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(54) **A BARIUM SUBSTITUTED-SULFUR TOLERANT LEAN NOX TRAP**

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(57) **ABSTRACT**

The present invention provides a composition and method for storing and reducing NOx from lean burn internal combustion engines. The present invention uses composite metal oxides, in spinel structure, in conjunction with the typical lean NOx trap formulation to form an integrated lean NOx trap. The composite metal oxides in spinel structure act primarily as a SOx trapping element and also secondarily as a NOx trapping element within the integrated LNT. In this integrated LNT, the sulfur is trapped and released in a way that does not allow the sulfur to go to the primary NOx trapping element an alkali or earth metal - and thus prevents the integrated lean NOx trap from becoming poisoned, thereby leaving more reactive sites for NOx trapping and conversion.

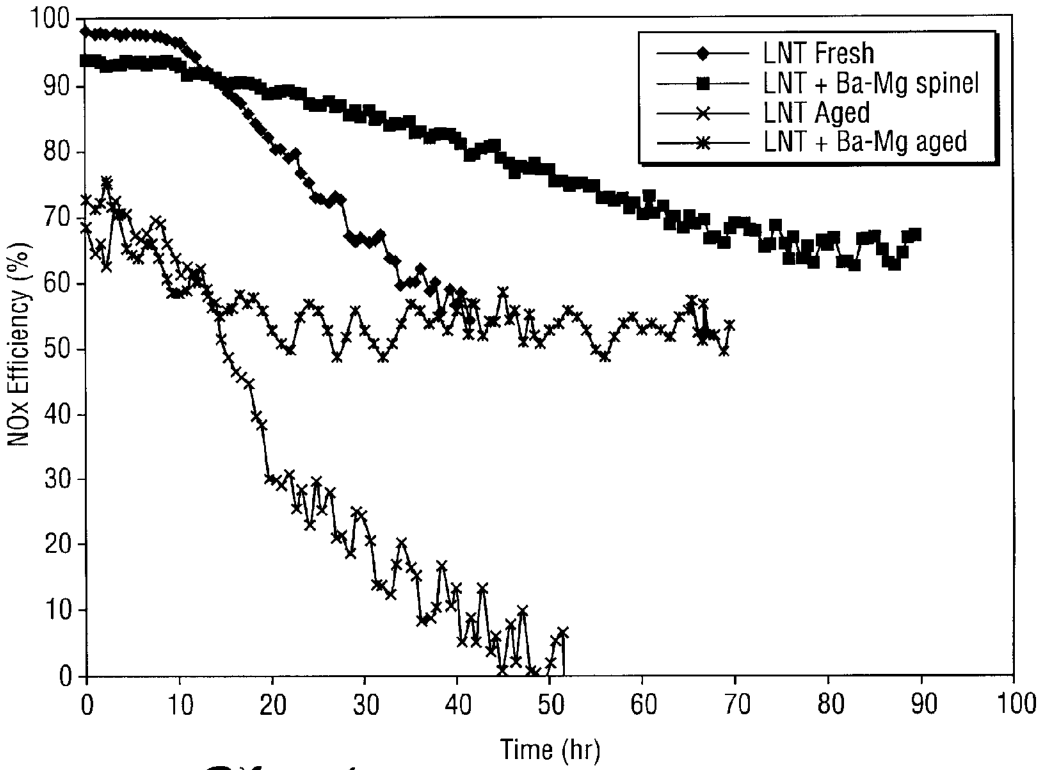

LNT Fresh
LNT + Ba-Mg spinel
LNT Aged
LNT + Ba-Mg aged
NOx Efficiency (%)
Time (hr)
0
10
20
30
40
50
60
70
80
90
100

Fig. 1

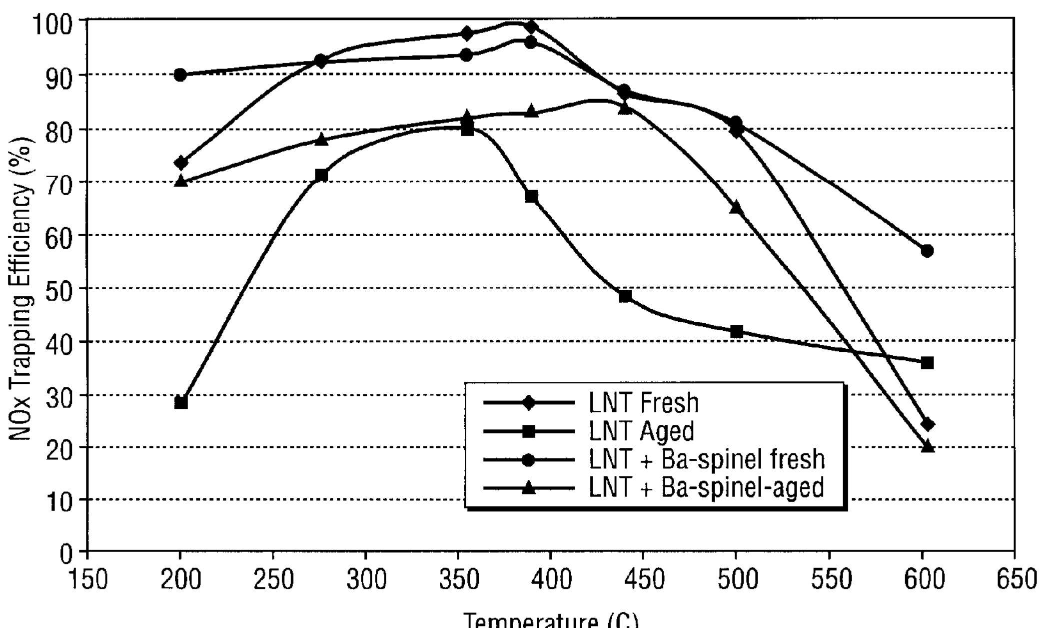
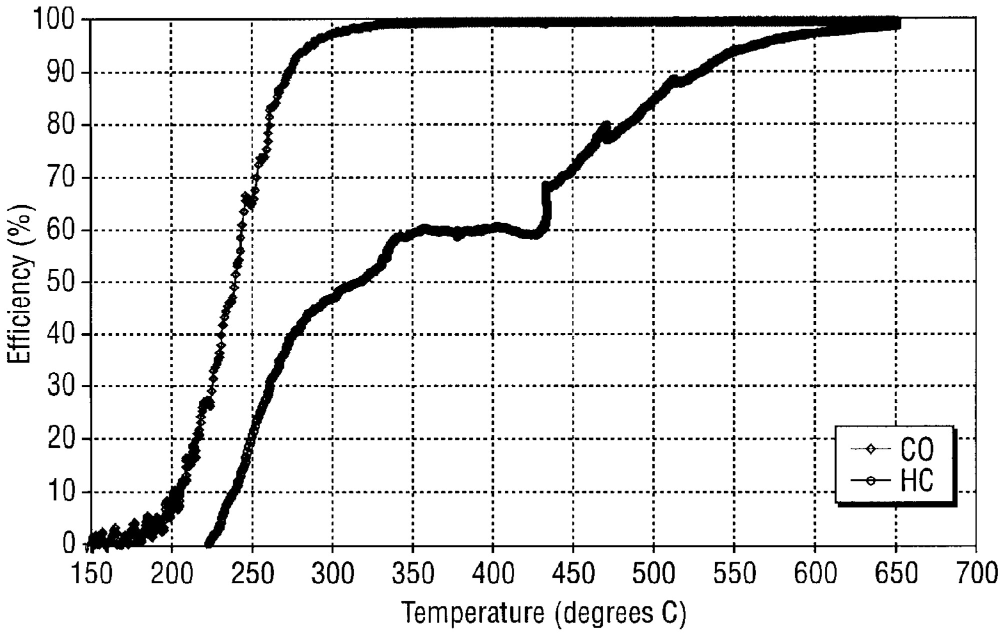

LNT Fresh
LNT Aged
LNT + Ba-spinel fresh
LNT + Ba-spinel-aged
NOx Trapping Efficiency (%)
Temperature (C)
150
200
250
300
350
400
450
500
550
600
650

Fig. 2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90
80
70
60
50
40
30
20
10
0
Efficiency (%)
150
200
250
300
350
400
450
500
550
600
650
700
Temperature (degrees C)
CO
HC

Fig. 3a

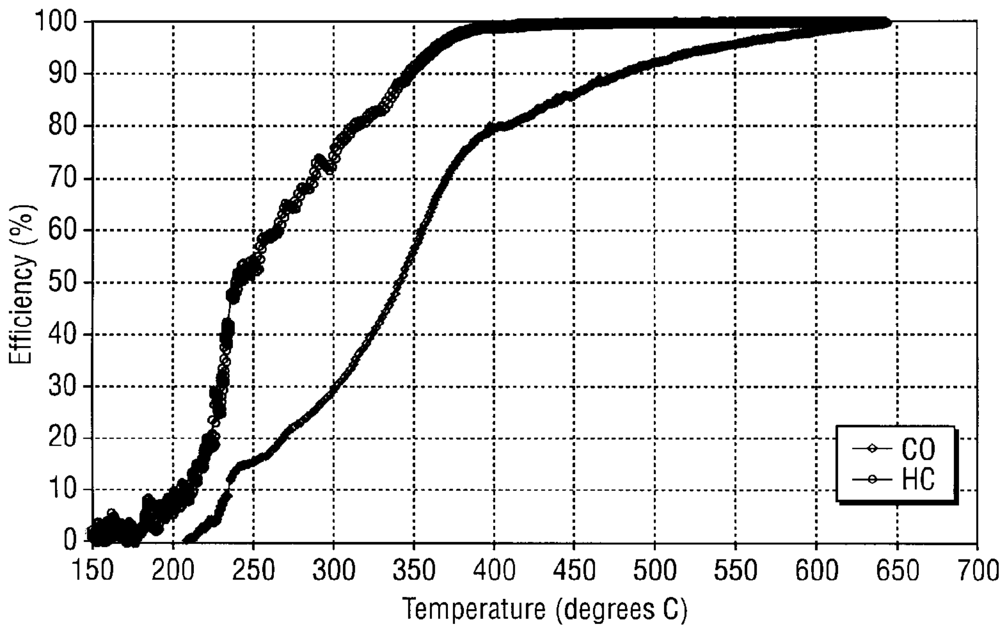
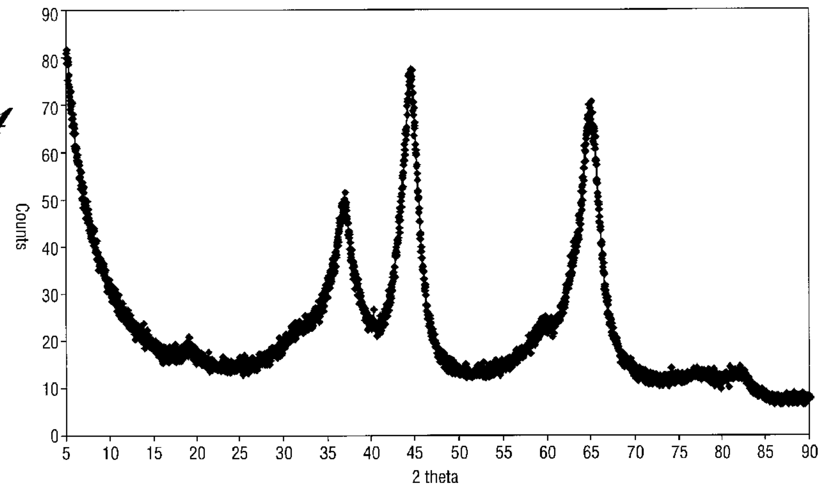

100
90
80
70
60
50
40
30
20
10
0
Efficiency (%)
150
200
250
300
350
400
450
500
550
600
650
700
Temperature (degrees C)
CO
HC

Fig. 3b

Fig. 4


Counts
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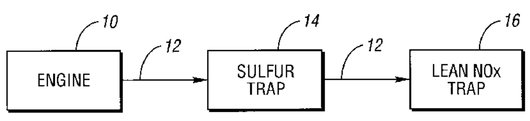
80
70
60
50
40
30
20
10
0
5 10 15 20 25 30 35 40 45 50 55 60 65 70 75 80 85 90
2 theta

Fig. 5


10
ENGINE
12
14
SULFUR TRAP
12
16
LEAN NOx TRAP

A BARIUM SUBSTITUTED-SULFUR TOLERANT LEAN NOX TRAP

Cross Reference to Related Applications

[0001] This application is a continuation-in-part of U.S. application Serial No. 09/682,781, filed October 18, 2001.

Background of Invention

[0002] 1. Field of the Invention

[0003] This invention is directed to the field of reducing noxious emissions from internal combustion engines. The invention is particularly directed to the field of reducing NOx emissions under lean conditions to improve the sulfur tolerance of a lean NOx trap.

[0004] 2. Background Art

[0005] The present invention relates to a composition and method for controlling exhaust emissions, especially nitrogen oxide emissions from combustion engines. More specifically, the present invention relates to a series of composite metal oxides that significantly improve the sulfur tolerance of a lean NOx trap (LNT).

[0006] An approach for treating the NOx emissions from lean-burn engines is the use of NOx traps. A lean NOx trap typically contains precious metals, alkali or alkali earth metals, and alumina. A generally accepted pathway for reactions of LNT is that under lean conditions, NO is oxidized to NO_2 which is followed by the subsequent formation of a nitrate with alkali or alkali earth metal(s), e.g., magnesium and barium. Under stoichiometric or rich operation, the stored nitrate is thermodynamically unstable. The stored NOx is released. On release, the NOx then catalytically reacts with reducing species in the exhaust gas to form N_2.

[0007] The alkali or alkali earth metal(s) that are typically used for NOx adsorption - trapping metals or elements - are readily poisoned by sulfur oxides in the exhaust gas. Over time, the sulfur oxides react with these trapping elements forming sulfates which are more stable than corresponding nitrates.

[0008] The present invention provides a new series of composite metal oxides that, combined with the active components of a lean NOx trap, significantly improve the sulfur tolerance of the lean NOx trap while improving the general performance of the lean NOx trap by improving the ability of the NOx trap to store NOx. More specifically, the present invention teaches the use of a barium-substituted spinel (AB_2O_4) that coats the lean NOx trap to improve the sulfur tolerance of the lean NOx trap - expanding the optimum temperature range for the NOx trap.

Summary of Invention

[0009] The present invention solves the problem of sulfur poisoning of lean NOx traps by providing a composition and method for storing and reducing NOx from lean burn internal combustion engines. The present invention uses composite metal oxides, specifically aluminum, magnesium and barium, in spinel structure, AB_2O_4, in conjunction with a typical LNT formulation to form an integrated LNT. The composite metal oxide in spinel structure acts primarily as a SOx trapping element and also a secondary NOx trapping element within the integrated LNT.

[0010] In the application of this integrated LNT, the sulfur oxides are mainly attached to the magnesium/barium oxides in spinel structure under a relatively low temperature (200-600°C). When the integrated LNT is saturated with sulfur for a specified NOx conversion, the LNT will be desulfated under rich conditions at a higher temperature (600-750°C), so that the capacity of the LNT for NOx trapping and conversion is regenerated. In this integrated LNT, the sulfur is trapped and released in a way that minimizes the sulfur from going to the primary NOx trapping element, i.e., the alkali or alkali earth metal oxides, to poison the integrated LNT (such as barium, aluminum and magnesium), thereby leaving more reactive sites for the NOx trapping and conversion.

[0011] The present invention provides a composition and method comprising a typical LNT formulation treated with the composite metal oxide in spinel structure. In one embodiment, the composite metal oxide is in powder form and made into a slurry and then coated into an LNT after all the other materials have been coated. The LNT is then dried and calcined. In another embodiment, the spinel oxide slurry is mixed with CeO_2 powder in an amount of 4-10 wt% of CeO_2 of the total mixture before coating onto the LNT. In yet another embodiment, the spinel oxide slurry is mixed with CeO_2-ZrO_2 powder, in an amount of 4-10 wt% of the total mixture before coating onto the LNT.

[0012] In this invention, magnesium is partially substituted with barium, to improve the sulfur tolerance of the lean NOx trap. Additionally, the partial substitution of magnesium with barium results in an expanded optimum temperature range for the NOx trap - increasing NOx reduction over the full range of operating temperature parameters for the catalyst.

[0013] The method for removing NOx and SOx impurities from exhaust gases provides a composition comprising an integrated LNT treated with a composite metal oxide having the spinel structure (AB_2O_4), and passing exhaust gas containing NOx and SOx over the composition. The NOx is stored under lean conditions between 200-600°C and released and converted under stoichiometric and rich conditions between 200-600°C. Meanwhile, SOx is stored between 200-600°C under both lean and rich conditions and is desulfated at a temperature between 600-750°C under rich conditions, when the sulfur oxides have reacted with the composite metal oxides and have thus reduced the NOx trapping efficiency to a predetermined value.

Brief Description of Drawings

[0014] **Figure 1** shows the sulfur tolerance of a fresh and aged lean NOx trap with and without the barium substituted spinel;

[0015] **Figure 2** shows the temperature operating profile of a fresh lean NOx trap with and without the barium substituted spinel;

[0016] **Figure 3a** shows the light-off test results of the lean NOx trap without the barium substituted spinel;

[0017] **Figure 3b** shows the light-off test results of the lean NOx trap with the barium substituted spinel;

[0018] **Figure 4** shows the X-ray diffraction pattern for a fresh barium spinel powder; and

[0019] **Figure 5** shows an alternate embodiment using the barium substituted spinel composition in a sulfur trap upstream of the lean NOx trap.

Detailed Description

[0020] The present invention teaches a series of composite metal oxides and a method to inhibit sulfur poisoning of lean NOx traps. A typical LNT can be doped with the current composite metal oxide, that are spinel in structure. The spinel oxides can also be added during the manufacturing of the typical LNT to form integrated new LNTs. The integrated new LNTs have significantly better sulfur tolerance than a LNT without the composite metal oxides. The composite metal oxide is made to function primarily as a sulfur trapping element and also function as a secondary NOx trapping element within the integrated LNT.

[0021] As stated in the background, a LNT trap typically contains precious metals, alkali or alkali earth metals, and alumina. A generally accepted pathway for reactions of LNT is that, under lean conditions, NO is oxidized to NO_2, which is followed by subsequent formation of a nitrate with alkali or alkali earth metal(s), e.g., magnesium or barium. Thus, the alkali or alkali earth metal(s) "trap" the NOx. The trapped nitrate is decomposed, or released, into NOx under stoichiometric and rich conditions. This NOx is then reacted with reductants such as HC, CO, and H_2 to form N_2, CO_2 and H_2O. While the primary trapping elements are the alkali or alkali earth metals, the secondary trapping element is the composite metal oxide. The combination of the primary and secondary NOx trapping elements, in conjunction with the precious metal, forms the sulfur tolerant integrated LNT.

[0022] The temperature for NOx trapping is around 200-600°C, with the optimum performance at around 350-400°C. The wider the temperature range or window, the more versatile the resultant trap and, therefore, better equipped the trap is for vehicle operation. In the present invention, by partially substituting magnesium with barium, the optimum operating temperature range becomes wider and thus enhances the versatility and use of the NOx trap.

[0023] The composite spinel metal oxides in the integrated LNT can trap the sulfur under both lean and rich conditions between 200-600°C. Once the spinel is saturated with attached sulfur so that the NOx trapping function is reduced to a specific value, e.g., 85%, then the LNT needs to be desulfated. This can be done by adjusting the exhaust to a rich condition, such as A/F = 8-14, and raising the LNT temperature to about 600-750°C for a short period of time, e.g., 1-5 minutes. The desulfated LNT will then have regenerated high NOx trapping efficiency.

[0024] The composite metal oxide is a substituted spinel having a formula of $Mg_{0.1\text{-}0.7}Ba_{0.3\text{-}0.9}Al_2O_4$. Additionally, the composite metal oxide can be a substituted spinel $Mg_{0.1\text{-}0.7}Ba_{0.3\text{-}0.9}Al_2O_4$ having BaO on the surface ($MgBaAl_2O_4{\cdot}BaO$) or a solid solution of barium substituted spinel $Mg_{0.1\text{-}0.7}Ba_{0.3\text{-}0.9}Al_2O_4$ and excess BaO. It is believed that the substituted spinel $Mg_{0.1\text{-}0.7}Ba_{0.3\text{-}0.9}Al_2O_4$ and/or the BaO on the surface of the composite metal oxide or in the solid solution forms a chemical bond with the adsorbed SOx, forming surface sulfates and bulk complex sulfates with the composite metal oxides. Therefore, the primary NOx trapping element within the LNT is protected for NOx trapping. The sulfur tolerance of the LNT is thus improved. On the other hand, we found that surface sulfates and bulk complex sulfates are easier to remove under reducing conditions than those bulk sulfates formed with the primary NOx trapping element, when no spinel oxides are included in the LNT. From test results, the desulfation of the integrated LNT with composite spinel metal oxides is also easier than the typical lean NOx trap.

[0025] The composite metal oxide is in powder form. The powder is then made into a slurry in an amount between 2-30 wt% of the total trap. Preferably, the powder is made into a slurry in an amount between 2-20 wt% of the total trap. Most preferably, the powder is made into a slurry in an amount between 4-10 wt% of the total trap. The trap is then dipped into the slurry, dried at 120°C for six hours, and calcined under 600°C for ten hours. The coating of the slurry can be conducted after all the other components are fixed or at the same time with the primary NOx trapping element.

[0026] Another option is to mix spinel oxide with CeO_2 powder in an amount between 0.1-20 wt% of CeO_2 of the total mixture. Preferably, the CeO_2 powder is mixed in an amount between 2-15 wt% of the total mixture. The trap is then dipped into the slurry of spinel oxide with CeO_2 dried at 120°C in six hours and calcined under 600°C for ten hours. Similarly, the coating of the slurry can be conducted after all the other components are fixed or conducted at the same time with the primary NOx trapping elements. Using spinel/CeO_2 ($Mg_{0.1\text{-}0.7}Ba_{0.3\text{-}0.9}Al_2O_4{\cdot}CeO_2$) provides better sulfur tolerance than using spinel alone. It is believed that CeO_2 promotes the oxidation of SO_2 through its surface and lattice oxygen thereby promoting the sulfur oxides oxidation and attachment to the spinels, thus improving the sulfur tolerance of the lean NOx trap.

[0027] Another option is to mix the oxide with CeO_2-ZrO_2 powder, in an amount between 0.1-20 wt% of the total mixture. Preferably, the CeO_2-ZrO_2 powder is mixed in an amount between 2-15 wt% of the total mixture. Most preferably, the CeO_2-ZrO_2 powder is mixed in an amount between 4-10 wt% of the total mixture. The trap is then dipped into the slurry, dried at 120°C in six hours and calcined under 600°C for ten hours. Again, the coating of the slurry can be conducted after all the other components are fixed or in the same time with the primary NOx trapping elements.

[0028] The method for removing NOx and SOx impurities from the exhaust gases involves adding a composite metal oxide in spinel structure to a typical LNT. The composite metal oxide is added in an amount between 2-30 wt%. Preferably, the composite metal oxide is added in an amount between 2-20 wt%. Most preferably, the composite metal oxide is added in an amount between 4-10 wt%. The composite metal oxides are then coated onto the typical lean NOx trap after all the other components are fixed or at the same time with the primary NOx trapping elements. The composite metal oxide is spinel in structure. The composite metal oxides are preferably $Mg_{0.1\text{-}0.7}Ba_{0.3\text{-}0.9}Al_2O_4$, $Mg_{0.1\text{-}0.7}Ba_{0.3\text{-}0.9}Al_2O_4{\cdot}xBaO$, $Mg_{0.1\text{-}0.7}Ba_{0.3\text{-}0.9}Al_2O_4{\cdot}\,yCeO_2$, or $Mg_{0.1\text{-}0.7}Ba_{0.3\text{-}0.9}Al_2O_4{\cdot}zCeO_2\text{-}ZrO_2$, where x, y and z are a number which would provide a correct weight percent in accordance with the amount of composite metal oxides that is added to the total mixture. The lean NOx trap is doped with the composite metal oxide comprising between about 70-98 wt% lean NOx trap and about 2-30 wt% composite metal oxide.

[0029] The SOx impurities are mostly attached to the composite metal oxide in the form of surface sulfate and bulk composite sulfate at a temperature between 200-600°C under lean and rich conditions. The SOx impurities are released at a temperature between 600-750°C under rich conditions. For this integrated lean NOx trap with composite spinel oxides, the storage and release conditions for NOx are similar to a typical NOx trap application condition. For example, NOx is stored under lean conditions (an air fuel ratio greater than 15) between 200-600°C, and then released and converted under stoichiometric and rich conditions (air fuel ratios less than or equal to 14.7) for a shorter period than the lean period between 200-600°C. This cycling continues and during this cycling the sulfur is attached mainly to spinel oxide sites. When the NOx efficiency is reduced to a predetermined value due to sulfur poisoning, the trap is ready for a desulfation cycle. The temperature of the trap is raised to about 600-750°C under rich conditions, the sulfur attached to the spinel oxides is thus released, probably in the form of H_2S and COS.

[0030] Having described the invention in detail and by reference to preferred embodiments thereof, it will be apparent that modifications and variations are possible without departing from the scope of the invention defined in the attached claims. More specifically, although some aspects of the present invention are identified herein, as preferred or particularly advantageous, it is contemplated that the present invention is not necessarily limited to these preferred aspects of the invention.

[0031] Example 1

[0032] The partial substitution of magnesium with barium, improves the sulfur tolerance of the lean NOx trap even more significantly. A co-precipitation method was used to synthesize the barium-spinel. Solutions of $Mg(NO_3)_2$, with concentrated HNO_3 added, $Na_2Al_2O_4$ contains 0.45 mole Al_2O_3 and 0.67 mole Na_2O, with NaOH added, and $Ba(NO_3)_2$ of desired concentration were used in the preparation process. The magnesium solution was added to a vessel containing 850 ml deionized H_2O and then the barium and $Na_2Al_2O_4$ solutions were simultaneously added over 30 minutes while stirring vigorously. During the titration, a pH between 7-8 was maintained by adding concentrated HNO_3. After the titration was complete, the final pH was adjusted to 10.0 by slowly adding an appropriate amount of 20 wt% NaOH solution over 45 minutes with constant stirring. The solution stood for 14 hours before being filtered and washed with 14 L of dionized H_2O. The sample was dried at 120°C for 16 hours in a circulating air oven, ground and then calcined in flowing O_2 at 750°C for three hours. The materials were added to produce a final formula of $Mg_{0.5}Ba_{0.5}Al_2O_4$ spinel.

[0033] Example 2 (Doping Of the Spinel to LNT)

[0034] A fully formulated lean NOx trap with relatively good sulfur tolerance was obtained from a catalyst supplier. The specific LNT formulation is not critical. One preferred LNT comes from Johnson Matthey. A block of fully formulated LNT was cut from the brick. This block was doped with 4 wt% of spinel made from example 1. The block was then dried at 120°C for six hours and calcined at 600°C for six hours. Cores with one inch (length) by 3/4″ (diameter) were cut. Two pieces were subject to standard hydrothermal aging with 850°C inlet temperature (maximum trap bed temperature at 1000°C) using a pulse flame combustor (pulsator). Both fresh and aged cores were evaluated in a flow reactor.

[0035] **Figure 1** shows the sulfur tolerance of fresh and aged LNT with and without the barium substituted spinel. With 9 ppm SO_2 in the feed gas, as can be seen in **Figure 1**, the sulfur tolerance of the LNT for both the fresh and aged samples has been improved significantly.

[0036] **Figure 2** shows the temperature window, which reflects the easiness and effectiveness of the trap to be fitted in the vehicle exhaust system. As can be seen, the doping of the spinel actually improved the performance of the trap, by not only improving sulfur tolerance but widening the temperature window, especially in the high temperature region.

[0037] **Figure 3** shows the light-off behavior of the LNT doped with barium substituted spinel (**Figure 3b**) and without barium substituted spinel (Figure 3a). The light-off before and after the doping of the barium spinel for CO and HC behaves differently. For CO (the top line of **Figure 3a**, and the bottom line of Figure 3b), the doping of barium spinel increased T_{80} from 260°C to 310°C. For HC (the bottom line of Figure 3a and the top line of Figure 3b), the doping decreased T_{80} from 480°C to 400°C. Because in general CO is easier to light-off than hydrocarbons, the overall impact to light-off temperature is improved.

[0038] **Figure 4** shows the X-ray diffraction pattern of the powder made from example 1. The X-ray diffraction shows a strong $MgAl_2O_4$ spinel pattern, with significant intensity alteration for relatively small peak shift. No comparative $Mg_{0.5}Ba_{0.5}Al_2O_4$ pattern existed in the database. No peaks related to other barium compounds such as BaO, $BaCO_3$, etc. were detected. The X-ray diffraction results show that the main structure of the powder is in spinel form. All the peaks can be assigned as spinel in structure except significant intensity alteration at 36 and 45 degrees. The two main peaks at 45 and 66 degrees have been shifted to approximately 1 degree lower compared to a $MgAl_2O_4$ structure. Part of the barium is incorporated into the spinel structure, however, not all is incorporated into the structure, because Ba divalent cations are larger than magnesium divalent cations and aluminum trivalent cations, so more peak shift or unit size change are believed to appear. The barium is nevertheless extremely well dispersed in the spinel structure, so well that even if free barium is forming barium carbonate, this carbonate is rather amorphous, and not detected by XRD.

[0039] As can be seen from these figures, the overall improvement of the trap performance is significant under the current invention. The examples used are only an illustration of the present invention.

[0040] As shown in **Figure 5**, another option is to use this barium substituted spinel composition as a sulfur trap 14 placed downstream of the LNT 16 to remove sulfur emissions from the exhaust stream 12. For such a composition, the sulfur trap substrate is preferably alumina.

[0041] Other variations are likely and within the spirit of the present invention. For example, the barium substituted spinel may be produced with methods other than co-precipitation, and the ratio of barium substitution can also be varied. Incorporation of the barium spinel may be carried out after the lean NOx trap is prepared or as an integral step of the trap preparation process. The amount of the barium substituted spinel can be between 2-30 wt% of the total weight of the lean NOx trap.

[0042] While the best mode for carrying out the invention has been described in detail, those familiar with the art to which this invention relates will recognize various alternative designs and embodiments for practicing the invention as defined by the following claims.

Claims

1. A sulfur-tolerant lean NOx trap, comprising: a lean NOx trap doped with a composite metal oxide having a formula of $Mg_xBa_yAl_2O_4$, wherein x is a number in the range of 0.1-0.7 and y is a number in the range of 0.3-0.9.

2. The lean NOx trap of claim 1, wherein the composite metal oxide is spinel in structure.

3. The lean NOx trap of claim 1, wherein the composite metal oxide comprises $Mg_xBa_yAl_2O\cdot_4BaO$, wherein x is a number in the range of 0.1-0.7 and y is a number in the range of 0.3-0.9.

4. The lean NOx trap of claim 1, wherein the composite metal oxide comprises $Mg_xBa_yAl_2O\cdot_4CeO_2$,wherein x is a number in the range of 0.1-0.7 and y is a number in the range of 0.3-0.9.

5. The lean NOx trap of claim 4, wherein the trap is doped with said composite metal oxide to provide a composition comprising between 0.1 20 wt% of the lean NOx trap.

6. The lean NOx trap of claim 4, wherein the trap is doped with said composite metal oxide to provide a composition comprising between 2-15 wt% of the lean NOx trap.

7. The lean NOx trap of claim 1, wherein the composite metal oxide comprises $Mg_xBa_yAl_2O\cdot_4zCeO_2\text{-}ZrO_2$, wherein x is a number in the range of 0.1-0.7, y is a number in the range of 0.3-0.9, and z is a number in the range of 1-20 wt%.

8. The lean NOx trap of claim 7, wherein z is a number in the range of 2-15 wt%.

9. The lean NOx trap of claim 1, wherein the trap is doped with said composite metal oxide to provide a composition comprising between 2-30 wt% of the lean NOx trap.

10. The lean NOx trap of claim 1, wherein the trap is doped with said composite metal oxide to provide a composition comprising between 2-20 wt% of the lean NOx trap.

11. The lean NOx trap of claim 1, wherein the trap is doped with said composite metal oxide to provide a composition comprising between 4-10 wt% of the lean NOx trap.

12. The lean NOx trap of claim 1, wherein the trap is doped with said metal oxide after preparation of the lean NOx trap.

13. The lean NOx trap of claim 1, wherein the trap is doped with said metal oxide during preparation of the lean NOx trap.

14. A method for removing NOx and SOx from an exhaust gas stream, comprising: placing a lean NOx trap in the exhaust gas stream, wherein the lean NOx trap is doped with a composite metal oxide having a formula of $Mg_xBa_yAl_2O_4$, wherein x is a number in the range of 0.1-0.7 and y is a number in the range of 0.3-0.9.

15. The method of claim 14, wherein the composite metal oxide is added in the ratio of 2 to 30.

16. The method of claim 14, wherein the composite metal oxide is added in the ratio of 2 to 20.

17. The method of claim 14, wherein the composite metal oxide is added in the ratio of 4 to 10.

18. The method of claim 14, wherein the composite metal oxide is spinel in structure.

19. The method of claim 14, wherein the metal oxide is $Mg_{0.1\text{-}0.7}Ba_{0.3\text{-}0.9}Al_2O_4$.

20. The method of claim 14, wherein the composite metal oxide is $Mg_{0.1\text{-}0.7}Ba_{0.3\text{-}0.9}Al_2O\cdot_4BaO$.

21. The method of claim 14, wherein the composite metal oxide is $Mg_{0.1\text{-}0.7}Ba_{0.3\text{-}0.9}Al_2O\cdot_4CeO_2$.

22. The method of claim 14, wherein the composite metal oxide is $Mg_{0.1\text{-}0.7}Ba_{0.3\text{-}0.9}Al_2O\cdot_4zCeO_2\text{-}ZrO_2$.

23. A sulfur trap for the removal of sulfur in an exhaust stream, comprising: an alumina substrate and a composite metal oxide having a formula of $Mg_xBa_yAl_20_4$, wherein x is a number in the range of 0.1-0.7 and y is a number in the range of 0.3-0.9.

24. The sulfur trap of claim 23, wherein the composite metal oxide is spinel in structure.

25. The sulfur trap of claim 23, wherein the sulfur trap is positioned upstream from any lean NOx trap in the exhaust system.

* * * * *