AN ALUMINA-BASED LEAN NOX TRAP SYSTEM AND METHOD OF USE IN DUAL-MODE HCCI ENGINES

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An alumina-based lean NOx trap system for use in a HCCI engine exhaust is provided which includes at least one alumina-based lean NOx trap comprising a catalyst, an alumina NOx absorbent material, and optionally, from 0 to about 4 wt % of an alkaline earth metal oxide; and a conventional three-way catalyst. The lean NOx trap system substantially oxidizes HC and CO and converts at least a portion of NOx contained in the exhaust gas to N2 at a temperature between about 150° C. to about 250° C. in HCCI mode. The system also effectively removes HC, CO and NOx at high temperature when the engine is in SI mode (stoichiometric conditions). The alumina-based lean NOx trap in the system also undergoes efficient desulphurization and maintains its activity with extended use.
**Fig. 3**

Engine Exhaust → Al LNT → TWC → Al LNT

12 14 18

**Fig. 4**

De-Sox of alumina-based LNT + a typical TWC at 650°C

\( \lambda = 0.984 \)

![Graph showing concentration of SO2, NO, COS, H2S, and O2 over time.](image)
ALUMINA-BASED LEAN NOX TRAP SYSTEM AND METHOD OF USE IN DUAL-MODE HCCI ENGINES

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Application No. 60/649,331, entitled SYSTEM FOR TREATING EMISSIONS FROM DIESEL EXHAUST GAS, filed Feb. 2, 2005. The entire contents of said application are hereby incorporated by reference.

BACKGROUND OF THE INVENTION

[0002] The present invention relates to a lean NOx trap system for treating emissions from dual-mode HCCI engines, and more particularly, to a system including at least one lean NOx trap which utilizes alumina as a NOx storage material. The alumina-based lean NOx trap achieves high NOx, HC and CO conversion efficiencies at the low temperatures encountered in the lean exhaust gas of HCCI engines. In addition, the alumina-based lean NOx trap maintains its activity with extended use and undergoes efficient desulphurization.

[0003] Government regulations, created in response to environmental and health concerns, have necessitated the treatment of exhaust gas from vehicle engines in order to reduce the level of certain combustion by-products, including carbon monoxide (CO), hydrocarbons (HC), and nitrogen oxides (NOx). In conventional gasoline engines (i.e., engines that operate at a stoichiometric air-to-fuel ratio), such treatment generally includes the use of a three-way catalyst (TWC). In recent years, the development of HCCI (homogeneous-charge-compression-ignition) engines has been found to have the potential to significantly improve fuel efficiency (up to 50%) over conventional gasoline engines which operate in an SI (spark-ignition) mode. In such engines, the charge is compression-ignited, and the engine runs in very lean conditions (λ from about 30 to 80, where λ represents the actual air/fuel ratio divided by the stoichiometric air/fuel ratio), or in highly diluted conditions (very large residual gas fraction), which provides high efficiency, low emissions of NOx and low cost when compared with a diesel engine.

[0004] However, at high loads, operation of the engine in HCCI mode is difficult. Accordingly, it is common for the HCCI engine to employ both SI and HCCI combustion mode technology (referred to herein as HCCI-SI or dual-mode), which allows the engine to operate in HCCI mode to achieve high fuel efficiency and low NOx emissions at low and medium loads, and then switch to SI mode at higher loads.

[0005] However, such a dual-mode engine requires a treatment system for emissions in order to meet future emission regulations. When the dual-mode engine is in SI mode, it is relatively easy to reduce emissions with the use of a conventional three-way catalyst due to the high exhaust temperature (about 450 to 600° C.) and stoichiometric air/fuel ratio in the exhaust gas. In the SI mode, such a three-way catalyst is effective in reducing HC, CO and NOx.

[0006] However, during HCCI mode, the exhaust temperature is low, ranging from about 150 to 250° C. (engine out temperature is from about 190 to 300° C.), and the exhaust gas is very lean. A three-way catalyst cannot effectively reduce the level of NOx, CO and HC under these conditions. In addition, the engine exhaust has a large variation, with NOx ranging from 2 to 150 ppm, CO from 300 to 6000 ppm, and HC from 1000 to 4000 ppm. Thus, when the engine operates in HCCI mode, a treatment system is needed which can operate efficiently at low temperatures (150 to 250° C.) to oxidize HC, CO and to reduce NOx (when NOx concentration is higher than a certain threshold level) under lean conditions.

[0007] Lean NOx traps (LNTs), which conventionally include a catalyst comprising one or more precious metals and an alkaline earth metal oxide provided on a support material such as alumina, are known for use in lean-burn engines. Such LNTs are capable of absorbing or storing nitrogen oxides during lean-burn engine operation. Periodically, engine operation changes in order to release and reduce NOx to nitrogen when the exhaust gas is in rich condition. However, conventional lean NOx traps currently in use are most effective at an operating temperature range of about 200° C. to about 500° C., while the exhaust gas temperature (catalyst inlet) during HCCI mode is typically less than 200° C. Thus, a conventional LNT cannot remove NOx in HCCI exhaust gas.

[0008] Another disadvantage of conventional LNTs is that they become poisoned over time by the accumulation of sulfur (SOx) on the LNT due to combustion of the sulfur contained in the fuel. Accordingly, it is necessary to perform a periodic (about every 5,000 miles) desulphurization (de- SOx) procedure to maintain the activity and effectiveness of the trap. However, desulphurization of a conventional LNT requires high temperatures (650° C. to 800° C.) for relatively long times (5 to 10 minutes). This thermally damages the conventional LNT with each de-SOx cycle, which reduces the activity of the LNT. In addition, the de-SOx process results in a considerable fuel consumption penalty (up to 5%).

[0009] Accordingly, there is still a need in the art for a system of treating exhaust emissions from a dual-mode HCCI engine which provides effective treatment at the lower temperatures encountered during the HCCI mode of the engine, which maintains its activity with extended use, and which undergoes efficient desulphurization.

SUMMARY OF THE INVENTION

[0010] The present invention meets those needs by providing a lean NOx trap (LNT) system for use in a dual-mode HCCI engine which includes at least one lean NOx trap which utilizes alumina as a NOx storage (absorbent) material. The alumina-based LNT, when incorporated in a HCCI engine exhaust system along with a conventional three-way catalyst, effectively converts HC, CO and NOx at the low temperatures (about 150° C.) encountered during the HCCI operational mode of such engines. In addition, the alumina-based LNT system functions as an oxidation catalyst in the HCCI engine exhaust and provides effective oxidation of HC and CO (above 90%) at low exhaust temperature. Furthermore, the alumina-based LNT maintains its activity with extended use and undergoes efficient desulphurization.

[0011] When the engine operates in SI mode, the engine exhaust gas is at stoichiometric conditions with high tem-
temperatures (500 to 600° C.), and the gas includes all three pollutants (HC, CO and NOx). For such conditions, the three-way catalyst in the lean NOx trap system of the present invention effectively converts these pollutants.

[0012] According to one aspect of the present invention, a lean NOx trap system for use in a HCCI engine is provided. The system comprises a first lean NOx trap comprising a catalyst, a NOx absorbent material comprising alumina, and optionally, from 0 to 4 wt % of an alkaline earth metal oxide (also referred to herein as an alumina-based LNT); and a three-way catalyst.

[0013] The lean NOx trap system oxidizes HC and CO, and converts at least a portion of NOx contained in lean exhaust gas from the engine exhaust to N2 at a temperature range of between about 150° C. to about 250° C. The system preferably has a NOx conversion efficiency of at least 50% at a temperature between about 150° C. to about 250° C. In addition, the system has a conversion efficiency for HC and CO of at least 70% in lean conditions at a temperature between about 150° C. to about 250° C. By conversion efficiency, it is meant the difference between the levels of NOx, HC and CO entering the trap and leaving the trap divided by the level entering the trap, multiplied by 100%.

[0014] Preferably, the alumina-based lean NOx trap comprises from 0 to about 4.0 wt % of the alkaline earth metal oxide, which is preferably selected from Mg, Sr, Ba, and Ca.

[0015] The catalyst in the alumina-based LNT is preferably selected from platinum, rhodium, and combinations thereof. The alumina-based lean NOx trap preferably further includes less than about 4 wt % of a stabilizing metal selected from La, Ce, and Ba.

[0016] In the system of the present invention, the three-way catalyst is preferably positioned downstream from the lean NOx trap. Alternatively, the alumina-based lean NOx trap and the three-way catalyst may be combined.

[0017] In an alternative embodiment of the invention, a second alumina-based lean NOx trap may be included in the system. In this embodiment, the second alumina-based lean NOx trap is positioned downstream from the three-way catalyst.

[0018] The present invention further provides a method for treating HCCI engine exhaust gases which comprises providing a lean NOx trap system in an exhaust gas passage of a HCCI engine, where the system comprises a first lean NOx trap comprising a catalyst, a NOx absorbent material comprising alumina, and optionally, from 0 to 4.0 wt % of an alkaline earth metal oxide; and a three-way catalyst.

[0019] The lean NOx trap system is exposed to lean HCCI engine exhaust gas containing HC, CO and NOx such that the HC and CO is substantially oxidized and at least a portion of the NOx contained in the exhaust gas is converted to N2 at a temperature between about 150° C. to 250° C. By “substantially oxidized,” it is meant that at least 85% of the HC and CO is oxidized.

[0020] It should be noted that when the lean NOx trap system is exposed to SI engine exhaust gas (stoichiometric) containing HC, CO and NOx, the HC, CO and NOx are converted to H2O, CO2 and N2 at a temperature above about 450° C. During the transition of HCCI mode to SI mode, this system can oxidize HC and CO at low temperature (<350° C.) and raise the temperature of the exhaust gas to shorten the light-off time of the downstream three-way catalyst.

[0021] In one embodiment of the method, the three-way catalyst is positioned downstream from the first lean NOx trap. In another embodiment, the first lean NOx trap is positioned downstream from the three-way catalyst. In yet another embodiment, the lean NOx trap and three-way catalyst are combined. In yet another embodiment of the method, a second alumina-based lean NOx trap is included in the system which is positioned downstream from the three-way catalyst.

[0022] The present invention also provides a method for desulfurization of an alumina-based lean NOx trap system used in a HCCI engine, where the system comprises at least one lean NOx trap comprising a catalyst, a NOx absorbent material comprising alumina, and optionally, from 0 to about 4.0 wt % of an alkaline earth metal oxide, and a three-way catalyst.

[0023] In the desulfurization method, the LNT system is exposed to exhaust gases in the HCCI engine. The exhaust gases are heated to a temperature of between about 550 and 650° C. for at least 60 seconds by operating the engine in SI mode. Preferably, during desulfurization, λ is between about 0.98 and 0.99. The desulfurization of the lean NOx trap system causes the alumina-based lean NOx trap to release a sulfur product comprising at least 90% SO2. In addition, the alumina-based lean NOx trap maintains its activity after the desulfurization process.

[0024] Accordingly, it is a feature of the present invention to provide a lean NOx trap system including an alumina-based lean NOx trap which operates effectively at the low temperatures and lean conditions encountered in the HCCI operational mode of dual-mode HCCI engines, which maintains its activity over time, and which undergoes efficient desulfurization. It is a further feature of the invention to provide a lean NOx trap system including a three-way catalyst which operates effectively at the high temperatures and stoichiometric conditions encountered in the SI operational mode of dual-mode HCCI engines. Other features and advantages will be apparent from the following description and the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0025] FIG. 1 is a schematic illustration of the system of the present invention including an alumina-based LNT and a conventional three-way catalyst;

[0026] FIG. 2 is a schematic illustrations of the system including a first alumina-based LNT and a three-way catalyst which are combined on a single brick; and

[0027] FIG. 3 is a schematic illustration of the system including first and second alumina-based LNTs and a three-way catalyst; and

[0028] FIG. 4 is a graph illustrating the desulfurization (de-SO2) performance of system of the present invention including the alumina-based LNT and a three-way catalyst at 650° C. and λ=0.984.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

[0029] We have found that the use of alumina as a NOx storage (absorbent) material in a lean NOx trap provides
more efficient release of NO\textsubscript{x} at low temperatures than conventional lean NO\textsubscript{x} traps which utilize alkali metal oxides or alkaline earth metal oxides as NO\textsubscript{x} storage materials. Because alkali metals and alkaline earth metals are very basic in nature, such storage materials have a strong interaction with NO\textsubscript{x}, which interaction takes place at higher temperatures. As alumina has a relatively weak interaction with NO\textsubscript{x}, it can absorb and release NO\textsubscript{x} at much lower temperatures. While alumina has been widely used in conventional LNTs as a support material for catalysts, such LNTs include large amounts (e.g., about 20 to 35 wt %) of alkali metal oxides and/or alkaline earth metal oxides. Such large amounts of metal oxides dominate the NO\textsubscript{x} absorption properties of the LNT, thus determining the activity of the LNT and its other properties, i.e., operating temperature window, de-NO\textsubscript{x} temperature, etc.

[0035] We have found that the use of an alumina-based lean NO\textsubscript{x} trap system including at least one alumina-based trap containing little or no alkaline earth metal oxides allows the alumina to dominate the NO\textsubscript{x} absorption properties of the lean NO\textsubscript{x} trap, resulting in high NO\textsubscript{x} conversion efficiency at relatively low temperatures, e.g., about 150° C. to 200° C. The alumina-based LNT is also resistant to degradation by aqueous-based processes previously found to cause conventional traps to lose a substantial fraction of their initial NO\textsubscript{x} storage capacity. The catalysts (Pt, Rh, etc.) in the alumina-based LNT also function as very good HC and CO oxidation catalysts in lean conditions to remove HC and CO at low temperatures (above 150° C.).

[0036] In addition, we have found that because the alumina-based LNT has very strong oxidation capability at low temperatures, it can shorten the light-off time for the three-way catalyst when the engine operation transits from HCCI mode (≤200° C.) to SI mode (about 500 to 600° C.) by burning off the HC and CO and raising the exhaust temperature before the three-way catalyst lights off downstream from the LNT.

[0037] Desulphurization (de-NO\textsubscript{x}) of the alumina-based LNT system is also achieved more efficiently than in a conventional LNT as desulphurization can take place at lower temperatures for much shorter periods of time. The alumina-based LNT system of the present invention is resistant to SO\textsubscript{2} poisoning since the alumina-based LNT does not degrade when subjected to the desulphurization process. Also, production of unwanted H\textsubscript{2}S during desulphurization is minimized.

[0038] The alumina-based lean NO\textsubscript{x} trap of the present invention is preferably prepared by coating a cordierite monolith with a catalyst washcoat (about 5 to 7 kg/m\textsuperscript{3}) comprising from about 95 to 99% by weight alumina. Optionally, a stabilizing metal comprising less than about 4% by weight of the total washcoat may be added to stabilize the alumina surface area during the high-temperature exposure and to increase the durability of the LNT. Suitable stabilizing metals include La, Ce, and Ba.

[0039] In addition, the alumina-based lean NO\textsubscript{x} trap optionally includes from 0 to about 4.0% by weight of the total washcoat of an alkaline earth metal oxide. Preferred alkaline earth metals include Mg, Sr, Ba, and Ca. The alkaline earth metal oxide may be included in the LNT for the purpose of shifting the operating temperature window of the LNT, for example, to achieve higher operating temperatures.

[0040] We have found that the addition of such a small amount of an alkaline earth metal oxide (i.e., less than about 4.0 wt %) does not impact the basic properties of the alumina-based LNT, e.g., high NO\textsubscript{x} conversion efficiency at low temperatures and efficient desulphurization of the LNT. The alkaline earth metal oxide may be added to the washcoat by a conventional aqueous solution ion exchange method. For example, the alumina coated monolith is ion exchanged from one to four times with an aqueous solution of Ca\textsubscript{2+}. In the present invention, a (Ca(NO\textsubscript{3})\textsubscript{2}) solution is preferred. The ion exchanges are preferably carried out at room temperature with solutions of 0.5 mol/L. After each solution ion exchange step, the coated monolith is preferably washed, dried, and calcined at about 773° K for about 4 hours prior to performing the next ion exchange step.

[0041] Precious metal catalysts are then added to the washcoated monolith. Preferred for use in the present invention are Pt and Rh, which may be added at loadings of about 100 g Pt/m\textsuperscript{3} and 20 g Rh/m\textsuperscript{3}. The precious metals are loaded onto the alumina coated monolith by the Subtractive Deposition Method, which includes 1) measuring the volume of the monolith and calculating the amount (Mg) of precious metal compound (e.g., H\textsubscript{2}PtCl\textsubscript{6}) needed for the monolith to reach a certain precious metal loading (e.g., 100 g Pt/m\textsuperscript{3}); 2) measuring the total volume (V\textsubscript{H\textsubscript{2}O}) of water that can be absorbed by the washcoat onto the monolith at room temperature; 3) preparing a solution of the precious metal compound with the concentration Mol/V\textsubscript{H\textsubscript{2}O}; 4) dipping the monolith into the prepared solution with a total volume of 2.5 times V\textsubscript{H\textsubscript{2}O} at room temperature, wetting the monolith thoroughly, blowing away the residual solution and drying the monolith at 130° C. for 1 hour; and 5) where the precious metal compounds contain chlorine, removing the chlorine (Cl) at 500° C. in a flow reactor with a mixed gas of 1% H\textsubscript{2} and 10% H\textsubscript{2}O balanced by nitrogen for 4 hours. Where more than one precious metal is loaded onto the same monolith, the procedure is repeated.

[0042] The three-way catalyst included in the system is preferably a conventional three-way catalyst which is well known in the art and typically comprises Pt, Pd and Rh on an alumina or silica support.

[0043] Referring now to FIG. 1, the lean NO\textsubscript{x} trap system 10 of the present invention is illustrated, which, in a preferred embodiment, includes an alumina-based lean NO\textsubscript{x} trap 12 and a three-way catalyst 14. The system is preferably coupled to the HCCI engine such that exhaust gases flow through an exhaust manifold into the system 10.

[0044] As shown, the three-way catalyst is positioned downstream from the alumina-based lean NO\textsubscript{x} trap. Alternatively, the alumina-based lean NO\textsubscript{x} trap may be positioned downstream from the three-way catalyst. In yet another alternative embodiment, the alumina-based trap and the three-way catalyst may be combined on a single brick 16 as shown in FIG. 2. This may be achieved by coating a single catalyst brick with two different compositions, i.e., the alumina-based LNT composition and a conventional three-way catalyst composition. In the embodiment shown, the alumina-based LNT is positioned in front of the three-way catalyst; however, it should be appreciated that the three-way catalyst may also be positioned in front of the alumina-based LNT.

[0045] Referring now to FIG. 3, an alternative embodiment of the invention is illustrated in which the system
comprises first and second alumina-based lean NO\(_x\) traps (12, 18) in addition to a three-way catalyst 14, where the second lean NO\(_x\) trap is positioned downstream from the three-way catalyst.

[0041] In use, the system of the present invention including at least one alumina-based LNT is placed in the exhaust of a vehicle having a HCCI engine. The system is exposed to the exhaust gas such that HC and CO contained in the gas is oxidized and at least a portion of the NO\(_x\) in the gas is converted to N\(_2\), preferably at a temperature between about 150° C. and 250° C. (HCCI mode). When the engine operates in SI mode, the engine exhaust gas is at stoichiometric conditions with high temperatures (500 to 600° C.), such that the three-way catalyst in the lean NO\(_x\) trap system of the present invention effectively converts HC, CO and NO\(_x\).

[0042] It should be noted that in instances where the lean burn exhaust gas temperature exceeds the operating temperature window of the first LNT (150 to 300° C.), the second alumina-based LNT, which is at a lower inlet temperature, can perform the NO\(_x\) reduction under lean conditions.

[0043] It should also be noted that when the engine operation mode switches from SI mode to medium HCCI mode, if the first LNT is exposed to a temperature higher than its operating temperature window (above 350° C.), the second alumina-based LNT located downstream from the three-way catalyst can be active in reducing NO\(_x\) since the second LNT is located at such a distance away from the first LNT that its inlet temperature is at least 100° C. lower than that of the first LNT.

[0044] A desulphurization (de-SO\(_x\)) process may be performed on the system when the sulfur content on the alumina-based lean NO\(_x\) trap reaches a certain threshold level (HT). This threshold level is determined by the amount of SO\(_x\) storage materials in the trap, the temperature, the inlet SO\(_x\) level, the exhaust gas flow rate, the operating history of the trap, etc. The de-SO\(_x\) timing may also be determined by a SO\(_x\) sensor (not shown) which may be positioned downstream from the alumina-based LNT.

[0045] Each time the engine switches from HCCI mode to SI mode during normal operations (except the rich time during the lean/rich cycle for lean NO\(_x\) trap operation) a de-SO\(_x\) process should be performed unless the sulfur content on the LNT is below a low threshold value (LT) since the de-SO\(_x\) condition is easily achieved when the engine is in SI mode.

[0046] The alumina-based trap of the present invention has a unique de-SO\(_x\) procedure which is believed to occur because of a weak interaction between the SO\(_x\) and the alumina-based storage materials. The release of sulfur from the alumina-based trap is very efficient and provides the advantage of minimum thermal exposure and fuel penalty during de-SO\(_x\) over the use of a conventional LNT alone.

[0047] During the desulphurization process, exhaust gases in the alumina-based lean NO\(_x\) trap 12 are heated to a temperature of between about 550° C. and about 650° C. for at least 60 seconds (during SI mode). The resulting de-SO\(_x\) product is comprised mainly of SO\(_2\) (more than 90 wt %), which is a more favorable sulfur product than the H\(_2\)S product typically achieved with de-SO\(_x\) of a conventional LNT.

[0048] In order that the invention may be more readily understood, reference is made to the following examples which are intended to illustrate the invention, but not limit the scope thereof.

EXAMPLE 1

A lean NO\(_x\) trap system in accordance with the present invention comprising an alumina-based LNT and a three-way catalyst was applied to simulated dual mode HCCI exhaust gases in a laboratory reactor to verify the efficiencies of the system in converting the pollutants in various engine operation modes. Table 1 below lists the emission data and exhaust gas temperatures from a single cylinder dual mode HCCI engine at different engine modes (#1 to #5), and the emission results after the alumina-based LNT and three way catalyst.

<table>
<thead>
<tr>
<th>Engine Operation Mode</th>
<th>Engine out emission</th>
<th>After catalyst (Lab results)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1 - HCCI</td>
<td>AF ratio = 94</td>
<td>T catalyst inlet = 150° C.</td>
</tr>
<tr>
<td></td>
<td>T engine out = 190° C.</td>
<td>NO(_x) = 0 ppm; HC = 0 ppm</td>
</tr>
<tr>
<td></td>
<td>NO(_x) = 5 ppm; HC = 1100 ppm</td>
<td>CO = 0.001 ppm</td>
</tr>
<tr>
<td>#2 - HCCI</td>
<td>AF ratio = 96</td>
<td>T catalyst inlet = 180° C.</td>
</tr>
<tr>
<td></td>
<td>T engine out = 190° C.</td>
<td>lean/rich (30/4)</td>
</tr>
<tr>
<td></td>
<td>NO(_x) = 10 ppm; HC = 1500 ppm</td>
<td>NO(_x) = 4.0 ppm; HC = 150 ppm</td>
</tr>
<tr>
<td></td>
<td>CO = 7 ppm</td>
<td>CO = 8 ppm</td>
</tr>
<tr>
<td>#3 - HCCI</td>
<td>AF ratio = 34</td>
<td>T catalyst inlet = 170° C.</td>
</tr>
<tr>
<td></td>
<td>T engine out = 230° C.</td>
<td>lean/rich (60/4)</td>
</tr>
<tr>
<td></td>
<td>NO(_x) = 5 ppm; HC = 3500 ppm</td>
<td>NO(_x) = 1.0 ppm; HC = 180 ppm</td>
</tr>
<tr>
<td></td>
<td>CO = 10 ppm</td>
<td>CO = 9 ppm</td>
</tr>
<tr>
<td>#4 - SI</td>
<td>AF ratio = 14.7</td>
<td>T catalyst inlet = 500° C.</td>
</tr>
<tr>
<td></td>
<td>T engine out = 590° C.</td>
<td>NO(_x) = 0 ppm; HC = 18 ppm</td>
</tr>
<tr>
<td></td>
<td>NO(_x) = 2000 ppm; HC = 5000 ppm; CO = 12,500 ppm</td>
<td>CO = 35 ppm</td>
</tr>
</tbody>
</table>

TABLE 1
TABLE 1-continued

<table>
<thead>
<tr>
<th>Engine Operation Mode</th>
<th>Engine out emission</th>
<th>After catalyst (Lab results)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#5 - SI</td>
<td>AF ratio = 14.6</td>
<td>T catalyst inlet = 500°C</td>
</tr>
<tr>
<td></td>
<td>T engine out = 600°C</td>
<td>NOx = 0 ppm; HC = 32 ppm</td>
</tr>
<tr>
<td></td>
<td>NOx = 2000 ppm</td>
<td>CO = 12 ppm</td>
</tr>
<tr>
<td></td>
<td>HC = 8000 ppm</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CO = 9500 ppm</td>
<td></td>
</tr>
</tbody>
</table>

[0050] At engine mode #1—HCCI with relatively low loads, NOx concentration was low (3 ppm) and engine out temperature was at 190°C, the catalyst system was running at 150°C in lean conditions and effectively removed all the pollutants. At mode #2—HCCI with medium loads, engine exhaust temperature of about 240°C, and NOx concentration at about 140 ppm, a lean/rich cycle of 30 second lean/4 second rich was applied to the system at about 180°C. The NOx, HC and CO had high conversion efficiencies (above 90%). Mode #3—HCCI with a NOx concentration of 80 ppm, and a lean/rich cycle of 60/4 was applied to the LNT system. The pollutants (HC, CO and NOx) were converted at high efficiencies (above 90%). Modes #4 and #5—SI with stoichiometric conditions (air/fuel ratio of about 14.7) at high temperature (600°C). The pollutants were converted efficiently (above 90%) by the three way catalyst without running the lean/rich cycle.

[0051] It is clear that in the median engine loads when the engine operates in HCCI mode, the NOx concentration in the lean exhaust gas is relatively high such that the lean/rich cycles are needed for converting the NOx in the lean exhaust gas, e.g., the LNT system functions as a lean NOx trap. The lean/rich cycle can be realized by quickly switching the engine from HCCI mode to SI mode. The ratio of the lean/rich time can be adjusted with the feedback of in-situ NOx conversion efficiencies (e.g. obtained by one or more downstream NOx sensors) compared with the engine out NOx concentration (which is measured either by a NOx sensor upstream of the catalyst system or from engine map) by changing the length of rich time and the frequency (length of the lean time) to reach the minimum fuel penalty (R-x/y, the higher, the R, the less the fuel penalty) and maximum NOx conversion efficiency (see commonly assigned U.S. application Ser. No. ____ entitled ALUMINA-BASED LEAN NOx TRAP SYSTEM AND METHOD OF USE, the disclosure of which is hereby incorporated by reference).

[0052] During the low load of HCCI mode (mode #1—HCCI), when the NOx concentration is low (e.g., <10 ppm), the lean/rich cycle is not needed (a NOx sensor for measuring the engine out NOx or engine mapping can provide guidance if lean/rich cycle is necessary), and the catalyst system of present invention can effectively convert HC and CO in lean condition (above 150°C). When the engine operates at SI mode (modes #4 and #5—SI), these are also no need of modification of the air/fuel ratio (or lean/rich cycle). Since the exhaust gas is at stoichiometric (air/fuel ratio about 14.7) and high temperature (500 to 600°C), the three way catalyst can effectively remove the pollutants (HC, CO and NOx).

[0053] FIG. 4 illustrates the de-SOX process of the LNT system of the present invention (with sulfur loading of 1.14 gram/liter) under the unique de-SOX method of the alumina-based LNT. It is clear that sulfur can be removed (out of the system) very efficiently (in about 60 seconds) at 550 to 650°C under slightly rich condition without being captured by the downstream three way catalyst.

[0054] While certain representative embodiments and details have been shown for purposes of illustrating the invention, it will be apparent to those skilled in the art that various changes in the methods and apparatus disclosed herein may be made without departing from the scope of the invention, which is defined in the appended claims.

What is claimed is:

1. A lean NOx trap system for use in a HCCI engine exhaust comprising:
   a first lean NOx trap comprising a catalyst, a NOx absorbent material comprising alumina, and optionally, from 0 to about 4 wt % of an alkaline earth metal oxide; and a three-way catalyst; wherein said system oxidizes HC and CO and converts at least a portion of NOx contained in exhaust gas from said engine to N2 at a temperature range of between about 150°C to about 250°C.

2. The system of claim 1 wherein said catalyst in said lean NOx trap is selected from platinum, rhodium, and combinations thereof.

3. The system of claim 1 having a NOx conversion efficiency of at least 50% at a temperature between about 150°C to about 250°C.

4. The system of claim 1 having a HC and CO conversion efficiency of at least 70% at a temperature between about 150°C to about 250°C.

5. The system of claim 1 wherein said catalyst in said first lean NOx trap is selected from platinum, rhodium, and combinations thereof.

6. The system of claim 1 wherein said alkaline earth metal in said metal oxide is selected from Mg, Sr, Ba, and Ca.

7. The system of claim 1 wherein said lean NOx trap further includes less than about 4 wt % of a stabilizing metal selected from La, Ce, and Ba.

8. The system of claim 1 wherein said three-way catalyst is positioned downstream from said lean NOx trap.

9. The system of claim 1 wherein said lean NOx trap and said three-way catalyst are combined.

10. The system of claim 1 further including a second lean NOx trap comprising a catalyst, a NOx absorbent material comprising alumina, and optionally, from 0 to 4 wt % of an alkaline earth metal oxide.
11. The system of claim 10 wherein said second lean NO\textsubscript{x} trap is positioned downstream from said three-way catalyst.

12. A method for treating HCCI engine exhaust gases comprising:

- providing a lean NO\textsubscript{x} trap system in an exhaust gas passage of a HCCI engine said system comprising a first lean NO\textsubscript{x} trap comprising a catalyst, a NO\textsubscript{x} absorbent material comprising alumina, and optionally, from 0 to about 4 wt % of an alkaline earth metal oxide; and a three-way catalyst;
- exposing said lean NO\textsubscript{x} trap system to HCCI engine exhaust gas containing NO\textsubscript{x} such that HC and CO are substantially oxidized, and at least a portion of said NO\textsubscript{x} contained in said exhaust gas is converted to N\textsubscript{2} at a temperature between about 150° C. to 250° C.

13. The method of claim 12 wherein said three-way catalyst is positioned downstream from said first lean NO\textsubscript{x} trap.

14. The method of claim 12 wherein said first lean NO\textsubscript{x} trap is positioned downstream from said three-way catalyst.

15. The method of claim 12 wherein said first lean NO\textsubscript{x} trap and said three-way catalyst are combined.

16. The method of claim 12 wherein said system includes a second lean NO\textsubscript{x} trap positioned downstream from said three-way catalyst, said second lean NO\textsubscript{x} trap comprising a catalyst, a NO\textsubscript{x} absorbent material comprising alumina, and optionally, from 0 to about 4 wt % of an alkaline earth metal oxide.

17. A method for desulphurization of a lean NO\textsubscript{x} trap system in a HCCI engine comprising:

- providing a lean NO\textsubscript{x} trap system including a first lean NO\textsubscript{x} trap comprising a catalyst, a NO\textsubscript{x} absorbent material comprising alumina, and optionally, from 0 to about 4 wt % of an alkaline earth metal oxide; and a three-way catalyst positioned downstream from said first lean NO\textsubscript{x} trap; said system being positioned in the exhaust passage of said HCCI engine such that it is exposed to exhaust gases therein; and
- heating said exhaust gases to a temperature of between about 550 and 650° C. for at least 60 seconds by operating said engine in SI mode.

18. The method of claim 17 wherein said desulphurization of said lean NO\textsubscript{x} trap system produces a sulfur product comprising at least 90% SO\textsubscript{2}.

19. The method of claim 17 wherein during said desulphurization, x is between 0.98 and 0.99.

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