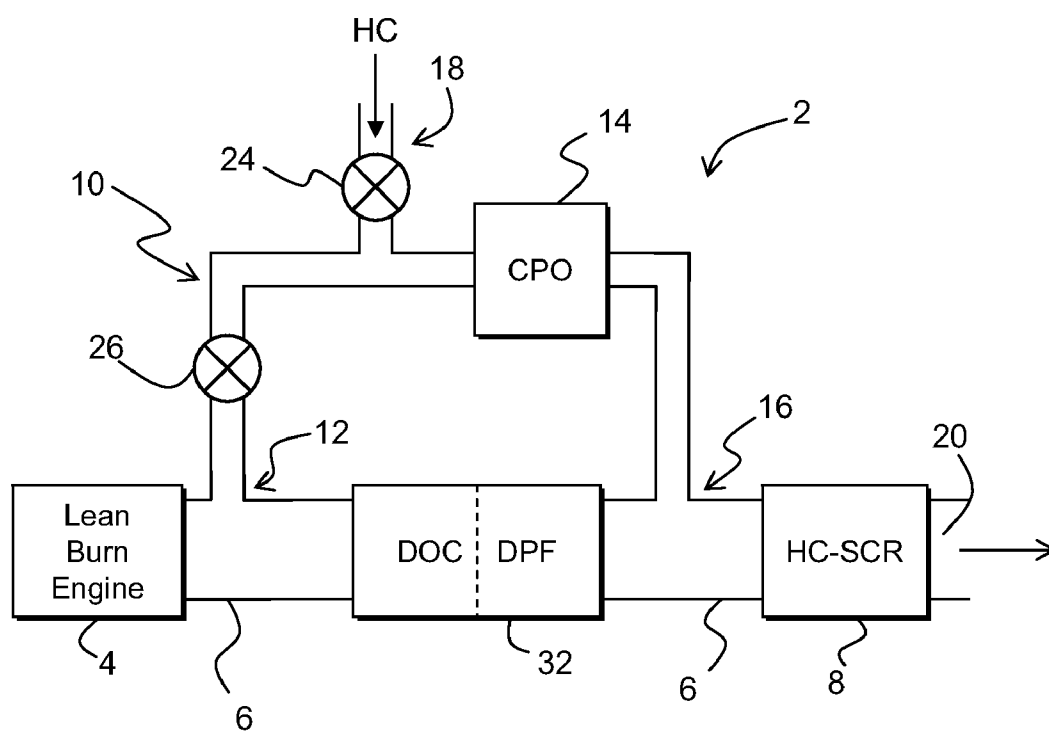


FIG. 4

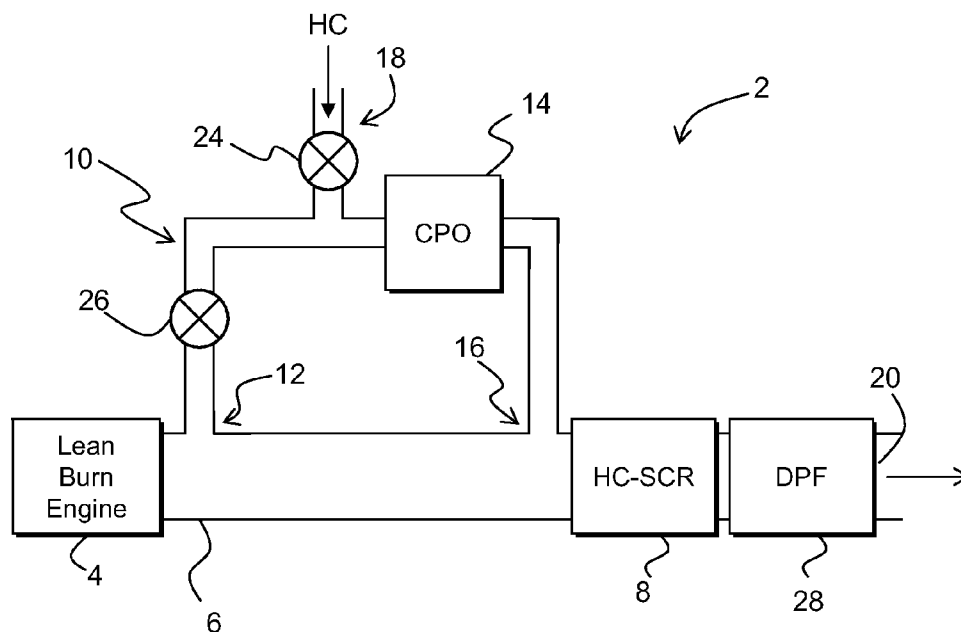


FIG. 5

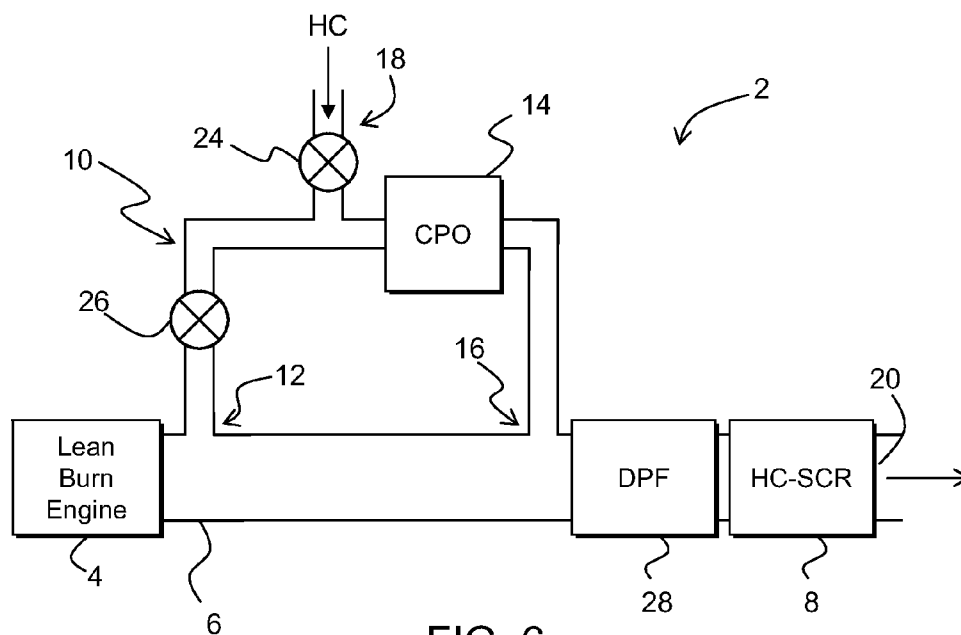


FIG. 6

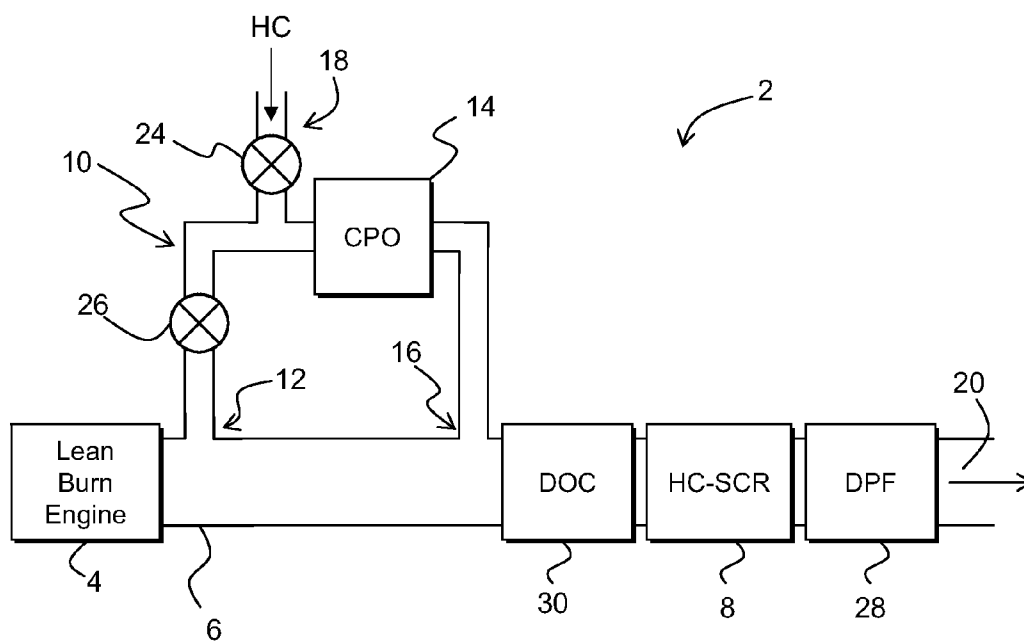


FIG. 7

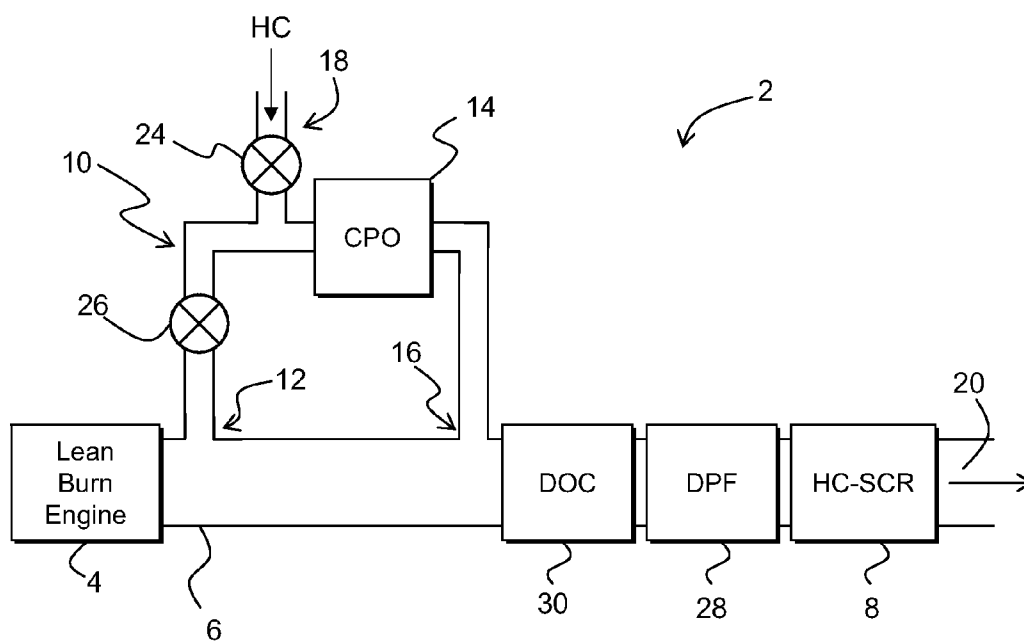


FIG. 8

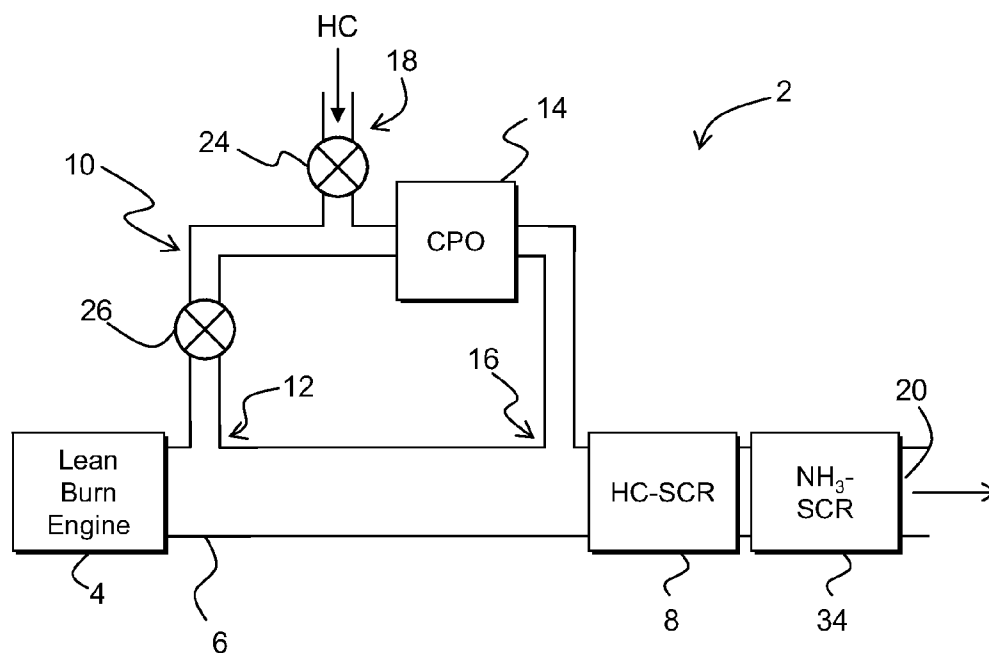


FIG. 9

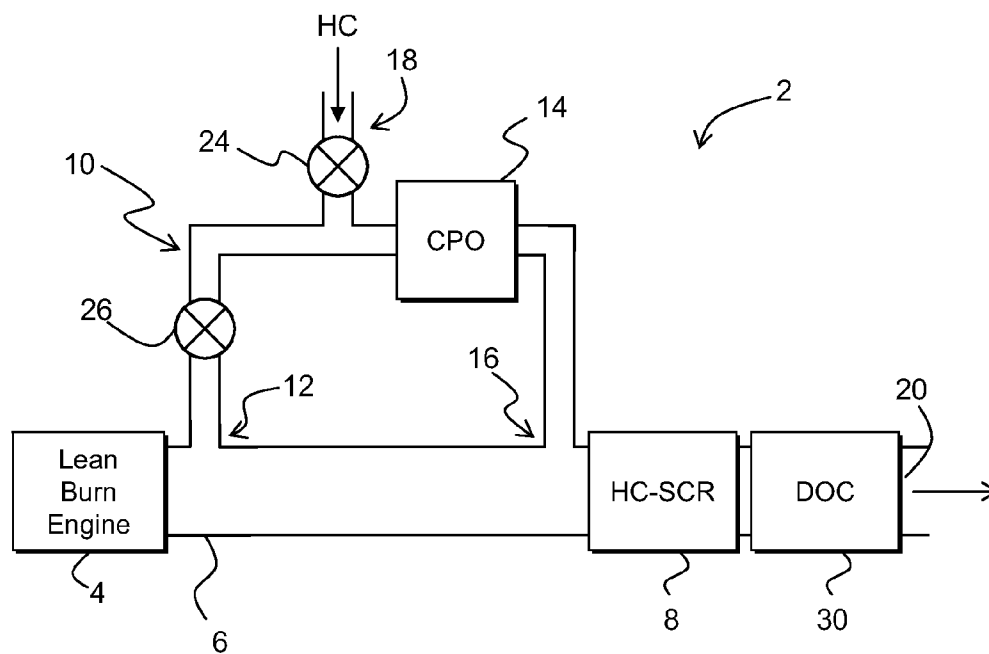


FIG. 10

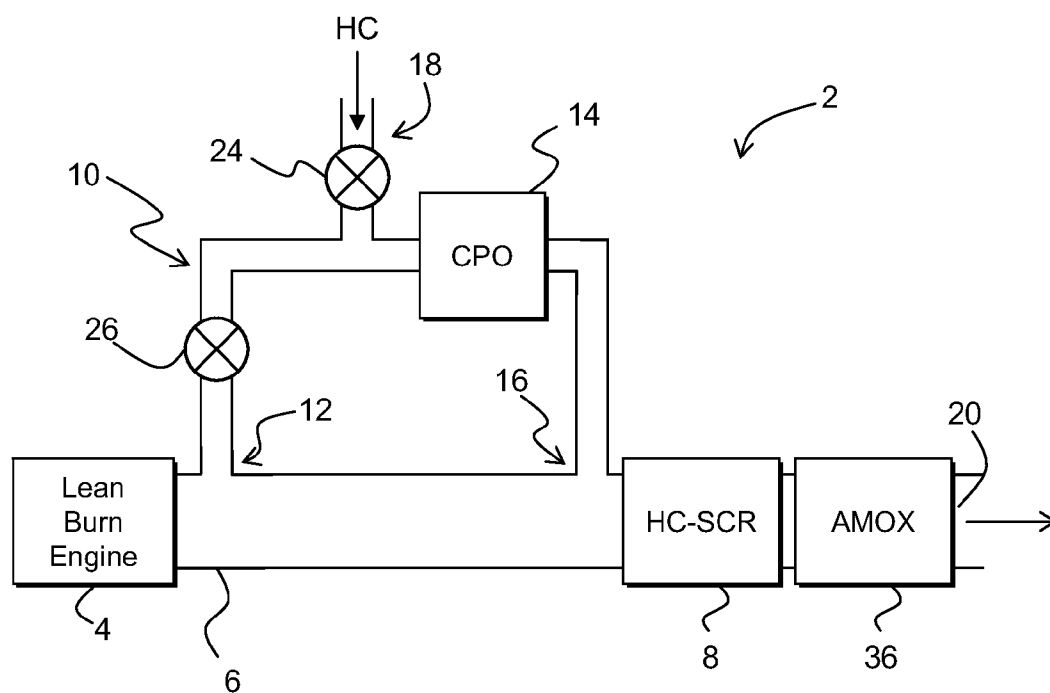


FIG. 11

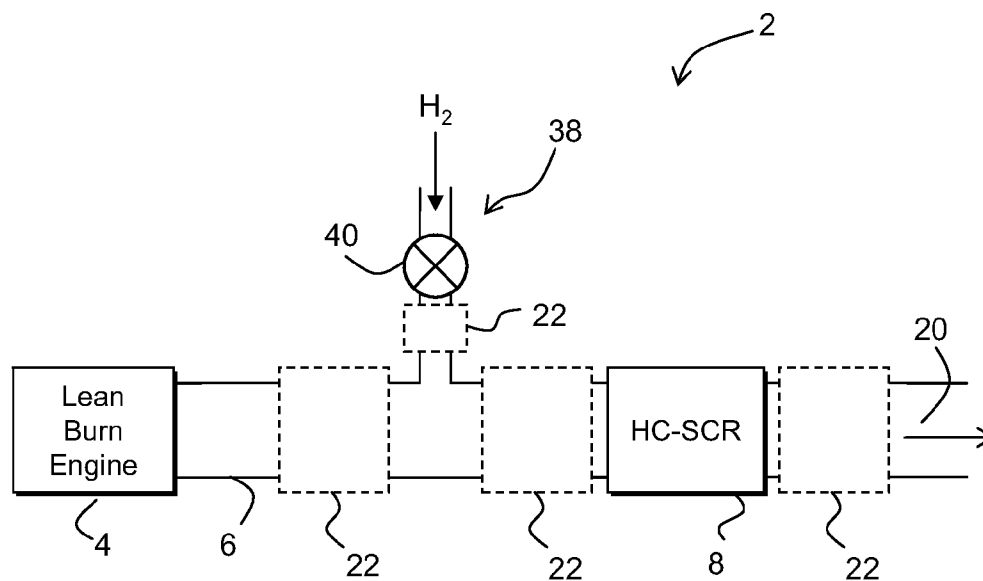


FIG. 12

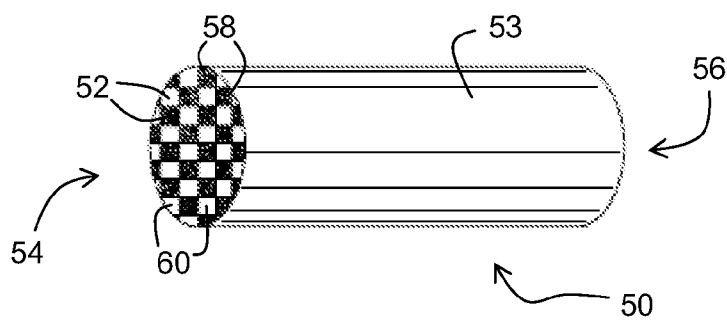


FIG. 13

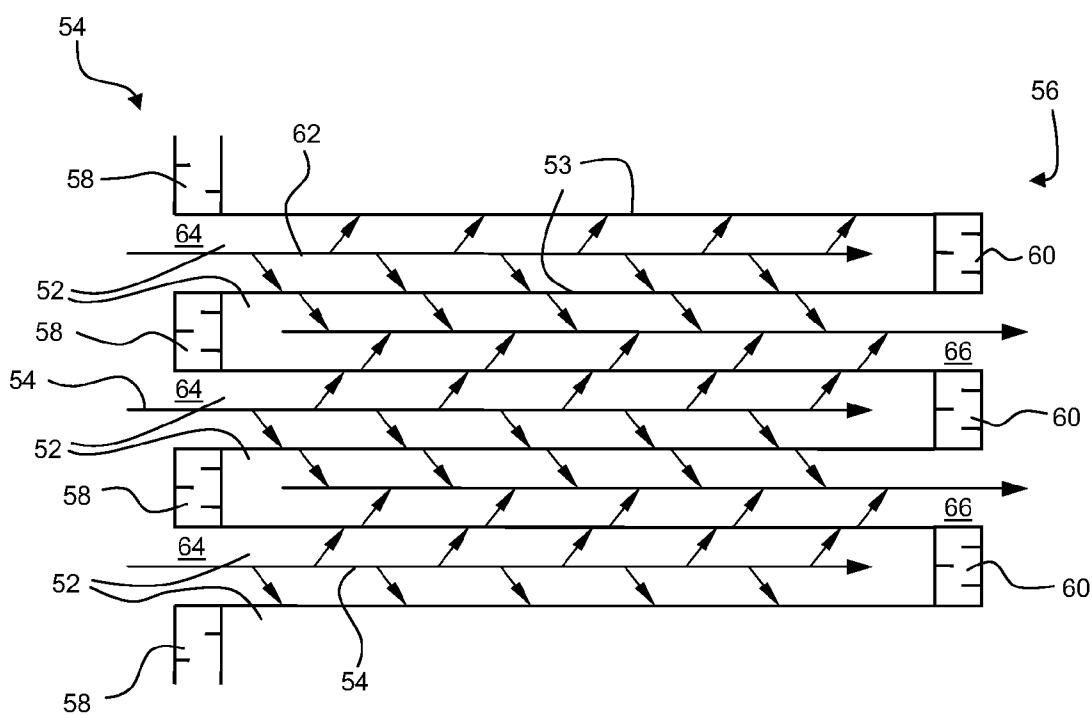


FIG. 14

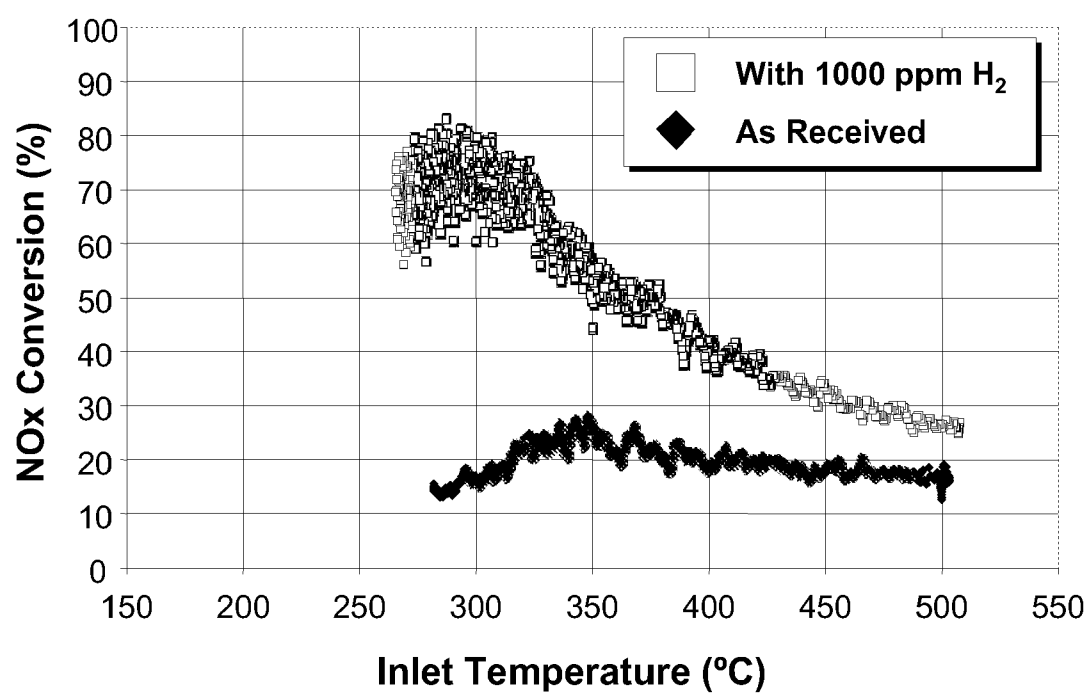


FIG. 15

HC-SCR SYSTEM FOR LEAN BURN ENGINES

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of priority under 35 USC §119(e) to U.S. Provisional Application Ser. No. 61/166,047, filed Apr. 2, 2009, U.S. Provisional Application Ser. No. 61/166,603 filed Apr. 2, 2009 and U.S. Provisional Application Ser. No. 61/169,932 filed Apr. 16, 2009 which are incorporated herein by reference.

TECHNICAL FIELD

[0002] The present invention relates to emissions treatment systems and methods useful for reducing contaminants in exhaust gas streams. Specifically, embodiments of the invention are directed to emissions treatment systems, and methods of use, for reducing NO_x, the systems including hydrocarbon conversion over a partial oxidation catalyst to generate hydrogen and exhaust gas stream partition.

BACKGROUND

[0003] Operation of lean burn engines, e.g., diesel engines, lean burn gasoline engines and locomotive engines, provide excellent fuel economy, and have very low emissions of gas phase hydrocarbons and carbon monoxide due to their operation at high air/fuel ratios under fuel lean conditions. Diesel engines, in particular, also offer significant advantages over gasoline engines in terms of their durability, and their ability to generate high torque at low speed. Effective abatement of NO_x from lean burn engines is difficult to achieve because NO_x conversion rates under fuel lean conditions is very low. Thus, conversion of the NO_x component of exhaust streams to innocuous components generally requires specialized NO_x abatement strategies for operation under fuel lean conditions.

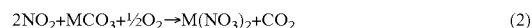
[0004] One such strategy for the abatement of NO_x in the exhaust stream from lean burn engines uses NO_x storage reduction (NSR) catalysts, which are also known in the art as "lean NO_x traps (LNT)." LNT catalysts contain NO_x sorbent materials capable of adsorbing or "trapping" oxides of nitrogen under lean conditions and platinum group metal components to provide the catalyst with oxidation and reduction functions. In operation, the LNT catalyst promotes a series of elementary steps which are depicted below in Equations 1-5. In an oxidizing environment, NO is oxidized to NO₂ (Equation 1), which is an important step for NO_x storage. At low temperatures, this reaction is typically catalyzed by a platinum group metal component, e.g., a platinum component. The oxidation process does not stop here. Further oxidation of NO₂ to nitrate, with incorporation of atomic oxygen, is also a catalyzed reaction (Equation 2). There is little nitrate formation in the absence of the platinum group metal component even when NO₂ is used as the NO_x source. The platinum group metal component has the dual functions of oxidation and reduction. For its reduction role, the platinum group metal component first catalyzes the release of NO_x upon introduction of a reductant, e.g., CO (carbon monoxide), H₂ (hydrogen) or HC (hydrocarbon) to the exhaust (Equation 3). This step may recover some NO_x storage sites but contribute to limited reduction of NO_x species. The released NO_x is then further reduced to gaseous N₂ in a rich environment (Equations 4 and 5). NO_x release can be induced by fuel injection even in a net oxidizing environment. However, the efficient

reduction of released NO_x by H₂, CO or HC requires overall net rich conditions. A temperature surge can also trigger NO_x release because metal nitrate is less stable at higher temperatures. NO_x trap catalysis is a cyclic operation. Metal compounds are believed to undergo a carbonate/nitrate conversion, as a dominant path, during lean/rich operations.

[0005] Oxidation of NO to NO₂



[0006] NO_x Storage as Nitrate



[0007] NO_x Release



[0008] NO_x Reduction to N₂



[0009] In Equations 2 and 3, M represents a divalent metal cation. M can also be a monovalent or trivalent metal compound in which case the equations need to be rebalanced.

[0010] While the reduction of NO and NO₂ to N₂ occurs in the presence of the NSR catalyst during the rich period, it has been observed that ammonia (NH₃) can also form as a by-product of a rich pulse regeneration of the NSR catalyst. For example, the reduction of NO may proceed with Equations 6 and 7.

[0011] Reduction of NO to NH₃



[0012] This property of the NSR catalyst mandates that NH₃, which is itself a noxious component, must also now be converted to an innocuous species before the exhaust is vented to the atmosphere.

[0013] An alternative strategy for the abatement of NO_x under development of mobile applications (including treating exhaust from lean burn engines) uses selective catalytic reduction (SCR) catalyst technology. The strategy has been proven effective as applied to stationary sources, e.g., treatment of flue gases. In this strategy, NO_x is reduced with a reductant, e.g., NH₃, to nitrogen (N₂) over an SCR catalyst that is typically composed of base metals. This technology is capable of NO_x reduction greater than 90%, thus it represents one of the best approaches for achieving aggressive NO_x reduction goals.

[0014] Ammonia is one of the most effective reductants for NO_x at lean condition using SCR technologies. One of the approaches being investigated for abating NO_x in diesel engines (mostly heavy duty diesel vehicles) utilizes urea as a reductant. Urea, which upon hydrolysis produces ammonia, is injected into the exhaust in front of an SCR catalyst in the temperature range 200-600° C. One of the major disadvantages for this technology is the need for an extra large reservoir to house the urea on board the vehicle. Another significant concern is the commitment of operators of these vehicles to replenish the reservoirs with urea as needed, and the requirement of an infrastructure for supplying urea to the operators. Therefore, less burdensome and alternative technology utilizing on board fuel as reductant for the NO_x treatment of exhaust gases are desirable.

[0015] Selective catalytic reduction of NO_x using hydrocarbons (HC-SCR) has been studied extensively as a potential

alternative method for the removal of NO_x under oxygen-rich conditions. Ion-exchanged base metal zeolite catalysts (e.g., Cu-ZSM5) have typically not been sufficiently active under typical vehicle operating conditions, and are susceptible to degradation by sulfur dioxide and water exposure. Catalysts employing platinum-group metals (e.g., Pt/Al₂O₃) operate effectively over a narrow temperature window between 180° C. and 220° C. and are highly selective towards N₂O production.

[0016] Catalytic devices using alumina-supported silver (Ag/Al₂O₃) have received attention because of their ability to selectively reduce NO_x under lean exhaust conditions with a wide variety of hydrocarbon species. The use of hydrocarbons and alcohols, aldehydes and functionalized organic compounds over Ag/Al₂O₃ allows reduction of NO_x at temperatures below 450° C. In addition to the molecules listed above, diesel fuel could also be used as a reductant. Diesel fuel does not require additional tanks for diesel-powered vehicles. The diesel fuel can be supplied to the emissions system by changing engine management or by supplying an additional injector of diesel fuel to the exhaust train. However, current HC-SCR catalyst systems exhibit insufficient durability. Catalyst coking caused by fuel decomposition and deposition on catalyst and sulfur poisoning derived from fuel and oil cause catalyst performance deterioration in relatively short periods of operation time. The catalyst has to undergo frequent and costly regeneration to sustain desirable performance.

[0017] Despite these various alternatives, there is no commercially available practical hydrocarbon SCR catalyst using diesel fuel as reductant. Therefore, there is a need in the art for systems and methods for providing durable NO_x reduction activity with HC-SCR technology.

SUMMARY

[0018] One or more embodiments of the invention are directed to emissions treatment systems for NO_x abatement in an exhaust stream from a lean burn engine. One embodiment of a system comprises a main exhaust conduit in flow communication with the engine exhaust stream, and a hydrocarbon selective catalytic reduction catalyst (HC-SCR) in flow communication with the main exhaust conduit. A slip exhaust stream conduit branches off of the main exhaust conduit and is connected to the main exhaust conduit by a first junction to divert a portion of the exhaust stream from the main exhaust conduit into the slip exhaust stream conduit to provide a slip exhaust stream to flow through a catalytic partial oxidation (CPO) catalyst in flow communication with the slip exhaust stream conduit. A hydrocarbon injector is located upstream of the CPO catalyst in the slip stream. A second junction downstream from the first junction reintroduces the slip exhaust stream to the main exhaust conduit upstream of the HC-SCR. The CPO is effective to convert a portion of the hydrocarbons to carbon monoxide and hydrogen.

[0019] In one or more embodiments, the CPO is designed to provide sufficient hydrogen and adequate amount of hydrocarbons for the downstream HC-SCR catalyst. In one or more embodiments, the hydrocarbon injector device includes a metering device adapted to control the amount of hydrocarbon injected into the slip exhaust stream conduit. The hydrocarbon is fuel according to one or more embodiments.

[0020] In one or more embodiments, the portion of the exhaust gas diverted into the slip exhaust stream conduit is up

to about 10% of the total exhaust flow. One or more embodiments further comprise a metering device at the first junction of the slip exhaust stream conduit to regulate the percentage of exhaust gas diverted to the slip exhaust stream conduit. In one or more embodiments the CPO catalyst contains platinum group metals. Examples of the platinum group metals of CPO catalyst include platinum, palladium, rhodium and mixtures thereof.

[0021] In one or more embodiments, one or both of the CPO catalyst and the HC-SCR are disposed on a flow through monolith. In one or more embodiments, the system includes a diesel particulate filter (DPF) downstream of the HC-SCR catalyst. In one or more embodiments, the system includes a diesel particulate filter (DPF) upstream of the HC-SCR catalyst. In one or more embodiments, the diesel particulate filter (DPF) is located between the first junction and the second junction in flow communication of the main exhaust conduit. In one or more embodiments, the system includes a diesel oxidation catalyst (DOC) upstream of the DPF and HC-SCR catalyst. In one or more embodiments, the system includes a diesel oxidation catalyst (DOC) upstream of the DPF and HC-SCR catalyst. In one or more embodiments, the system includes a diesel oxidation catalyst (DOC) upstream of the DPF and HC-SCR catalyst. In one or more embodiments, the system includes the diesel oxidation catalyst (DOC) is located downstream of the first junction in flow communication with the main exhaust conduit. In one or more embodiments, the system includes the diesel oxidation catalyst (DOC) is located downstream of the first junction in flow communication with the main exhaust conduit. In one or more embodiments, the system includes the diesel oxidation catalyst (DOC) is located downstream of the first junction in flow communication with the main exhaust conduit.

[0022] In one or more embodiments, the system includes the diesel oxidation catalyst (DOC) is located downstream of the first junction and upstream of the DPF and in flow communication with the main exhaust conduit. In one or more embodiments, the system includes the DOC and DPF are integrated into a single component. In one or more embodiments, the system includes a NH₃-SCR catalyst downstream of the HC-SCR catalyst. In one or more embodiments, the system includes an oxidation catalyst downstream of the HC-SCR catalyst.

[0023] Another aspect of the invention pertains to methods of treating an exhaust stream. In one method embodiment, the exhaust stream is passed through a main exhaust conduit and a portion of the exhaust stream through a slip exhaust stream conduit. The main exhaust conduit comprises a hydrocarbon selective catalytic reduction catalyst (HC-SCR), and the slip exhaust stream conduit comprises a catalytic partial oxidation (CPO) catalyst in flow communication with the slip stream conduit and a hydrocarbon injector upstream of the CPO. The slip exhaust stream conduit branches-off of the main exhaust conduit at a first junction and is in flow communication with the CPO. The slip exhaust stream conduit rejoins the main exhaust conduit at a second junction upstream of the HC-SCR. The CPO is adapted to convert a portion of the hydrocarbons in the slip exhaust stream conduit to carbon monoxide and hydrogen.

[0024] In one or more method embodiments, the amount of hydrocarbon injector into the slip exhaust stream conduit is controlled by a metering device. The hydrocarbon is onboard fuel in one or more embodiments. In one or more embodiments, a first percentage of the exhaust stream passes through

the main exhaust conduit and a second percentage of the exhaust stream passes through the slip exhaust stream conduit, where the first percentage is greater than the second percentage. In one or more embodiments, the second percentage of the exhaust stream is controlled by a metering device located within the slip exhaust stream conduit near the first junction. One or more embodiments of the method further comprise passing the exhaust stream in the main exhaust conduit through a diesel particulate filter located upstream of the HC-SCR catalyst.

[0025] One or more method embodiments may include passing the exhaust stream in the main exhaust conduit through a diesel particulate filter located downstream of the HC-SCR catalyst. One or more method embodiments may include passing the exhaust stream in the main exhaust conduit through a diesel particulate filter located downstream of the first junction and upstream of the second junction. One or more method embodiments may include passing the exhaust stream in the main exhaust conduit through a diesel oxidation catalyst located upstream of the diesel particulate filter. One or more method embodiments may include passing the exhaust stream in the main exhaust conduit through a diesel oxidation catalyst located upstream of the diesel particulate filter. One or more method embodiments may include passing the exhaust stream in the main exhaust conduit through a diesel oxidation catalyst located downstream of the first junction. One or more method embodiments may include passing the exhaust stream in the main exhaust conduit through a diesel oxidation catalyst located downstream of the first junction.

[0026] One or more method embodiments may include passing the exhaust stream in the main exhaust conduit through a diesel oxidation catalyst located downstream of the first junction. One or more method embodiments may include passing the exhaust stream in the main exhaust conduit through a diesel oxidation catalyst located downstream of the first junction and upstream of the diesel particulate filter. One or more method embodiments may include passing the exhaust stream in the main exhaust conduit through a diesel oxidation catalyst located downstream of the first junction and upstream of the diesel particulate filter. One or more method embodiments may include passing the exhaust stream in the main exhaust conduit through a diesel oxidation catalyst located downstream of the first junction and upstream of the diesel particulate filter.

[0027] In one or more method embodiments, the diesel oxidation catalyst and the diesel particulate filter are integrated. In one or more method embodiments, the diesel oxidation catalyst and the diesel particulate filter are integrated. The method can comprise according to one or more embodiments passing the exhaust stream in the main exhaust conduit through a NH₃-SCR catalyst located downstream of the HC-SCR catalyst. One or more method embodiments include passing the exhaust stream in the main exhaust conduit through an oxidation catalyst located downstream of the HC-SCR catalyst.

[0028] The various embodiments of the invention may include, in a multitude of configurations, various components including, but not limited to, diesel oxidation catalysts, catalyzed soot filters, HC-selective catalytic reduction catalysts, NH₃—selective catalytic reduction catalyst and oxidation

catalysts. The exhaust gas may be passed through these optional components in a variety of sequences.

BRIEF DESCRIPTION OF THE DRAWINGS

[0029] FIG. 1 is a schematic view showing an engine emission treatment system according to a detailed embodiment; [0030] FIG. 2 is a schematic view showing an engine emission treatment system according to another embodiment; [0031] FIG. 3 is a schematic view showing an integrated engine emission treatment system according to an embodiment; [0032] FIG. 4 is an alternative emission treatment system according to one or more embodiments of the invention; [0033] FIG. 5 is an alternative emission treatment system according to one or more embodiments of the invention; [0034] FIG. 6 is an alternative emission treatment system according to one or more embodiments of the invention; [0035] FIG. 7 is an alternative emission treatment system according to one or more embodiments of the invention; [0036] FIG. 8 is an alternative emission treatment system according to one or more embodiments of the invention; [0037] FIG. 9 is an alternative emission treatment system according to one or more embodiments of the invention; [0038] FIG. 10 is an alternative emission treatment system according to one or more embodiments of the invention; [0039] FIG. 11 is an alternative emission treatment system according to one or more embodiments of the invention; [0040] FIG. 12 is an alternative emission treatment system according to one or more embodiments of the invention; [0041] FIG. 13 is a perspective view of a wall flow filter substrate; [0042] FIG. 14 is a cut-away view of a section of a wall flow filter substrate; and [0043] FIG. 15 shows a graph of the percent NO_x conversion as a function of catalyst inlet temperature for an HC-SCR under various operating conditions.

DETAILED DESCRIPTION

[0044] Provided are emissions treatment systems that can be used for treating exhaust gas from lean burn engines, and methods of using these systems to treat engine exhaust. Lean burn engines include, but are not limited to, diesel engines, lean burn gasoline engines and locomotive engines.

[0045] Small amount of hydrogen (typically <2000 ppm) present in the lean exhaust can significantly enhance the performance of the HC-SCR catalyst, reversing damage done to the catalyst through normal operation. Embodiments of the invention are directed to systems and methods that can provide the fuel reductant and hydrogen to the HC-SCR catalyst. The system comprises a slip stream from the main exhaust to generate hydrogen with on-board fuel and a catalytic partial oxidation catalyst (CPO) in a net reducing condition. The slip stream containing unconverted fuel species and hydrogen is combined with the main exhaust to provide the favorable HC-SCR reaction conditions. Hydrogen can be generated from a hydrocarbon feed by a partial oxidation process in which a portion of the feed reacts with the oxygen in the slip stream under a fuel rich condition.

[0046] FIG. 1 shows a schematic description of one aspect of the present invention and is described in greater detail below. Briefly, a slip stream (typically 1-10% of the total exhaust flow emanating from the engine) is bypassed upstream of a HC-SCR catalyst located downstream from the

engine. A sufficient amount of the fuel is introduced into the slip stream to produce a fuel rich condition. A catalytic partial oxidation catalyst, as described further below, is placed in the slipstream downstream of the point of fuel introduction. The slip stream containing unconverted fuel species and hydrogen is combined with the main exhaust and introduced to the HC-SCR catalyst. In one embodiment of this invention, the HC-SCR may be placed downstream of a diesel oxidation catalyst and diesel particulate filter devices so that the HC-SCR can be regenerated at the same time as the regeneration of the DOC and DPF devices. The system can be optionally optimized with a bypass flow control valve and a fuel control delivery device to minimize the fuel penalty of the system.

[0047] The following terms shall have, for the purposes of this application, the respective meanings set forth below.

[0048] “Lean NOx catalyst”, “LNC”, “hydrocarbon selective catalytic reduction catalyst” and “HC-SCR” may be used interchangeably within the specification. These are different than a lean NOx trap (LNT) which has a NOx storage and release function.

[0049] “Lean gaseous streams” including lean exhaust streams mean gas streams that have a $\lambda > 1.0$.

[0050] “Lean periods” refer to periods of exhaust treatment where the exhaust gas composition is lean, i.e., has a $\lambda > 1.0$.

[0051] “Platinum group metal components” refer to platinum group metals or one of their oxides.

[0052] “Rare earth metal components” refer to one or more oxides of the lanthanum series defined in the Periodic Table of Elements, including lanthanum, cerium, praseodymium and neodymium.

[0053] “Rich gaseous streams” including rich exhaust streams mean gas streams that have a $\lambda < 1.0$.

[0054] “Rich periods” refer to periods of exhaust treatment where the exhaust gas composition is rich, i.e., has a $\lambda < 1.0$.

[0055] “Washcoat” has its usual meaning in the art of a thin, adherent coating of a catalytic or other material applied to a refractory substrate, such as a honeycomb flow through monolith substrate or a filter substrate, which is sufficiently porous to permit the passage there through of the gas stream being treated.

[0056] “Flow communication” means that the components and/or conduits are adjoined such that exhaust gases or other fluids can flow between the components and/or conduits.

[0057] “Downstream” refers to a position of a component in an exhaust gas stream in a path further away from the engine than the component preceding component. For example, when a diesel particulate filter is referred to as downstream from a diesel oxidation catalyst, exhaust gas emanating from the engine in an exhaust conduit flows through the diesel oxidation catalyst before flowing through the diesel particulate filter. Thus, “upstream” refers to a component that is located closer to the engine relate to another component.

[0058] Reference to an “ammonia-generating component” means a part of the exhaust system that supplies ammonia (NH_3) as a result of its design and configuration driven by engine-out emissions and dosing of reductant (H_2 , CO and/or HC) via engine management or via injection into exhaust. Such a component excludes gas dosing or other externally supplied sources of NH_3 . Examples of ammonia-generating components include NOx storage reduction (NSR) catalysts and lean NOx traps (LNT).

[0059] FIG. 1 shows an emissions treatment system 2 for NOx abatement in an exhaust stream from a lean burn engine

4 according to one embodiment. An exhaust gas stream containing gaseous pollutants (e.g., unburned hydrocarbons, carbon monoxide, nitrogen oxides) and particulate matter is conveyed via a main exhaust conduit 6 in flow communication with a lean burn engine 4. The exhaust gas stream in the main exhaust conduit 6 is passed through a hydrocarbon selective catalytic reduction catalyst (HC-SCR) 8 in flow communication with the conduit 6. A slip exhaust stream conduit 10 branches off of the main exhaust conduit 6. The slip exhaust stream conduit 10 is connected to the main exhaust conduit 6 by a first junction 12 to divert a portion of the exhaust stream from the main exhaust conduit 6 into the slip exhaust stream conduit 10 to provide a slip exhaust stream. The slip exhaust stream flows through a catalytic partial oxidation (CPO) catalyst 14 in flow communication with the slip exhaust stream conduit 10. A second junction 16 downstream from the first junction 12 reintroduces the slip exhaust stream from the slip exhaust stream conduit 10 to the main exhaust conduit 6 upstream of the HC-SCR 8. Line 20 leads to the tail pipe and out of the system.

[0060] Hydrocarbon feed can be introduced through the conduit 18 in the slip stream upstream of a CPO catalyst 14. The CPO 14 is effective to convert a portion of the hydrocarbons to carbon monoxide and hydrogen. The CPO 14 according to one or more embodiments is designed to provide sufficient hydrogen to enhance the performance of the HC-SCR 8.

[0061] In some embodiments, the main exhaust conduit 6 includes an optional additional exhaust system component 22 downstream of the first junction 12. The additional exhaust system component 22 can be, for example, one or more of a diesel oxidation catalyst, a diesel particulate filter, a reductant injector and an air injector in flow communication with the main exhaust conduit. In one specific embodiment, the optional additional exhaust system component 22, for example, one or more of a diesel oxidation catalyst and a diesel particulate filter, can be placed upstream of the first junction 12 of the main exhaust conduit 6.

[0062] As shown in the embodiment of FIG. 2, the hydrocarbon injector 18 can include a metering device 24 adapted to control the amount of hydrocarbon injected into the slip exhaust stream conduit 10. In specific embodiments, the injected hydrocarbon is on-board fuel.

[0063] Detailed embodiments of the invention include a metering device 26 at the first junction 12 of the slip exhaust stream conduit 10 to regulate the percentage of exhaust gas diverted to the slip exhaust stream conduit 10. In some embodiments of the invention, the portion of the exhaust gas diverted from the main exhaust conduit 6 into the slip exhaust stream conduit 10 is up to about 10% of the total exhaust flow. In other detailed embodiments, the portion of the exhaust gas diverted from the main exhaust conduit 6 is in the range of about 0.5% to about 15%, or in the range of about 1% to about 10%. In other detailed embodiments the portion of the exhaust gas diverted from the main exhaust conduit 6 is up to about 15%, 14%, 13%, 12%, 11%, 10%, 9%, 8%, 7%, 6%, 5%, 4%, 3% or 2% of the total exhaust flow.

[0064] In specific embodiments one or more of the CPO catalyst and the HC-SCR are disposed on a flow through monolith.

[0065] The emissions treatment system of various embodiments, as shown in FIG. 2, further comprises a diesel particulate filter (DPF) 28 located between the first junction 12 and the second junction 16 in flow communication with the main

exhaust conduit 6. In other embodiments, a diesel oxidation catalyst (DOC) 30 is located downstream of the first junction 12 and upstream of the DPF 28 and in flow communication with the main exhaust conduit 6.

[0066] In an alternative embodiment, shown in FIGS. 3 and 4, the DOC 30 and DPF 28 are integrated into a single component or substrate 32. For example, the DOC 30 and DPF 28 may be disposed in separate zones of the same substrate 32, where the DOC 30 is disposed on the upstream segment of the substrate 32, and the CSF 28 is disposed on the downstream segment of the substrate 32.

[0067] Additional embodiments of the invention are directed to methods of treating an exhaust stream from a lean burn engine. Referring to FIGS. 1, 2 and 4, the exhaust stream is passed through a main exhaust conduit 6 and a portion of the exhaust stream through a slip exhaust stream conduit 10. The main exhaust conduit 6 comprises a hydrocarbon selective catalytic reduction catalyst (HC-SCR) 8. The slip exhaust stream conduit 10 comprises a catalytic partial oxidation (CPO) catalyst 14 and hydrocarbons can be injected into the slip exhaust stream conduit 10 upstream of the CPO 14 using a hydrocarbon injector 18. The slip exhaust stream conduit 10 branches-off of the main exhaust conduit 6 at a first junction 12 and is in flow communication with the CPO 14. The slip exhaust stream conduit 10 rejoins the main exhaust conduit 6 at a second junction 16. The second junction 16 is located upstream of the HC-SCR 8. The CPO 14 is adapted to convert hydrocarbons in the slip exhaust stream conduit 10 to carbon monoxide and hydrogen.

[0068] The amount of hydrocarbon injected into the slip exhaust stream conduit 10 may be controlled by a metering device 24. In detailed embodiments, the hydrocarbon is on-board fuel.

[0069] According to one or more embodiments of the invention, a first percentage of the exhaust stream passes through the main exhaust conduit 6 and a second percentage of the exhaust stream passes through the slip exhaust stream conduit 10, where the first percentage is greater than the second percentage. The second percentage of the exhaust stream in some embodiments is controlled by a metering device 26 located within the slip exhaust stream conduit 10 near the first junction 12.

[0070] Various embodiments of the invention further comprise passing the exhaust stream in the main exhaust conduit 6 through a diesel particulate filter 28 located downstream of the first junction 12 and upstream of the second junction 16. In other embodiments, the exhaust stream in the main exhaust conduit 6 is passed through a diesel oxidation catalyst 30 located downstream of the first junction 12 and upstream of the diesel particulate filter 28. In detailed embodiments, as shown in FIG. 4, the diesel oxidation catalyst 30 and the diesel particulate filter 28 are integrated into a single component 32.

[0071] The CPO 14, DOC 30, DPF 28 as well as optional components 22 can be made of compositions well known in the art and may comprise base metals (e.g., ceria) and/or platinum group metals as catalytic agents. In the upstream position, the DOC and/or particulate filter provides several advantageous functions. The catalyst serves to oxidize unburned gaseous and non-volatile hydrocarbons (i.e., the soluble organic fraction of the diesel particulate matter) and carbon monoxide to carbon dioxide and water. Removal of substantial portions of the SOF, in particular, assists in preventing too great a deposition of particulate matter on the

HC-SCR 8. In specific embodiments, the platinum group metal is selected from the group consisting of platinum, palladium, rhodium and combinations thereof.

[0072] In certain embodiments of the invention, one or more of the DOC 30, DPF 28 and optional components 22 are coated on a soot filter, for example, a wall flow filter to assist in the removal of the particulate material in the exhaust stream, and, especially the soot fraction (or carbonaceous fraction) of the particulate material. The DOC, in addition to the other oxidation function mentioned above, lowers the temperature at which the soot fraction is oxidized to CO₂ and H₂O. As soot accumulates on the filter, the catalyst coating assists in the regeneration of the filter. As shown in FIG. 5, a DPF 28 may be located downstream of the HC-SCR 8 to convert the CO and unconverted fuel species. FIG. 6 shows another alternate embodiment where the DPF 28 is located upstream of the first junction 12 to minimize or prevent fouling of the downstream HC-SCR with particulate material. FIG. 7 shows an alternate embodiment where a DOC 30 is located upstream of the first junction 12 and the HC-SCR 8 and DPF 28 are located downstream of the second junction. FIG. 8 shows an alternate embodiment where a DOC 30 and DPF 28 are located upstream of the first junction. In another alternate embodiment, as shown in FIG. 9 the system further comprises a NH₃-SCR catalyst downstream of the HC-SCR to convert any NH₃ emissions generated in the system. In another specific embodiment, shown in FIG. 10, the system further comprises an oxidation catalyst downstream of the HC-SCR to oxidize CO and any unconverted fuel species. FIG. 11 shows an alternative embodiment of an emission treatment system comprising an ammonia oxidation (AMOX) catalyst 36 located downstream of the HC-SCR 8 catalyst. The ammonia oxidation catalyst 36 may be useful for removing or abating residual ammonia, which may be referred to as slipped ammonia through the system.

[0073] FIG. 12 shows an alternate embodiment where the hydrogen source 38 is an off-line source or component other than a CPO catalyst. The hydrogen source 38, as shown here, may include a metering device 40 capable of controlling the amount of hydrogen being injected into the main exhaust conduit 6. The off-line H₂ source (and HC reductant) can include the output from a CPO reaction (a partial oxidation of fuel with oxygen) as previously described.

[0074] Various optional components 22 can be included in the exhaust conduit 6. These optional components 22 can be located upstream of the hydrogen injector 38, downstream of the hydrogen injector 38 or downstream of the HC-SCR catalyst 8. It is conceivable that an optional component may be located within the hydrogen injector 38 prior to the junction with the main exhaust conduit 6. The alternate embodiments shown are merely indicative of various ways the invention can be practiced and should not be taken as limiting. The components can be arranged in other configurations and remain within the scope of the invention.

[0075] As will be understood by those skilled in the art, the various metering devices may also be connected to a controller. The controller can include, amongst other components, sensors and processors. The sensors can be suitable for measuring the components of the gaseous composition and can be placed at various locations within the exhaust conduits. The processor can evaluate data from the sensors and adjust the metering devices to optimize the function of the various catalytic components.

[0076] Optional components 22 for use with various embodiments of the invention can be, for example, one or more of a diesel oxidation catalyst, a diesel particulate filter, a reductant injector, an air injector, an ammonia oxidation catalyst, an ammonia selective catalytic reduction catalyst in flow communication with the main exhaust conduit. Additionally, the optional components 22 may be a combination of integrated components, including, but not limited to, those shown in FIG. 3.

Substrates

[0077] In detailed embodiments, any or all of the catalysts, including the HC-SCR 8, CPO 14, and DOC 30, are disposed on a substrate. The substrate may be any of those materials typically used for preparing catalysts, and will typically comprise a ceramic or metal honeycomb structure, for example, a flow through monolith. Any suitable substrate may be employed, such as a monolithic substrate of the type having fine, parallel gas flow passages extending therethrough from an inlet or an outlet face of the substrate, such that passages are open to fluid flow therethrough (referred to as honeycomb flow through substrates). The passages, which are essentially straight paths from their fluid inlet to their fluid outlet, are defined by walls on which the catalytic material is coated as a washcoat so that the gases flowing through the passages contact the catalytic material. The flow passages of the monolithic substrate are thin-walled channels, which can be of any suitable cross-sectional shape and size such as trapezoidal, rectangular, square, sinusoidal, hexagonal, oval, circular, etc. Such structures may contain from about 60 to about 600 or more gas inlet openings (i.e., cells) per square inch of cross section.

[0078] FIGS. 13 and 14 illustrate a wall flow filter substrate 50 which has a plurality of alternately blocked channels 52 and can serve as a particulate filter. The passages are tubularly enclosed by the internal walls 53 of the filter substrate. The substrate has an inlet end 54 and an outlet end 56. Alternate passages are plugged at the inlet end 54 with inlet plugs 58 and at the outlet end 56 with outlet plugs to form opposing checkerboard patterns at the inlet 54 and outlet 56. A gas stream enters through the unplugged channel inlet 60, is stopped by outlet plug and diffuses through channel walls 53 (which are porous) to the outlet side. The gas cannot pass back to the inlet side of walls because of inlet plugs 58. If such substrate is utilized, the resulting system will be able to remove particulate matters along with gaseous pollutants.

[0079] Wall flow filter substrates can be composed of ceramic-like materials such as cordierite, α -alumina, silicon carbide, aluminum titanate, silicon nitride, zirconia, mullite, spodumene, alumina-silica-magnesia or zirconium silicate, or of porous, refractory metal. Wall flow substrates may also be formed of ceramic fiber composite materials. Specific wall flow substrates are formed from cordierite, silicon carbide, and aluminum titanate. Such materials are able to withstand the environment, particularly high temperatures, encountered in treating the exhaust streams.

[0080] Wall flow substrates for use in the inventive system can include thin porous walled honeycombs (monoliths) through which the fluid stream passes without causing too great an increase in back pressure or pressure across the article. Ceramic wall flow substrates used in the system can be formed of a material having a porosity of at least 40% (e.g., from 40 to 75%) having a mean pore size of at least 10 microns (e.g., from 10 to 30 microns).

[0081] In specific embodiments where extra functionality is applied to the filter (DOC 30, DPF 28 and optional components 22), the substrates can have a porosity of at least 59% and have a mean pore size of between 10 and 20 microns. When substrates with these porosities and these mean pore sizes are coated with the techniques described below, adequate levels of desired catalyst compositions can be loaded onto the substrates. These substrates are still able to retain adequate exhaust flow characteristics, i.e., acceptable back pressures, despite the catalyst loading. U.S. Pat. No. 4,329,162 is herein incorporated by reference with respect to the disclosure of suitable wall flow substrates.

[0082] Typical wall flow filters in commercial use are typically formed with lower wall porosities, e.g., from about 42% to 50%. In general, the pore size distribution of commercial wall flow filters is typically very broad with a mean pore size smaller than 25 microns.

[0083] The porous wall flow filter can be catalyzed in that the wall of the element has thereon or contained therein one or more catalytic materials. Catalytic materials may be present on the inlet side of the element wall alone, the outlet side alone, both the inlet and outlet sides, or the wall itself may consist all, or in part, of the catalytic material. This invention includes the use of one or more washcoats of catalytic materials and combinations of one or more washcoats of catalytic materials on the inlet and/or outlet walls of the element. The filter may be coated by any of a variety of means well known to the art.

[0084] The substrates useful for the catalysts of the present invention may also be metallic in nature and be composed of one or more metals or metal alloys. The metallic substrates may be employed in various shapes such as corrugated sheet or monolithic form. Suitable metallic supports include the heat resistant metals and metal alloys such as titanium and stainless steel as well as other alloys in which iron is a substantial or major component. Such alloys may contain one or more of nickel, chromium and/or aluminum, and the total amount of these metals may advantageously comprise at least 15 wt. % of the alloy, e.g., 10-25 wt. % of chromium, 3-8 wt. % of aluminum and up to 20 wt. % of nickel. The alloys may also contain small or trace amounts of one or more other metals such as manganese, copper, vanadium, titanium and the like. The surface or the metal substrates may be oxidized at high temperatures, e.g., 1000° C. and higher, to improve the resistance to corrosion of the alloys by forming an oxide layer on the surfaces the substrates. Such high temperature-induced oxidation may enhance the adherence of the refractory metal oxide support and catalytically promoting metal components to the substrate.

[0085] In alternative embodiments, one or all of the HC-SCR 8, CPO 14, DOC 30, DPF 28 and optional components 22 may be deposited on an open cell foam substrate. Such substrates are well known in the art, and are typically formed of refractory ceramic or metallic materials.

CPO Catalyst

[0086] The principle of the CPO catalyst is the reaction of fuel with oxygen to yield carbon monoxide and hydrogen according to Equation 8.



[0087] The catalytic partial oxidation reaction prevails when sufficiently high temperature and limited contact time of reactive gas with the catalyst (high space velocity) are

provided. In detailed embodiments, the CPO 14 catalyst contains platinum and palladium. In specific embodiments, the platinum group metal loading is in the range of about 20 g/ft³ to about 200 g/ft³. In more specific embodiments, the platinum to palladium metal ratio in the CPO is in the range of about 1:9 to about 9:1. In one or more embodiments, the CPO operates between 600° C. and 700° C. in excess of 100,000 hr⁻¹ space velocity (sometimes >250,000 hr⁻¹). The platinum to palladium metal ratio of detailed embodiments can be in the range of about 1:5 to about 5:1, or about 1:4 to about 4:1, or about 1:3 to about 3:1, or about 1:2 to about 2:1, or about 1:1.

[0088] In a specific embodiment the CPO comprises a suitable high surface area refractory metal oxide support layer is deposited on a substrate as described above to serve as a support upon which finely dispersed catalytic metal may be distended. In particular embodiments, high surface area refractory metal oxide supports can be utilized, e.g., alumina support materials, also referred to as “gamma alumina” or “activated alumina,” typically exhibit a BET surface area in excess of 60 square meters per gram (“m²/g”), often up to about 200 m²/g or higher. Such activated alumina is usually a mixture of the gamma and delta phases of alumina, but may also contain substantial amounts of eta, kappa and theta alumina phases. Refractory metal oxides other than activated alumina can be used as a support for at least some of the catalytic components in a given catalyst. For example, bulk ceria, zirconia, alpha alumina and other materials are known for such use. Although many of these materials suffer from the disadvantage of having a considerably lower BET surface area than activated alumina, that disadvantage tends to be offset by a greater durability or performance enhancement of the resulting catalyst. “BET surface area” has its usual meaning of referring to the Brunauer, Emmett, Teller method for determining surface area by N₂ adsorption. Pore diameter and pore volume can also be determined using BET-type N₂ adsorption or desorption experiments.

[0089] A specific support coating is alumina, for example, a stabilized, high-surface area transition alumina. As used herein and in the claims, “transition alumina” includes gamma, chi, eta, kappa, theta and delta forms and mixtures thereof. It is known that certain additives such as, e.g., one or more rare earth metal oxides and/or alkaline earth metal oxides may be included in the transition alumina (usually in amounts comprising from 2 to 10 weight percent of the stabilized coating) to stabilize it against the generally undesirable high temperature phase transition to alpha alumina, which is a relatively low surface area. For example, oxides of one or more of lanthanum, cerium, praseodymium, calcium, barium, strontium and magnesium may be used as a stabilizer.

[0090] The platinum group metal catalytic component of the catalytic partial oxidation catalyst comprises palladium and platinum and, optionally, one or more other platinum group metals. As used herein and in the claims, “platinum group metals” means platinum, palladium, rhodium, iridium, osmium and ruthenium. Suitable platinum group metal components are palladium and platinum and, optionally, rhodium. Desirable catalysts for partial oxidation should have at least one or more of the following properties. They should be able to operate effectively under conditions varying from oxidizing at the inlet to reducing at the exit; they should operate effectively and without significant temperature degradation over a temperature range of about 427° C. to 1315° C.; they should operate effectively in the presence of carbon monox-

ide, olefins and sulfur compounds; they should provide for low levels of coking such as by preferentially catalyzing the reaction of carbon with H₂O to form carbon monoxide and hydrogen thereby permitting only a low level of carbon on the catalyst surface; they should resist poisoning from such common poisons as sulfur and halogen compounds. For example, in some otherwise suitable catalysts, carbon monoxide may be retained by the catalyst metal at low temperatures thereby decreasing or modifying its activity. The combination of platinum and palladium is a highly efficient oxidation catalyst for the purposes of the present invention. Generally, the catalytic activity of platinum-palladium combination catalysts is not simply an arithmetic combination of their respective catalytic activities; the disclosed range of proportions of platinum and palladium have been found to provide efficient and effective catalytic activity in treating a rather wide range of hydrocarbon feeds with good resistance to high temperature operation and catalyst poisons.

[0091] Rhodium may optionally be included with the platinum and palladium. Under certain conditions, rhodium is an effective oxidation as well as a steam reforming catalyst, particularly for light olefins. The combined platinum group metal catalysts can catalyze the autothermal reactions at quite low ratios of H₂O to carbon (atoms of carbon in the feed) and oxygen to carbon, without significant carbon deposition on the catalyst. This feature provides flexibility in selecting H₂O to C and O.sub.2 to C ratios in the inlet streams to be processed.

[0092] The platinum group metals employed in the catalysts of embodiments of the present invention may be present in the catalyst composition in any suitable form, such as the elemental metals, as alloys or intermetallic compounds with the other platinum group metal or metals present, or as compounds such as an oxide of the platinum group metal. As used in the claims, the terms palladium, platinum and/or rhodium “catalytic component” or “catalytic components” is intended to embrace the specified platinum group metal or metals present in any suitable form. Generally, reference in the claims or herein to platinum group metal or metals catalytic component or components embraces one or more platinum group metals in any suitable catalytic form. Suitable CPO catalysts are described in U.S. Pat. No. 4,522,894, the entire content of which is incorporated herein by reference.

HC-SCR Catalyst

[0093] A HC-SCR catalyst comprising silver on an alumina support is generally useful for the emissions treatment system of this invention. In a detailed embodiment, the catalyst contains “well dispersed” silver species on the surface of an alumina. In a specific embodiment, the catalyst substantially free of silver metal and/or silver aluminate.

[0094] The catalyst may be prepared by impregnation of an alumina support with ionic silver. The alumina support can be any suitable alumina, including but not limited to, boehmite pseudoboehmite, diaspore, norstrandite, bayerite, gibbsite, hydroxylated alumina, calcined alumina, and mixtures thereof. An exemplary silver-alumina catalyst comprises about 3 to 4 weight percent (wt. %) silver on an Ag₂O basis supported on alumina. In one embodiment, the catalyst is prepared by depositing ionic silver on highly hydroxylated alumina. As used herein, the term “hydroxylated” means that the surface of the alumina has a high concentration of surface hydroxyl groups in the alumina as it is obtained, for example boehmite, pseudoboehmite or gelatinous boehmite, diaspore,

norstrandite, bayerite, gibbsite, alumina having hydroxyl groups added to the surface, and mixtures thereof. Pseudo-boehmite and gelatinous boehmite are generally classified as non-crystalline or gelatinous materials, whereas diaspore, norstrandite, bayerite, gibbsite, and boehmite are generally classified as crystalline. According to one or more embodiments of the invention, the hydroxylated alumina is represented by the formula $\text{Al}(\text{OH})_x\text{O}_y$, where $x=3-2y$ and $y=0$ to 1 or fractions thereof. In their preparation, such aluminas are not subject to high temperature calcination, which would drive off many or most of the surface hydroxyl groups. In alternative embodiments, the alumina may be of a type subject to higher temperature calcinations to provide gamma, delta, theta and alpha-alumina and combinations thereof.

[0095] Impregnating the alumina with a water soluble, ionic form of silver such as silver acetate, silver nitrate, etc., and then drying and calcining the ionic silver-impregnated alumina at a temperature low enough to fix the silver and decompose the anion (if possible). Typically for the nitrate salt this would be about 450-550 degrees centigrade to provide an alumina that has substantially no silver particles greater than about 20 nm in diameter. In certain embodiments, the diameter of the silver is less than 10 nm, and in other embodiments, the silver is less than about 2 nm in diameter. In one or more embodiments, the processing is performed so that the silver is present in substantially ionic form and there is substantially no silver metal present as determined by UV spectroscopy. In one or more embodiments there is substantially no silver aluminate present. The absence of silver metal and silver aluminate can be confirmed by x-ray diffraction analysis. In the presence of small amount of hydrogen and adequate hydrocarbon fuel species, the catalyst can still perform well when it has been deposited with carbonaceous and sulfur species.

DOC Catalyst

[0096] The oxidation catalyst can be formed from any composition that provides effective combustion of unburned gaseous and non-volatile hydrocarbons (i.e., the VOF) and carbon monoxide. In addition, the oxidation catalyst should be effective to convert a substantial proportion of the NO of the NOx component to NO_2 . As used herein, the term "substantial conversion of NO of the NOx component to NO_2 " means at least 20%, and specifically between 30 and 60%. Catalyst compositions having these properties are known in the art, and include platinum group metal- and base metal-based compositions. The catalyst compositions can be coated onto honeycomb flow-through monolith substrates formed of refractory metallic or ceramic (e.g., cordierite) materials. Alternatively, oxidation catalysts may be formed on to metallic or ceramic foam substrates which are well-known in the art. These oxidation catalysts, by virtue of the substrate on which they are coated (e.g., open cell ceramic foam), and/or by virtue of their intrinsic oxidation catalytic activity provide some level of particulate removal. The oxidation catalyst may remove some of the particulate matter from the exhaust stream upstream of the wall flow filter, since the reduction in the particulate mass on the filter potentially extends the time before forced regenerations.

[0097] One specific oxidation catalyst composition that may be used in the emission treatment system contains a platinum group component (e.g., platinum, palladium or rhodium components) dispersed on a high surface area, refractory oxide support (e.g., γ -alumina) which is combined

with a zeolite component (e.g., a beta zeolite). A specific platinum group metal component comprises platinum and palladium. When the composition is disposed on a refractory oxide substrate, e.g., a flow through honeycomb substrate, the concentration of platinum group metal is typically from about 10 to 150 g/ft³. In specific embodiments, the platinum group metal is typically in the range of about 20 g/ft³ to about 130 g/ft³, or about 30 g/ft³ to about 120 g/ft³, or about 40 g/ft³ to about 110 g/ft³ or about 50 g/ft³ to about 100 g/ft³. In other detailed embodiments the platinum group metal is present in a concentration greater than about 10 g/ft³, about 20 g/ft³, about 30 g/ft³, about 40 g/ft³, about 50 g/ft³, about 60 g/ft³, about 70 g/ft³, about 80 g/ft³, about 90 g/ft³, about 100 g/ft³, about 110 g/ft³ or about 120 g/ft³. In still other detailed embodiments, the platinum group metal is present in a concentration less than about 120 g/ft³, about 110 g/ft³, about 100 g/ft³, about 90 g/ft³, about 80 g/ft³, about 70 g/ft³, about 60 g/ft³, about 50 g/ft³, about 40 g/ft³, or about 30 g/ft³. In further detailed embodiments, the range of platinum group metal concentrations is between any combination of the previously listed minimum and maximum concentrations.

[0098] Platinum group metal-based compositions suitable for use in forming the oxidation catalyst are also described in U.S. Pat. No. 5,100,632 (the '632 patent) hereby incorporated by reference. The '632 patent describes compositions that have a mixture of platinum, palladium, rhodium, and ruthenium and an alkaline earth metal oxide such as magnesium oxide, calcium oxide, strontium oxide, or barium oxide with an atomic ratio between the platinum group metal and the alkaline earth metal of about 1:250 to about 1:1, and specifically about 1:60 to about 1:6.

[0099] Catalyst compositions suitable for the oxidation catalyst may also be formed using base metals as catalytic agents. For example, U.S. Pat. No. 5,491,120 (the disclosure of which is hereby incorporated by reference) discloses oxidation catalyst compositions that include a catalytic material having a BET surface area of at least about 10 m²/g and consist essentially of a bulk second metal oxide which may be one or more of titania, zirconia, ceria-zirconia, silica, alumina-silica, and α -alumina.

[0100] Also useful are the catalyst compositions disclosed in U.S. Pat. No. 5,462,907 (the '907 patent, the disclosure of which is hereby incorporated by reference). The '907 patent teaches compositions that include a catalytic material containing ceria and alumina each having a surface area of at least about 10 m²/g, for example, ceria and activated alumina in a weight ratio of from about 1.5:1 to 1:1.5. Optionally, platinum may be included in the compositions described in the '907 patent in amounts effective to promote gas phase oxidation of CO and unburned hydrocarbons but which are limited to preclude excessive oxidation of SO_2 to SO_3 . Alternatively, palladium in any desired amount may be included in the catalytic material.

NH₃-SCR Catalyst

[0101] In one specific embodiment of the present invention, the system may further comprise a NH_3 -SCR catalyst downstream of the HC-SCR catalyst. The NH_3 -SCR catalyst can prevent any NH_3 generated in the system from releasing to the environment. Suitable NH_3 -SCR catalysts can be any of the known SCR catalysts useful in the Urea-SCR application. It is advantageous that NH_3 -SCR catalyst comprising molecular sieves with CHA X-ray crystal structures (e.g. Cu-CHA, Cu-SAPO) are employed. These molecular sieves with CHA

structure exhibiting superior hydrothermal stability and durability are particularly useful in this invention.

Gasoline Lean Burn Engines

[0102] While the embodiments described above are with respect to a diesel engine having a DOC and a DPF downstream of a diesel engine, it will be appreciated that systems in accordance with one or more embodiments of the invention can be used in gasoline lean burn engines. Accordingly, an exemplary system would include a system of the type shown in FIG. 1, wherein exhaust from a lean burn engine is in flow communication with component 22, which may be a suitable catalyst for oxidizing carbon monoxides and hydrocarbons. An example of a suitable catalyst for a gasoline engine is a three-way catalyst (TWC). TWC catalysts which exhibit good activity and long life comprise one or more platinum group metals (e.g., platinum or palladium, rhodium, ruthenium and iridium) located upon a high surface area, refractory oxide support, e.g., a high surface area alumina coating.

Hydrogen Sources

[0103] In some alternative embodiments, the hydrogen may be generated by an external source or hydrogen generator. Suitable hydrogen sources include, but are not limited to, electrolyzers, plasma reformers, thermal decomposition devices, steam reformers, compressed gases container and liquefied gases containers.

[0104] Electrolyzers, such as proton exchange membranes (PEM), can be used to produce hydrogen on board the a vehicle. The PEM splits water into hydrogen and oxygen molecules which can then be compressed and injected into the exhaust. PEM systems require only small amounts of water maintained in the system.

[0105] Plasma reformers convert gaseous hydrocarbons, like gasoline, diesel fuel, methane, ethane, etc., to hydrogen. A reaction chamber is charged with sufficient fuel and air and a plasma is ignited. The plasma based reaction results in hydrogen evolution. The hydrogen evolution can be optimized with catalytic components.

[0106] Thermal decomposition devices can crack, or pyrolyze, fuel to yield hydrogen and carbon oxide species. Thermal decomposition generally requires high temperatures for efficient conversion.

[0107] Steam reformers can generate hydrogen by reacting fuel with water. The reaction is exothermic, resulting in an increased reaction rate. Like electrolysis, a small onboard water source is required for this type of hydrogen injector.

Example

[0108] To illustrate the effect of hydrogen present in the exhaust, separate experiments were conducted with an engine aged HC-SCR catalyst sample in a laboratory reactor. A simulated diesel exhaust containing 450 ppm carbon C1 (as diesel), 150 ppm NO, 5% CO₂, 5% H₂O, 10% O₂ balance N₂ was introduced to a core sample taken from the inlet section of an engine aged HC-SCR catalyst sample at 30,000 hr⁻¹. The evaluations were conducted with a down ramp of the catalyst inlet temperature from 500° C. to 260° C. The HC-SCR catalyst sample was silver containing monolithic catalyst. A 1 M solution of silver nitrate was prepared using deionized water. The resulting solution was stored in a dark bottle away from light sources. The available pore volume of the various supports was determined by titrating the bare support with

water while mixing until incipient wetness was achieved. This resulted in a liquid volume per gram of support. Using the final target Ag₂O level and the available volume per gram of support, the amount of 1M AgNO₃ solution needed was calculated. DI water was added to the silver solution, if needed, so that the total volume of liquid was equal to amount needed to impregnate the support sample to incipient wetness. If the amount of AgNO₃ solution needed exceeds the pore volume of the support, then multiple impregnations were done.

[0109] The appropriate AgNO₃ solution was added slowly to the support with mixing. After incipient wetness is achieved, the resulting solid was dried at 90° C. for 16 h, then calcined at 540° C. for 2 hours. The catalyst was also optionally subjected to a flowing stream of about 10% steam in air for at least about, typically about 16 hours at 650° C.

[0110] Catalysts were prepared as described above using commercially available pseudoboehmite (Catapal® C1, 270 m²/g, 0.41 cc/g pore volume, 6.1 nm average pore diameter, produced by Sasol, North America) and boehmite (P200 (from Sasol), 100 m²/g, 0.47 cc/g pore volume, 17.9 nm average pore diameter) alumina supports. Each alumina was processed until the silver content of the finished catalyst was about 3% by weight on an Ag₂O basis. A monolith having about 300 cells per square inch was washcoated with the alumina, resulting in a loading of about 2 g/in³. The HC-SCR catalyst was placed in front of a DOC/DPF in a configuration in an engine exhaust system and aged on an engine for 50 hours. During the aging, a number of fuel burning cycles to simulate the regeneration of DOC/DPF were employed.

[0111] The NOx conversion results are shown in FIG. 13. The engine aged sample as received without any treatment shows about 20% NOx conversion in the entire temperature range evaluated. The catalyst exhibits 10% better NOx conversion at 500° C., 20% better NOx conversion at 400° C., and 50% better NOx conversion at 300° C. when 1000 ppm H₂ is introduced into the simulated exhaust. The presence of hydrogen in the exhaust drastically enhances the NOx performance of the severely deactivated catalyst.

[0112] While this invention has been described with an emphasis upon preferred embodiments, it will be obvious to those of ordinary skill in the art that variations in the preferred devices and methods may be used and that it is intended that the invention may be practiced otherwise than as specifically described herein. Accordingly, this invention includes all modifications encompassed within the spirit and scope of the invention as defined by the claims that follow.

What is claimed is:

1. An emissions treatment system for NOx abatement in an exhaust stream from a lean burn engine, comprising:

- a main exhaust conduit in flow communication with the engine exhaust stream, and a hydrocarbon selective catalytic reduction catalyst (HC-SCR) in flow communication with the main exhaust conduit;
- a slip exhaust stream conduit branched off of the main exhaust conduit connected to the main exhaust conduit by a first junction to divert a portion of the exhaust stream from the main exhaust conduit into the slip exhaust stream conduit to provide a slip exhaust stream to flow through a catalytic partial oxidation (CPO) catalyst in flow communication with the slip exhaust stream conduit, and second junction downstream from the first junction to reintroduce the slip exhaust stream to the main exhaust conduit upstream of the HC-SCR; and

a hydrocarbon injector upstream of the CPO, wherein the CPO is effective to convert a portion of the hydrocarbons to carbon monoxide and hydrogen.

2. The emissions treatment system of claim 1, wherein the CPO is designed to provide sufficient hydrogen and adequate amount of hydrocarbons for the downstream HC-SCR catalyst.

3. The emissions treatment system of claim 1, wherein the hydrocarbon injector device includes a metering device adapted to control the amount of hydrocarbon injected into the slip exhaust stream conduit.

4. The emissions treatment system of claim 1, wherein the hydrocarbon is fuel.

5. The emissions treatment system of claim 1, wherein the portion of the exhaust gas diverted into the slip exhaust stream conduit is up to about 10% of the total exhaust flow.

6. The emissions treatment system of claim 1, further comprising a metering device at the first junction of the slip exhaust stream conduit to regulate the percentage of exhaust gas diverted to the slip exhaust stream conduit.

7. The emissions treatment system of claim 6, wherein the percentage of exhaust gas diverted to the slip exhaust stream conduit is regulated up to about 10% of the total exhaust flow.

8. The emissions treatment system of claim 1, wherein the CPO catalyst contains platinum group metals.

9. The emissions treatment system of claim 8, where the platinum group metals of CPO catalyst are selected from of platinum, palladium, rhodium and mixtures thereof.

10. The emissions treatment system of claim 1, wherein one or both of the CPO catalyst and the HC-SCR are disposed on a flow through monolith.

11. The emissions treatment system of claim 1, further comprising a diesel particulate filter (DPF) downstream of the HC-SCR catalyst.

12. The emissions treatment system of claim 1, further comprising a diesel particulate filter (DPF) upstream of the HC-SCR catalyst.

13. The emissions treatment system of claim 12, wherein the diesel particulate filter (DPF) is located between the first junction and the second junction in flow communication of the main exhaust conduit.

14. The emissions treatment system of claim 11, further comprising a diesel oxidation catalyst (DOC) upstream of the DPF and HC-SCR catalyst.

15. The emissions treatment system of claim 12, further comprising a diesel oxidation catalyst (DOC) upstream of the DPF and HC-SCR catalyst.

16. The emissions treatment system of claim 13, further comprising a diesel oxidation catalyst (DOC) upstream of the DPF and HC-SCR catalyst.

17. The emissions treatment system of claim 14, wherein the diesel oxidation catalyst (DOC) is located downstream of the first junction in flow communication with the main exhaust conduit.

18. The emissions treatment system of claim 15, wherein the diesel oxidation catalyst (DOC) is located downstream of the first junction in flow communication with the main exhaust conduit.

19. The emissions treatment system of claim 16, wherein the diesel oxidation catalyst (DOC) is located downstream of the first junction in flow communication with the main exhaust conduit.

20. The emissions treatment system of claim 13, wherein the diesel oxidation catalyst (DOC) is located downstream of the first junction and upstream of the DPF and in flow communication with the main exhaust conduit.

21. The emissions treatment system of claim 20, wherein the DOC and DPF are integrated into a single component.

22. The emissions treatment system of claim 1, further comprising a NH₃-SCR catalyst downstream of the HC-SCR catalyst.

23. The emissions treatment system of claim 1, further comprising an oxidation catalyst downstream of the HC-SCR catalyst.

24. A method of treating an exhaust stream comprising: passing the exhaust stream through a main exhaust conduit and a portion of the exhaust stream through a slip exhaust stream conduit, the main exhaust conduit comprising a hydrocarbon selective catalytic reduction catalyst (HC-SCR), the slip exhaust stream conduit comprising a catalytic partial oxidation (CPO) catalyst, the slip exhaust stream conduit branching-off of the main exhaust conduit at a first junction and in flow communication with the CPO, the slip exhaust stream conduit rejoining the main exhaust conduit at a second junction upstream of the HC-SCR, a hydrocarbon injector upstream of the CPO, where the CPO is adapted to convert a portion of the hydrocarbons to carbon monoxide and hydrogen.

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