

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
7 October 2010 (07.10.2010)

PCT

(10) International Publication Number
WO 2010/114873 A2

(51) International Patent Classification:
B01D 53/94 (2006.01) *F01N 3/035* (2006.01)
B01D 53/58 (2006.01)

(21) International Application Number:
PCT/US2010/029329

(22) International Filing Date:
31 March 2010 (31.03.2010)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/166,584 3 April 2009 (03.04.2009) US
12/750,001 30 March 2010 (30.03.2010) US

(71) Applicant (for all designated States except US): **BASF CATALYSTS LLC** [US/US]; 100 Campus Drive, Florham Park, NJ 07932 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **WAN, Chung-Zong** [US/US]; 4 Scaletti Court, Somerset, NJ 08873 (US). **ZHENG, Xiaolai** [US/US]; 44 Cubbery Road, Princeton Junction, NJ 08550 (US). **STIEBELS, Susanne** [DE/DE]; In Den Ackern 5, 38528 Adenbuttel (DE). **WENDT, Claudia** [DE/DE]; Haltenhoffstr. 189B, 30419 Hannover (DE). **BOORSE, Samuel, R.** [US/US]; 172 Fairview Road, Skillman, NJ 08558 (US).

(74) Agents: **BROWN, Melanie** et al.; BASF Catalysts LLC, 100 Campus Drive, Florham Park, NJ 07932 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— without international search report and to be republished upon receipt of that report (Rule 48.2(g))

(54) Title: EMISSIONS TREATMENT SYSTEM WITH AMMONIA-GENERATING AND SCR CATALYSTS

(57) Abstract: Provided are emissions treatment systems for an exhaust stream having an ammonia- generating component, such as a NOx storage reduction (NSR) catalyst or a lean NOx trap (LNT) catalyst, and an SCR catalyst disposed downstream of the ammonia-generating catalyst. The SCR catalyst can be a molecular sieve having the CHA crystal structure, for example SSZ- 13 or SAPO-34, which can be ion-exchanged with copper. The LNT can be layered, having an undercoat washcoat layer comprising a support material, at least one precious metal, and at least one NOx sorbent selected from the group consisting of alkaline earth elements, rare earth elements, and combinations thereof and a top washcoat layer comprising a support material at least one precious metal, and ceria in particulate form, the top washcoat layer being substantially free of alkaline earth components. The emissions treatment system is advantageously used for the treatment of exhaust streams from diesel engines and lean burn gasoline engines.



WO 2010/114873 A2

EMISSIONS TREATMENT SYSTEM WITH AMMONIA-GENERATING AND SCR CATALYSTS

TECHNICAL FIELD

5 [0001] The present invention relates to emissions treatment systems having ammonia-generating and SCR catalysts, and methods useful for reducing contaminants in exhaust gas streams, especially exhaust gas streams containing nitrogen oxides (NO_x). More specifically, the present invention is concerned with emissions treatment systems containing ammonia-generating catalysts such as NO_x storage reduction (NSR) or lean NO_x trap (LNT) catalysts in
10 combination with Selective Catalytic Reduction (SCR) catalysts, and methods for their use with lean burn engines, including diesel engines and lean burn gasoline engines.

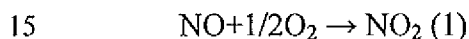
BACKGROUND

[0002] Operation of lean burn engines, e.g., diesel engines and lean burn gasoline engines,
15 provide the user with 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 high NO_x conversion
20 rates typically require reductant-rich conditions. 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.

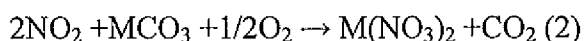
[0003] One such strategy for the abatement of NO_x in the exhaust stream from lean burn engines uses NO_x storage reduction (NSR) catalysts, which are also known in the art as “lean
25 NO_x trap (LNT)”. NSR catalysts contain NO_x sorbent materials capable of adsorbing or “trapping” oxides of nitrogen under lean conditions and platinum group metal components to provide the catalyst with oxidation and reduction functions. In operation, the NSR 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
30 storage. At low temperatures, this reaction is typically catalyzed by the 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 an atomic oxygen, is also a catalyzed reaction

(Equation 2). There is little nitrate formation in 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) or HC (hydrocarbon) (Equation 3) to the exhaust. This step recovers NO_x storage sites but induces release 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 also be induced by reductants in a net oxidizing environment. However, the efficient reduction of released NO_x by CO requires 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.

Oxidation of NO to NO₂



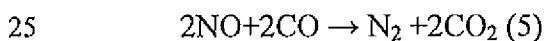
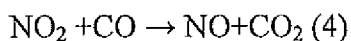
NO_x Storage as Nitrate



20 NO_x Release



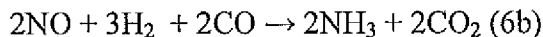
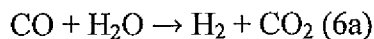
NO_x Reduction to N₂



[0004] 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.

[0005] 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 with CO and H₂O is shown below in equation (6).

Reduction of NO to NH₃



5

[0006] 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.

[0007] 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.

[0008] 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 sources for supplying the reductant NH₃ for the SCR treatment of exhaust gases are desirable.

[0009] Emissions treatment systems that utilize the catalytic reduction of NO_x in the exhaust to generate NH₃, in place of an external reservoir of NH₃ or NH₃ precursor have been described, but these systems have limitations. In such systems, a portion of the NO_x component of the exhaust is used as an NH₃ precursor in such systems. For instance, United States Patent No. 6,176,079 discloses a method for treating an exhaust gas from a combustion system that is operated alternately in lean and rich conditions. In the method, nitrogen oxides are intermediately stored during lean operation, and released during rich operation to form NH₃ that

is stored. The stored NH_3 can be released, and thereby reduce nitrogen oxides during a subsequent lean operation.

[0010] European Patent Publication No. 773 354 describes a device for purifying the exhaust gas of an engine that has a three way catalyst connected to an NH_3 adsorbing and oxidizing (NH_3 -AO) catalyst. The engine is operated with alternating rich and lean periods. During a rich operation the three way catalyst synthesizes NH_3 from NO_x in the inflowing exhaust gas, and the NH_3 is then adsorbed on the NH_3 -AO catalyst. During the lean operation NO_x passes through the three way catalyst and the adsorbed NH_3 is desorbed and reduces the inflowing NO_x .

[0011] International Published Patent Application WO 97/17532 discloses a method and device for purifying the exhaust gas from an engine, and in particular, describes a method and device for purifying NO_x in the exhaust gas. In one embodiment, the publication describes a device that has a three way catalyst upstream of, and on the same carrier as a NO_x occluding and reducing catalyst. Downstream of the NO_x occluding and reducing (NO_x -OR) catalyst is a NH_3 adsorbing and oxidation (NH_3 -AO) catalyst. To prevent any NH_3 breakthrough, the device is also equipped with a NH_3 purifying catalyst downstream of the NH_3 -AO catalyst. The air/fuel ratio of the cylinders of the engine are alternately and repeatedly rendered lean and rich to thereby render the exhaust gas air/fuel ratio, alternately and repeatedly rich and lean.

[0012] In the method described for this device in the WO97/17532 publication, when the air/fuel ratio of the exhaust gas is lean, NO_x passes through the three way catalyst, and NO_x is occluded in the NO_x -OR catalyst. It is described that any NO_x passing through the NO_x -OR catalyst is purified in the following NH_3 -AO catalyst. NH_3 is desorbed from the NH_3 -AO catalyst when the air/fuel ratio of the exhaust gas is lean, and the desorbed NH_3 reduces the NO_x .

[0013] When the air/fuel ratio of the exhaust gas is rich, a part of the NO_x in the exhaust gas is converted to NH_3 in the three way catalyst. The NH_3 then passes into the NO_x -OR catalyst, where the NO_x is released, reduced and purified by the inflowing NH_3 . Any NH_3 passing through the NO_x -OR catalyst that is not consumed by the reduction of NO_x is adsorbed on the NH_3 -AO catalyst, or is purified further downstream in the NH_3 purifying catalyst.

[0014] A problem associated with methods that utilize a portion of the NO_x in the exhaust gas as an NH_3 precursor is that, depending on operating conditions, NH_3 generated during rich operating periods often is insufficient to treat the NO_x during lean periods (i.e., when the

exhaust gas composition has a $\lambda \gg 1$). This deficiency can limit the range of operating conditions where NO_x can be effectively treated by other emissions treatment systems.

[0015] As the conditions that emission treatment systems operate under vary for different vehicles powered by lean burn engines, flexible approaches for the design of emission treatment systems are needed to achieve ever more stringent requirements for NO_x abatement. In particular, approaches that account for the effect on NO_x storage and NH₃ formation during lean and rich periods of operation of altering the NSR catalyst composition offer more reliable and practical pathways to achieving this goal.

10 SUMMARY

[0016] Provided are emissions treatment systems that can be used in methods for treating exhaust gas from internal combustion engines, including diesel engines and lean burn gasoline engines, and methods of using these systems to treat internal combustion engine exhaust.

[0017] In one aspect, the invention relates to an emissions treatment system for an exhaust stream from, for example, a diesel engine or a lean burn gasoline engine. The system has an ammonia-generating component; and an SCR catalyst disposed downstream of the ammonia-generating component, wherein the SCR catalyst comprises a molecular sieve having the CHA crystal structure. In a specific embodiment, the ammonia-generating component is a lean NO_x trap (LNT) catalyst, which also provides functionality for NO_x abatement. The LNT and SCR combination can be configured as desired and as space permits in the exhaust system. For example, the LNT and SCR catalysts can each be on a separate substrate brick, or, alternatively, each can be placed in a front zone and a rear zone, respectively, on a single substrate brick. In another example, the LNT and SCR catalysts can be combined with a diesel particulate filter (DPF) that is downstream of the SCR. This combination can be such that each component is on its own substrate, or as desired, the SCR can be coated on a front zone of the DPF or along the entire length of the DPF.

[0018] In one embodiment, the ammonia-generating component comprises a lean NO_x trap (LNT) catalytic material disposed on a carrier, the catalytic material comprising: an undercoat washcoat layer comprising a support material, at least one precious metal, and at least one NO_x sorbent selected from the group consisting of alkaline earth elements, rare earth elements, and combinations thereof wherein the undercoat washcoat layer is on the carrier; and a top washcoat layer comprising a support material, at least one precious metal, and ceria in particulate form,

the top washcoat layer being substantially free of alkaline earth components; and the SCR catalyst comprises a molecular sieve having the CHA crystal structure that comprises a copper chabazite (CuCHA) and a copper SAPO (CuSAPO), and the molecular sieve is disposed on a carrier. In specific embodiments, the CuCHA is a copper-SSZ-13 and a CuSAPO such as
5 CuSAPO-34, which have good thermal stability. In one specific embodiment, Cu/SSZ-13 is particularly useful in light duty applications such as light duty diesel applications where the SCR should be effective at lower exhaust gas temperatures. In another specific embodiment, Cu/SAPO is useful in medium duty and heavy duty applications where the exhaust temperature will be higher.

10 [0019] The emissions treatment system typically has a controller to periodically lower the air/fuel ratio in the exhaust stream upstream of the ammonia-generating catalyst. In some embodiments, the controller is an engine management system that periodically operates the engine in a rich mode. The controller may also comprise an injector that periodically meters a reducing agent selected from at least one of a hydrocarbon fuel, carbon monoxide and hydrogen
15 into the exhaust stream upstream of the NSR catalyst to form a rich gaseous stream.

[0020] In an optional embodiment, the emissions treatment system also has an oxidation catalyst either upstream of the ammonia-generating catalyst or downstream of the SCR catalyst. The oxidation catalyst may be, for example, disposed on a soot filter. In a detailed embodiment, the SCR catalyst and the oxidation catalyst are both disposed on a soot filter. In this regard, the
20 soot filter can be zoned to have the SCR catalyst in an upstream zone and the oxidation catalyst in a downstream zone. For example, the SCR catalyst can be disposed along the first 10-90% (or 20-80%, or 30-70%, or 40-60%, or even 50%) of the axial length of the filter and the oxidation catalyst can be disposed along the back 90-10% (or 80-20%, or 70-30%, or 60-40%, or even 50%) of the axial length of the filter.

25 [0021] In another aspect, the invention relates to a method for converting NO_x in an exhaust gas from a diesel engine or lean burn gasoline engine to N₂. The method includes: routing the exhaust gas stream through the emissions treatment system of the present invention. In a detailed embodiment, the method comprises (a) contacting the exhaust gas stream comprising NO_x in a lean period with the ammonia-generating component that is an LNT to adsorb NO_x
30 from the exhaust gas stream; (b) periodically altering the air/fuel ratio of the exhaust stream to provide a rich gaseous stream during a rich period; (c) contacting the rich gaseous stream with

the LNT to reduce the adsorbed NO_x and generate NH₃ ; and (d) subsequently contacting a mixture of the NH₃ and the NO_x in the exhaust gas with an SCR catalyst to form N₂.

BRIEF DESCRIPTION OF THE DRAWINGS

- 5 [0022] FIG. 1A is a schematic view showing an engine emission treatment system according to a detailed embodiment;
- [0023] FIG. 1B is a schematic view showing an engine emission treatment system according to a detailed embodiment;
- [0024] FIG. 2 is a schematic view showing an integrated engine emission treatment system
10 according to an embodiment;
- [0025] FIG. 3 is a perspective view of a wall flow filter substrate;
- [0026] FIG. 4 is a cut-away view of a section of a wall flow filter substrate;
- [0027] FIG. 5A is graph showing ammonia removal from a system including copper SSZ-13 catalyst;
- 15 [0028] FIG. 5B is graph showing ammonia removal from a system including Cu SAPO catalyst;
- [0029] FIG. 5C is a graph showing cycle NO_x conversion for various samples to show the effect of a downstream SCR catalyst in accordance with one or more embodiments;
- [0030] FIG. 5D is a graph showing NO_x trapping at 80% conversion for various samples to
20 show the effect of a downstream SCR catalyst in accordance with one or more embodiments; and
- [0031] FIG. 6 is a graph showing accumulated NO_x emissions in grams for Examples 4 and 5.

25 DETAILED DESCRIPTION

- [0032] The invention relates to an emissions treatment system effective for the treatment of the components of exhaust gases from lean burn engines including unburned gaseous hydrocarbons, carbon monoxide, particulate matter (e.g., in diesel exhaust) and especially, NO_x. The system has an upstream ammonia-generating catalyst, such as a lean NO_x trap with dual
30 catalytic function, and a downstream SCR catalyst, and is operated with alternating lean and rich exhaust gases. The LNT catalyst promotes the storage of NO_x during a lean period of operation ($\lambda \gg 1.0$) according to equations (1) and (2), and during a rich period ($\lambda < 1.0$), it catalyzes not

only the reduction of stored NO_x to N₂ (equation 5), but also the formation of NH₃ (equation 6). Applicants have recognized that through selection of components of LNT catalyst and lean/rich operating conditions, adequate amounts of NH₃ can be generated when the exhaust gas is rendered rich.

5 [0033] As to the SCR catalysts, not all of known SCR catalysts that have previously proven to effectively treat NO_x in a lean exhaust are suitable for use downstream of an LNT catalyst. For instance, base metal (e.g., copper, iron) exchanged zeolite compositions (e.g Cu-Y and Fe-beta) or vanadia-based compositions (e.g., V₂O₅/WO₃/TiO₂/SiO₂) are insufficient to provide the desirable NH₃ conversion. These SCR catalysts either do not have sufficient thermal stability
10 during the lean and rich LNT operation or exhibit low NH₃ storage to capture the produced NH₃ from LNT. Thus, the art continues to search for a SCR catalyst that can be used effectively in combination with the LNT. The selection of suitable SCR catalyst components, such as Cu-SSZ-13 or Cu/SAPO-34, that provide good thermal stability permits locating the SCR catalyst close to the LNT catalyst where it can be subjected to high temperature and rich conditions
15 associated with LNT catalyst regeneration and/or particulate filter burn-off. In addition, it has been discovered that Cu/SSZ-13-based SCR catalyst can reduce hydrocarbon (HC) slip during the rich conditions. Such an SCR catalyst, therefore, not only benefits an LNT catalyst-based system from a NO_x and NH₃ standpoint, but also from a HC standpoint. Moreover, it has been discovered that catalyst systems comprising Cu-CHA SCR or Cu-SAPO SCR placed behind an
20 LNT can substantially reduce and/or effectively eliminate large NH₃ breakthrough (ammonia spike) during the cyclic operations where large amounts of NH₃ generated by the LNT during the rich transient.

[0034] The approaches described herein offer flexible, efficient, and predictable ways for designing emissions treatment systems capable of accommodating exhaust gases emitted from a
25 variety of lean burn engines, including diesel engines and lean burn gasoline engines.

[0035] The following terms shall have, for the purposes of this application, the respective meanings set forth below.

[0036] "Lean gaseous streams" including lean exhaust streams mean gas streams that have a $\lambda > 1.0$.

30 [0037] "Lean periods" refer to periods of exhaust treatment where the exhaust gas composition is lean, i.e., has a $\lambda > 1.0$.

[0038] “Platinum group metal components” refer to platinum group metals or one of their oxides.

[0039] “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.

[0040] “Rich gaseous streams” including rich exhaust streams mean gas streams that have a $\lambda < 1.0$.

[0041] “Rich periods” refer to periods of exhaust treatment where the exhaust gas composition is rich, i.e., has a $\lambda < 1.0$.

[0042] “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 gas stream being treated to pass through.

[0043] 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 operations. Such a component excludes gas dosing or other externally supplied sources of NH_3 . Examples of ammonia-generating components include NO_x storage reduction (NSR) catalysts, lean NO_x trap (LNT) catalysts.

[0044] Turning to FIG. 1A, an exhaust gas stream containing gaseous pollutants (e.g., unburned hydrocarbons, carbon monoxide, nitrogen oxides) and particulate matter is conveyed via line 6 from a lean burn engine 4 to an optional oxidation catalyst (DOC) catalyst 8. The exhaust stream is next conveyed via line 10 to a NO_x trap 12, which adsorbs NO_x during lean periods, and reduces NO_x to N_2 , desorbs NO_x and generates NH_3 during rich periods. Some of the NO_x during lean periods can remain unadsorbed, resulting in NO_x slip. The exhaust stream including NO_x slip or NH_3 , depending on the conditions, is routed through line 14 into an SCR catalyst 16. The NH_3 is adsorbed in the SCR. During lean periods, any NO_x slip from the NO_x trap can be reduced to N_2 by the NH_3 in the SCR. Optionally, a diesel particulate filter (DPF) (also referred to as a soot filter) 20, which received the exhaust stream through line 18, is provided downstream of the SCR 16. The particulate filter can be catalyzed with a soot burning catalyst for regeneration. Line 22 leads to the tail pipe and out of the system.

[0045] In FIG. 1B, an emissions treatment system 30 comprises a diesel engine 34 that conveys exhaust through line 36 to an optional DOC catalyst 38, which receives the exhaust

stream through line 36. Line 40 leads the exhaust stream to the NO_x trap 42, which in turn feeds the exhaust through line 44 to an SCR/DPF combination. In the SCR/DPF combination, the SCR catalyst can be coated onto the DPF in a front zone or along the entire length of the DPF.

[0046] In an alternative embodiment shown in FIG. 2, the LNT 52 and SCR 54 catalysts may be disposed in separate zones on the same substrate 50, where the LNT catalyst is disposed on the upstream segment of the substrate, and the SCR catalyst is disposed on the downstream segment.

[0047] The emissions treatment system as shown in FIGS. 1A and 1B can optionally contain an oxidation (DOC) catalyst 8 and 38 upstream of the NO_x trap catalyst 12 and 42.

DOC compositions are well known in the art and may comprise platinum group metals as catalytic agents and optionally base metals (e.g., ceria). In the upstream position (i.e., as 12 and 42), the DOC 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 using the DOC catalyst, in particular, assists in preventing too great a deposition of particulate matter on the NO_x trap and SCR catalysts. In another function, DOC can protect and prolong the useful life of the NO_x trap catalyst.

[0048] Alternatively (not shown), the DOC can be located downstream of the SCR catalyst, where the DOC not only serves to combust unburned hydrocarbon and CO as described above, but also serves as an ammonia slip oxidation catalyst to prevent any unreacted NH₃ from venting to the atmosphere, especially with DOC compositions containing platinum group metal components.

[0049] In certain embodiments of the invention, the DOC is 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. Although the soot filter may be located downstream of the SCR catalyst it is preferred that the catalyzed soot filter be located upstream of the NO_x trap catalyst to minimize or prevent fouling of the NO_x trap catalyst and the SCR catalyst downstream with particulate material.

Substrates

[0050] Preferably, each of the LNT and the SCR catalyst compositions are disposed on a substrate. The substrate may be any of those materials typically used for preparing catalysts, and will preferably comprise a ceramic or metal honeycomb structure. 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.

[0051] FIGS. 3 and 4 illustrate a wall flow filter substrate 50 which has a plurality of having alternately blocked channels 52 and can serve as a DPF. 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 with inlet plugs 58, and at the outlet end with outlet plugs 60 to form opposing checkerboard patterns at the inlet 54 and outlet 56. A gas stream 62 enters through the unplugged channel inlet 64, is stopped by outlet plug 60 and diffuses through channel walls 53 (which are porous) to the outlet side 66. 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. Thus a suitable wall flow filter is a honeycomb substrate having has a plurality of longitudinally extending passages formed by longitudinally extending walls bounding and defining said passages, wherein the passages comprise inlet passages having an open inlet end and a closed outlet end, and outlet passages having a closed inlet end and an open outlet end. Other suitable filters in addition to honeycomb wall flow filters, include, but are not limited to wound or packed fiber filters, open cell foams, sintered metal filters, etc.

[0052] 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.

[0053] 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 50% (e.g., from 50 to 75%) having a mean pore size of at least 5 microns (e.g., from 5 to 30 microns). In a specific embodiment, 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 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.

[0054] 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.

[0055] 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. Preferred 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. A representative commercially-available metal substrate is manufactured by Emitec. However, it will be understood that the invention is not limited to a particular substrate type, material, or

geometry. The surface of 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 of 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.

[0056] In alternative embodiments, one or both of the LNT or SCR catalyst compositions 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.

[0057] The use of the LNT catalysts described herein provides a significant advantage for the design of emissions treatment systems for lean burn engines. As the LNT catalyst has both a NO_x storage function during lean periods of operation and an NH₃ generating function during rich periods of operation, inclusion of separate catalyst substrates to perform these two functions is unnecessary. As a consequence, the burden of preparing and housing separate catalyst substrates is absent. Moreover, overall platinum group metal usage is diminished with the dual function LNT catalyst; since catalysts that promote NO_x storage and catalysts that promote NH₃ formation both generally have platinum group metal components in their compositions. Emissions treatment systems that have a single LNT catalyst instead of separate catalysts for NO_x storage and NH₃ formation therefore can afford the system designer with significant cost savings.

[0058] The air/fuel ratio of the exhaust gas composition may be altered to provide a rich gaseous stream by a number of methods known to those of skill in the art. Controllers that periodically operate the lean burn engine in a rich mode, or more directly alter the air/fuel ratio of the exhaust stream can be used. For instance, the air/fuel ratio can be made rich by periodically operating the engine in a rich mode using well known engine management controls. Alternatively, the exhaust gas stream may be rendered rich by periodically metering a hydrocarbon reductant (e.g., diesel fuel) upstream of the NSR catalyst.

[0059] The amount of NH₃ produced during a rich period depends both on the length and intensity of the rich pulse used to generate the rich gaseous stream. For purposes of operating the emissions treatment system of the invention during a rich period, the rich gaseous stream generally has a λ of from 0.80 to 0.995. Preferably, the rich gaseous stream has a λ of from 0.90 to 0.95. During a lean period, the lean gaseous stream preferably has a λ much greater than 1, for example in the range of 1.5 to 1.8 or higher. The length of the rich period is generally 1 to

10% of the lean period. Such operating parameters ensure that adequate levels of NH_3 are generated with minimum fuel penalty.

[0060] Space velocities for treating NO_x with the inventive emissions treatment system through the NSR catalyst are from 10,000 to 200,000 h^{-1} . More preferably, the space velocity of the exhaust gas is from 10,000 to 100,000 h^{-1} . The space velocities of the exhaust gas through the SCR catalyst are preferably from 10,000 to 300,000 h^{-1} , and more preferably, from 15,000 to 150,000 h^{-1} .

LNT Catalyst Composition

[0061] The LNT catalyst composition used in the inventive system contains a NO_x sorbent and a platinum group metal component dispersed on a refractory metal oxide support. In addition, the LNT catalyst composition optionally contains other components such as oxygen storage components that significantly affect the quantity of NH_3 formed during a rich period of operation.

[0062] The LNT catalyst may take any form such as self-supporting particles (e.g., tablets, beads) or as a solid honeycomb monolith formed of the catalyst composition. However, the LNT catalyst composition is preferably disposed as a washcoat or as a combination of washcoats (to form a layered catalyst composite) on a ceramic or metallic substrate. In preferred embodiments of the invention the LNT catalyst is either in the form of a single layer, or a bi-layer catalyst composite with the bottom layer adhered to the substrate and the top layer overlying to the bottom layer.

[0063] The LNT catalyst composition comprises at least a NO_x trapping component (e.g. Ba, Mg etc) and a support. The support is composed of at least a high surface area refractory metal oxide such as alumina, titania, zirconia; mixtures of alumina with one or more of titania, zirconia and ceria; ceria coated on alumina or titania coated on alumina. The refractory metal oxide may contain an oxide or a mixed oxide such as silica-alumina, aluminosilicates which may be amorphous or crystalline, alumina-zirconia, alumina-chromia, alumina-ceria and the like. The preferred refractory metal oxides are gamma alumina, ceria coated on alumina and titania coated on alumina. It is advantageous that the preferred support may contain dispersed alkaline earth elements (e.g. Barium) and the catalyst may further comprise ceria in particulate form.

[0064] Typically, the refractory metal oxide will have a specific surface area of about 50 to about 300 m^2/g . The support is typically presents in an amount of about 1.5 to about 7.0 g/in^3 ,

this amount being the total amount in embodiments with two or more catalyst layers. In embodiments of the invention where there are two layers, the support chosen for the bottom layer need not be, but is conveniently, the same as that chosen for the top layer. Moreover, the amount of the support in the bottom layer need not be the same as that in the top layer, so long as the amounts of the supports in the bottom and top layers are sufficient for providing desirable performance.

[0065] Dispersed on the support will be one or more platinum group metal components, e.g., platinum, palladium, rhodium and mixtures thereof. These components of the LNT catalyst promote oxidation and reduction of nitrogen species. The amount of loading of the platinum group metal component will be in the range of about 10 to about 250 g/ft³, and preferably, the amount will be in the range of 50 to 200 g/ft³, these amounts being the total amount in embodiments with two or more catalyst layers. Here again, in embodiments of the invention where a bi-layer catalyst composite is used, the platinum group metal component chosen for the bottom layer need not be, but is conveniently, the same as that chosen for the top layer. Moreover, the amount of the platinum group metal component in the bottom layer need not be the same as that in the top layer, so long as the amounts of the platinum group metal components in the bottom and top layers are within the foregoing range.

[0066] For the purposes of the present invention, the LNT catalyst also contains at least one NOx sorbent component to ensure an adequate NOx storage capacity. In addition, the NOx storage capacity significantly affects the ability of the LNT catalyst to form NH₃, since the formation of NH₃ during a rich period of operation is in part limited by the supply of stored NOx (i.e., as a metal nitrate). Typically, the NOx sorbent component is present in an amount of at least 0.1 g/in³, such as from 0.1 to 4.0 g/in³ to ensure adequate NOx storage. More preferably there is at least about 0.2 g/in³ of NOx sorbent, and still more preferably at least 0.3 g/in³ of NOx sorbent in the composition. A suitable NOx sorbent component comprises a basic oxygenated compound of alkaline earth element selected from magnesium, calcium, strontium or barium and mixtures thereof and an oxygenated compound of rare earth element consisting of cerium. The cerium may further contain lanthanum, neodymium and praseodymium as impurity.

[0067] A component of the LNT catalyst composition that affects NOx storage and formation of NH₃ is the ceria. While the ceria component improves the NOx trapping capacity at lower temperatures, too great a concentration of the component may limit the quantity of NH₃ that can be formed during normal lean and rich operation. Applicants believe that the presence of too

high an amount of the ceria component will consume a large portion of the reductants during the rich transient. As a result, an additional amount of reductant is needed to induce the formation of an adequate amount of NH_3 , which results in an increase in fuel penalty.

[0068] The ceria component may be dispersed on the refractory metal oxide support by, for example, dispersing a soluble precursor (e.g., cerium nitrate) on the refractory metal oxide support. Alternatively, the component is provided in particulate form in the composition. By particulate form it is meant that a composition is in a solid, preferably as fine particles which can be as small as 1 to 15 microns in diameter or smaller, as opposed to being dispersed in solution in the base metal washcoat. Other rare earth elements as an impurity may be present in the ceria.

[0069] In some embodiments, the ceria component may be composed of a bulk fine particulate material of co-formed rare earth metal-zirconia composite (e.g., a ceria-zirconia composite) such as are commercially available or are readily apparent to those of skill in the art. For instance, co-formed composites are described in United States Patent No. 5,057,483. These particles do not react with stabilized alumina washcoat and can maintain a BET surface area of above $40 \text{ m}^2/\text{g}$ upon exposure to 900°C for a long period of time.

[0070] Other components that may be added to the LNT composition include other transition metals such as zirconium. If used, such transition metal components are typically present in an amount of about 0.01 to about 0.5 g/in^3 .

[0071] The LNT catalyst composites may be readily prepared by processes well known in the prior art.

[0072] Specific desired LNT compositions are similar to those disclosed in United States Provisional Patent Application Serial No. 61/076,560 (Wan), filed June 27, 2008, which is incorporated herein by reference. Such LNT compositions exhibit good NO_x storage/ NO_x reduction activity at exhaust temperature of 100 to 600°C , and more particularly, at temperatures of 150 to 450°C . In addition, such LNT catalyst compositions exhibit outstanding thermal stability and the ability to remove sulfur compounds under moderate conditions. Interestingly, ceria in the LNT in particulate form with the presence of platinum group metals not only enhances the NO_x trapping efficiency at lower temperatures (especially below 250°C) in a net lean conditions, but also can activate the conversion of adsorbed nitrogen oxides in a net rich condition at the same low temperature.

[0073] The LNT catalyst composition can comprise a top washcoat layer and an undercoat washcoat layer. The top washcoat layer comprises at least one supported precious metal catalyst

and ceria as a NO_x trapping component. The top washcoat layer is substantially free of any alkaline earth components, which are believed to hinder the conversion of adsorbed nitrogen oxides over the precious metal components in a net rich conditions at low temperatures (typically <250°C). The top washcoat composition is capable of oxidizing NO_x at temperatures below 200°C. Additionally, the top washcoat layer is capable of effectively reducing unburned carbon monoxides at temperatures below 200°C. The undercoat layer comprises at least one NO_x trapping component in intimate contact with at least one supported precious metal catalyst for the treatment of exhaust gas emissions. Preferably, the undercoat layer comprises at least one alkaline earth element and/or rare earth element as NO_x trapping components.

[0074] In one embodiment, the lean NO_x trap/catalyst may comprise a trapping/catalyst composition, which comprises two distinct washcoat layers coated on a single substrate or carrier member, one layer (e.g., a top washcoat layer) over top of the other (e.g., an undercoat washcoat layer). In this embodiment, the undercoat washcoat layer is coated over the entire axial length of a substrate (e.g., a flow-through monolith) and the top washcoat layer is coated over the entire axial length of the undercoat washcoat layer. In accordance with the present invention, top washcoat layer comprises at least one supported precious metal for the treatment of exhaust gas emissions, and optionally may contain zirconia, but is devoid of any alkali or alkaline earth components. The undercoat layer may contain at least one NO_x trapping component or NO_x adsorbent, which selectively adsorbs and converts nitrogen oxides from exhaust gas streams at higher operating temperatures. The undercoat washcoat layer may also contain at least one precious metal catalyst for the treatment of exhaust gas emissions. Under lean burn conditions, the washcoat layers of the present invention can simultaneously store nitrogen oxides (NO_x) and catalyzes the conversion of hydrocarbons and carbon monoxide in exhaust gas streams. Under adequate rich regeneration conditions; stored NO_x may be converted by the catalysts contained in both the top and undercoat washcoat layers.

[0075] The LNT catalyst composite can be readily prepared in layers on a monolithic honeycomb substrate. For the bottom layer, finely divided particles of a high surface area refractory metal oxide such as gamma alumina and other catalyst components are slurried in an appropriate vehicle, e.g., water. The substrate may then be dipped one or more times in such slurry or the slurry may be coated on the substrate (e.g., honeycomb flow through substrate) such that there will be deposited on the substrate the desired loading of the metal oxide, e.g., about 1.5 to about 6.0 g/in³. Components such as the platinum group metals, transition metal

oxides, stabilizers, promoters and the NO_x sorbent component may be incorporated in the slurry as a mixture of water soluble or water-dispersible compounds or complexes. Thereafter the coated substrate is calcined by heating, e.g., at 400 to 600 °C for 1 to 3 hours.

[0076] Typically, the platinum group metal component, e.g., platinum component, is dispersed on the refractory metal oxide, e.g., activated alumina, using a platinum group metal salt or complex (or platinum group metal precursor). For the purposes of the present invention, the term "platinum group metal precursor" means any compound, complex, or the like which, upon calcination or use thereof, decomposes or otherwise converts to a catalytically active form, usually the metal or the metal oxide. Water-soluble compounds or water-dispersible compounds or complexes of the metal component may be used as long as the liquid medium used to impregnate or deposit the metal component onto the refractory metal oxide support particles does not adversely react with the metal or its compound or its complex or other components which may be present in the catalyst composition and is capable of being removed from the metal component by volatilization or decomposition upon heating and/or application of a vacuum. In some cases, the completion of removal of the liquid may not take place until the catalyst is placed into use and subjected to the high temperatures encountered during operation. Generally, both from the point of view of economics and environmental aspects, aqueous solutions of soluble compounds or complexes of the platinum-group metals are preferred. For example, suitable compounds are chloroplatinic acid, amine-solubilized platinum hydroxide, palladium nitrate or palladium chloride, rhodium chloride, rhodium nitrate, hexamine rhodium chloride, etc. During the calcination step, or at least during the initial phase of use of the composite, such compounds are converted into a catalytically active form of the metal or a compound thereof.

[0077] A preferred method of forming the bottom layer of the layered catalyst composite of the invention is to prepare a mixture of a solution of a platinum group metal precursor and at least one finely divided, high surface area, refractory metal oxide support, e.g., gamma alumina, which is sufficiently dry to absorb substantially all of the solution to form a slurry. Preferably, the slurry is acidic, having a pH of about 3 to less than 7. The pH of the slurry may be lowered by the addition of a minor amount of an inorganic or organic acid such as hydrochloric or nitric acid, preferably acetic acid, to the slurry. Thereafter, the NO_x sorbent component, and optional transition metal components, stabilizers and/or promoters may be added to the slurry.

[0078] In a particularly preferred embodiment, the slurry is thereafter comminuted to result in substantially all of the solids having particle sizes of less than 20 microns, i.e., 1-15 microns, in an average diameter. The comminution may be conducted in a ball mill or other similar equipment, and the solids content of the slurry may be, e.g., 20-60 wt.%, preferably 25-45 wt.%.
5 [0079] The top layer is thereafter prepared and deposited on the bottom layer of the calcined composite in a manner similar to that described above. After all coating operations have been completed, the composite is then again calcined by heating, e.g., at 400 to 600 °C for 1-3 hours.

SCR Catalyst

10 [0080] Not all of known SCR catalysts that were proven to effectively treat NO_x in a lean exhaust are suitable for use in downstream of the LNT catalyst. For instance, base metal (e.g., copper, iron) exchanged zeolite compositions (e.g. Cu-Y and Fe-beta) or vanadia-based compositions (e.g., V₂O₅/WO₃/TiO₂/SiO₂) are insufficient to provide the desirable NH₃ conversion. These SCR catalysts either do not have sufficient thermal stability during the lean
15 and rich LNT operation or exhibit low NH₃ storage to capture the produced NH₃ from LNT. Thus, the art continues to search for a SCR catalyst that can be used effectively in combination with the LNT.

[0081] In a specific embodiment of the emissions treatment system the SCR catalyst is formed from a base metal exchanged zeolite material. Such SCR catalyst compositions are
20 described, for example, in United States Patent Application Pub. No. 2008/0202107 (Boorse), which is hereby incorporated by reference. Compositions disclosed in Boorse include Cu-exchanged chabazite molecular sieve. In a preferred embodiment, the zeolite includes a copper component. In a particularly specific embodiment, the Cu/CHA is a copper-SSZ-13. Molecular sieves exhibiting structures similar to chabazite such as SAPO are also found effective. Thus, in
25 a specific embodiment, the Cu/SAPO is a copper- SAPO-34.

[0082] When deposited on the honeycomb monolith substrates, such SCR catalyst compositions are deposited at a concentration of at least 0.5 g/in³ to ensure that the desired NH₃ reduction is achieved and to secure adequate durability of the catalyst over extended use. One preferred embodiment provides that the SCR catalyst is loaded onto a carrier in an amount in the
30 range of 0.5 to 2.5 g/in³ (or 0.5 to 2.0 g/in³, or even 0.5 to 1.5 g/in³). In a specific embodiment, the SCR compositions are disposed on a wall flow monolith (e.g. a DPF).

[0083] Another particularly useful catalyst in accordance with one or more embodiments of the invention comprises a molecular sieve having the CHA crystal structure. Molecular sieves having the CHA crystal structure can include non-zeolitic molecular sieves (e.g. SAPO). Molecular sieves having the CHA crystal structure also include zeolites.

5 [0084] According to one or more embodiments, washcoats of metal-loaded zeolitic molecular sieves having the CHA structure can be prepared using a binder. According to one or more embodiments, use of a ZrO_2 binder derived from a suitable precursor such as zirconyl acetate or any other suitable zirconium precursor such as zirconyl nitrate. In one embodiment, zirconyl acetate binder provides a catalytic coating that remains homogeneous and intact after thermal
10 aging, for example, when the catalyst is exposed to high temperatures of at least about 600°C , for example, about 800°C and higher, and high water vapor environments of about 10% or more. Keeping the washcoat intact is beneficial because loose or free coating could plug the CSF itself if the CSF contains the SCR coating, or plug the downstream CSF if a flow-through SCR catalyst is placed in front of the CSF, causing the backpressure to increase. Other
15 potentially suitable binders include, but are not limited to, alumina and silica. Alumina binders include aluminum oxides, aluminum hydroxides, and aluminum oxyhydroxides. Aluminum salts and colloidal forms of alumina may also be used. Silica binders include various forms of SiO_2 , including colloidal silica. Furthermore, binder compositions may include any combination of zirconia, alumina, and silica.

20

Molecular Sieves Having the CHA Crystal Structure

[0085] One embodiment of the invention relates to a catalyst comprising a zeolite having the CHA crystal structure and a mole ratio of silica to alumina greater than about 15 and an atomic ratio of copper to aluminum exceeding about 0.25. In a specific embodiment, the mole ratio of
25 silica to alumina is from about 15 to about 256 and the atomic ratio of copper to aluminum is from about 0.25 to about 0.50. In a more specific embodiment, the mole ratio of silica to alumina is from about 25 to about 40. In an even more specific embodiment, the mole ratio of silica to alumina is about 30. In one particular embodiment, the atomic ratio of copper to aluminum is from about 0.30 to about 0.50. In a specific embodiment, the atomic ratio of
30 copper to aluminum is about 0.40. In a specific embodiment, the mole ratio of silica to alumina is from about 25 to about 40 and the atomic ratio of copper to aluminum is from about 0.30 to

about 0.50. In another specific embodiment, the silica to alumina is about 30 and the atomic ratio of copper to alumina is about 0.40.

[0086] In a particular embodiment, the catalyst contains ion-exchanged copper and an amount of copper sufficient to maintain NO_x conversion performance of the catalyst in an exhaust gas stream containing nitrogen oxides after hydrothermal aging of the catalyst. In a particular embodiment, the catalyst contains at least about 2.00 weight percent copper oxide.

[0087] In one embodiment, a catalyst article comprises a honeycomb substrate having a zeolite having the CHA crystal structure deposited on the substrate, the zeolite having a mole ratio of silica to alumina greater than about 15 and an atomic ratio of copper to aluminum exceeding about 0.25 and containing an amount of copper exceeding ion-exchanged capacity. In a specific embodiment, excessive copper may be present in an amount sufficient to prevent hydrothermal degradation of the structure of the catalyst. The catalyst may further comprise a binder.

[0088] In one embodiment of the invention, zeolites having the CHA structure such as chabazite are provided. In one or more embodiments, a zeolite having the CHA crystal structure and a mole ratio of silica to alumina greater than about 15 and an atomic ratio of copper to aluminum exceeding about 0.25 is provided. In specific embodiments, the mole ratio of silica to alumina is about 30 and the atomic ratio of copper to aluminum is about 0.40. Other zeolites having the CHA structure, include, but are not limited to SSZ-13, LZ-218, Linde D, Linde R, Phi, ZK-14, and ZYT-6.

[0089] In another embodiment of the invention, a catalyst article comprises a honeycomb substrate having a non-zeolitic molecular sieves having the CHA crystal structure such as SAPO deposited on the substrate. In a specific embodiment, a sufficient amount of copper is present to prevent hydrothermal degradation of the structure of the catalyst and to sustain the performance of the catalyst. The catalyst may further comprise a binder.

[0090] Synthesis of the molecular sieves having the CHA structure can be carried out according to various techniques known in the art. For example, in a typical SSZ-13 synthesis, a source of silica, a source of alumina, and an organic directing agent are mixed under alkaline aqueous conditions. Typical silica sources include various types of fumed silica, precipitated silica, and colloidal silica, as well as silicon alkoxides. Typical alumina sources include boehmites, pseudo-boehmites, aluminum hydroxides, aluminum salts such as aluminum sulfate, and aluminum alkoxides. Sodium hydroxide is typically added to the reaction mixture, but is

not required. A typical directing agent for this synthesis is adamantyltrimethylammonium hydroxide, although other amines and/or quaternary ammonium salts may be substituted or added to the latter directing agent. The reaction mixture is heated in a pressure vessel with stirring to yield the crystalline SSZ-13 product. Typical reaction temperatures are in the range of 150 and 180°C. Typical reaction times are between 1 and 5 days.

[0091] At the conclusion of the reaction, the product is filtered and washed with water. Alternatively, the product may be centrifuged. Organic additives may be used to help with the handling and isolation of the solid product. Spray-drying is an optional step in the processing of the product. The solid product is thermally treated in air or nitrogen. Alternatively, each gas treatment can be applied in various sequences, or mixtures of gases can be applied. Typical calcination temperatures are in the 400°C to 700°C range.

[0092] CuCHA zeolite catalysts and CuSAPO molecular sieve catalysts in accordance with one or more embodiments of the invention can be utilized in catalytic processes which involve oxidizing and/or hydrothermal conditions, for example in temperatures in excess of about 600°C, for example, above about 800°C and in the presence of about 10% water vapor. More specifically, it has been found that the catalysts which have been prepared in accordance with embodiments of the invention have superior hydrothermal stability compared to CuY and FeBeta zeolites. CuCHA zeolite catalysts and CuSAPO molecular sieve catalysts prepared in accordance with embodiments of the invention when combined with the LNT as a catalyst system can yield improved total NO_x reduction activity and substantially reduce or eliminate the large release of ammonia, especially after aging under high temperatures of at least about 600°C, for example, about 800°C, and high water vapor environments of about 10% or more. CuCHA and CuSAPO have high intrinsic activities that enable use of lower amounts of catalyst material, which in turn should reduce backpressure of honeycomb substrates coated with washcoats of the catalysts. In one or more embodiments, hydrothermal aging at high temperature refers to exposure of catalyst to a temperature of about 800°C in a high water vapor environments of about 10% or more, for at least about 1 to about 24 hours.

[0093] Experimentation has indicated that improved performance of CuCHA catalysts in accordance with embodiments of the invention is associated with Cu loading. While Cu can be exchanged to increase the level of Cu associated with the exchange sites in the structure of the zeolite, it has been found that it is beneficial to leave non-exchanged Cu in salt form, for example, as CuSO₄ within the zeolite catalyst. Upon calcination, the copper salt decomposes to

CuO, which may be referred to herein as "free copper" or "mobile copper." According to one or more embodiments, this free Cu is both active and selective, resulting in low N₂O formation when used in the treatment of a gas stream containing nitrogen oxides. Unexpectedly, this "free" Cu has been found to impart greater stability in CuCHA catalysts subjected to thermal aging at temperatures up to about 800°C.

[0094] While embodiments of the invention are not intended to be bound by a particular principle, it is believed that the relatively small channel openings of the molecular sieve having CHA structure do not permit large molecular weight hydrocarbons (HCs) typical of diesel fuel to enter and adsorb within the CHA structure. Unlike other zeolites like Beta or ZSM5, CHA catalysts prepared according to embodiments of the invention have a relatively low affinity for adsorbing these large molecular weight HC species. This is a beneficial property for use in selective catalytic reduction (SCR) catalysts.

[0095] In use, the exhaust gas stream can be contacted with a catalyst prepared in accordance with embodiments of the present invention. For example, the CuCHA and CuSAPO catalysts made in accordance with embodiments of the present invention are well suited to treat the exhaust of engines, including diesel engines.

[0096] Without intending to limit the invention in any manner, embodiments of the present invention will be more fully described by the following examples.

EXAMPLES

[0097] An emissions system was formed by preparing, in accordance with methods set forth herein, an oxidation catalyst, an LNT catalyst having an undercoat washcoat layer in conjunction with a topcoat washcoat layer and an SCR catalyst comprising copper-SSZ-13 (CuCHA) or copper-SAPO-34 (CuSAPO).

EXAMPLE 1

[0098] The oxidation catalyst was disposed on a flow-through monolith substrate, having a volume of 50 in³ (0.83 L), a cell density of 300 cells per square inch, and a wall thickness of approximately 125 µm. The catalyst contained a washcoat of 2.5 g/in³ activated alumina bearing 40 g/ft³ Pt and 8 g/ft³ Pd and 0.5 g/in³ H-beta zeolite.

[0099] The layered LNT catalyst was disposed on a flow-through monolith substrate, having a volume of 152 in³ (2.5 L), a cell density of 400 cells per square inch, and a wall thickness of approximately 100 μ m. The undercoat contained a washcoat of 3.84 g/in³ activated alumina containing 10% ceria and 18% BaO, 1.1 g/in³ ceria (87% of the ceria being in particulate form), 0.24 g/in³ MgO, and 0.096 g/in³ ZrO₂. The undercoat washcoat contained 34.3 g/ft³ Pt and 4.3 g/ft³ Pd. The topcoat contained a washcoat of 0.7 g/in³ activated alumina bearing 21.7 g/ft³ Pt and 2.7 g/ft³ Pd and 0.5 g/in³ ceria bearing 7.0 g/ft³ Rh, with no substantial alkaline earth component being present in the topcoat washcoat. The resulting layered LNT catalyst contained a total of 56 g/ft³ Pt, 7 g/ft³ Pd and 7 g/ft³ Rh.

[0100] The CuCHA SCR catalyst was disposed on a flow-through monolith substrate, having a volume of 91.5 in³ (1.5 L), a cell density of 400 cells per square inch, and a wall thickness of approximately 150 μ m. The CHA zeolite was the SSZ-13 composition. The copper loading on the zeolite was 3.2 wt% and the total washcoat loading on the monolith was 2.4 g/in³.

[0101] The CuSAPO SCR catalyst was disposed on a flow-through monolith substrate, having a volume of 91.5 in³ (1.5L), a cell density of 400 cells per square inch, and a wall thickness of approximately 150 μ m. The SAPO molecular sieve exhibited SAPO-34 composition having a silica to alumina molar ratio of about 0.67. The copper loading on the molecular sieve was 2.2 wt% and the total washcoat loading was 2.0 g/in³.

EXAMPLE 2

COMPARATIVE

[0102] An emissions system was formed by preparing the LNT catalyst of Example 1 in the absence of any of the SCR catalysts.

EXAMPLE 3

TESTING

[0103] Core samples were taken from each of the flow-through catalysts above-mentioned in Example 1. The size of the individual core sample was 0.75"(D) x 0.42" (L) for DOC, 0.75" (D) x 1.25" (L) for LNT and 0.75" (D) x 0.75" (L) for SCR. Three sets of system samples were assembled in individual laboratory reactor respectively. The distance of each catalyst elements in the laboratory reactor was 0.25". The emissions systems of Example 1 of this invention (i.e. DOC + LNT + Cu-CHA and DOC + LNT + Cu-SAPO) and Comparative Example 2 (i.e. (DOC

+ LNT only) were individually aged. The aging procedures consisted of two steps. First, the catalyst system was aged at 800°C in flowing air with 10% steam for 5 hours. Then, the catalyst system was subjected to a cyclic aging protocol consisting of a sulfation mode (1 g S/L loading) at 300°C and desulfation mode (cycle between 10 seconds lean and 15 seconds rich ($\lambda=0.9$) for 5 minutes) at 700°C (LNT bed temperature). The cyclic aging ran for 40 cycles. After the aging the catalyst system was evaluated on a reactor test rig with FTIR analytical apparatus. The evaluations were conducted with 12 cycles of a 120 seconds lean gas exposure and then followed by a 5 seconds rich gas exposure. The lean gas consisted of 200 ppm NO, 5% CO₂, 5% H₂O, 10% O₂ and balance N₂. The rich gas ($\lambda=0.95$) contained 2.36% CO, 0.78% H₂, 0.95% O₂, 5% CO₂, 5% H₂O, 1500 ppm C₃H₆ balance N₂. The space velocity during the test was kept constant at 60,000 hr⁻¹ (based on LNT volume). The percentage of NH₃ formation was monitored throughout the test and reported as a cycle average number based on the total NO_x input in the test. The NO_x trapping capacity of the system was measured after the end of 12th rich exposure and presented as the amount of NO_x removed from the system when 80% cycle NO_x conversion was reached.

[0104] As shown in FIG. 5A and FIG 5B, the catalyst system comprising Cu-CHA SCR or Cu-SAPO SCR (shown as the heavy or thick line in FIG. 5A and 5B) placed behind the LNT of Example 1 substantially reduced and/or effectively eliminated large NH₃ breakthrough (ammonia spike) during the cyclic operations where large amounts of NH₃ generated by the LNT during the rich transient. As can be seen in the Figures, according to embodiments including CuCHA SCR or CuSAPO SCR placed downstream of the LNT can substantially reduce and/or eliminate ammonia spikes during rich transient operation. As used herein, substantially reduce refers to a reduction of at least about 50%, 60%, 70%, 80% and 90% or greater in ammonia produced during rich transient operation. By eliminating a spike in ammonia emissions, the possibility of exceeding a regulatory limit for ammonia emissions can be avoided. Thus, by selecting the proper SCR catalyst and amount of catalyst the ammonia spike can be suppressed below a predetermined limit. As indicated in FIG. 5C and FIG. 5D, the catalyst system comprising Cu-CHA or Cu-SAPO placed behind the LNT of Example 1 greatly improved the system performance and significantly enhanced the system NO_x trapping capacity.

EXAMPLE 4

[0105] An emissions system was formed by preparing, in accordance with methods set forth herein, an LNT catalyst having a 2-layered structure and a downstream SCR catalyst comprising copper-SSZ-13 (CuCHA) on a diesel particulate filter (DPF).

[0106] The LNT catalyst was disposed on a flow-through monolith substrate, having a volume of 152 in³ (2.5 L), a cell density of 400 cells per square inch, and a wall thickness of approximately 100 μ m. The preparation of the LNT was essentially the same as that described in Example 1 except the PGM loading. The undercoat contained 63 g/ft³ Pt and 6.5 g/ft³ Pd and the topcoat bore 40 g/ft³ Pt and 4 g/ft³ Pd on activated alumina and 6.5 g/ft³ on ceria. The resulting layered LNT catalyst contained a total of 103 g/ft³ Pt, 10.5 g/ft³ Pd and 6.5 g/ft³ Rh.

[0107] The CuCHA SCR catalyst was disposed on a wall- flow filter substrate, having a volume of 152 in³ (2.5 L), a cell density of 300 cells per square inch, and a wall thickness of approximately 300 μ m. The washcoat loading on the filter was about 1.5 g/in³ and containing 3 wt% Cu. The SCR was coating along 100 % of the length of the DPF.

EXAMPLE 5

COMPARATIVE

[0108] An emissions system was formed by preparing the LNT catalyst of Example 4 and in the absence of the downstream SCR catalyst on a filter to show the effect of the downstream SCR catalyst on a filter.

EXAMPLE 6

TESTING

[0109] The emissions systems of Example 4 and comparative Example 5 were tested on a transient engine test cell in New European Drive Cycle (NEDC) conditions. A 6-cylinder state of the art engine was used. FIG. 6 shows accumulated NOx emissions over the course of the engine test, where the engine speed is shown by the bottom-most line and where NOx emissions are measured at (a) engine out, (b) after the NOx trap, and (c) after the SCRF. As show in FIG. 6, the total NOx conversion of the combined system of Example 4 was about 80%, which is depicted by the accumulated NOx emissions being reduced from approximately 2.67 g to approximately 0.56 g on line (c) at the end of the test cycle, whereas the system of comparative Example 5 was about 68%, which is depicted by the accumulated NOx emissions being reduced from approximately 2.67 g to approximately 0.86 g on line (b) at the end of the test cycle.

[0110] 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
5 all modifications encompassed within the spirit and scope of the invention as defined by the claims that follow.

What is claimed:

1. An emissions treatment system for an exhaust stream of a diesel engine or a lean burn gasoline engine comprising:
an in-situ ammonia-generating component; and
5 an SCR catalyst disposed downstream of the ammonia-generating component, wherein the SCR catalyst comprises a molecular sieve having the CHA crystal structure.
2. The emissions treatment system of claim 1, wherein the SCR catalyst is present in an amount in the range of 0.5 to 2.5 g/in³.
3. The emissions treatment system of claim 1, wherein the molecular sieve comprises a
10 copper chabazite (CuCHA) or a copper SAPO (CuSAPO), and the molecular sieve is disposed on a downstream carrier.
4. The emissions treatment system of claim 3, wherein the molecular sieve is a copper chabazite SSZ-13.
5. The emissions treatment system of claim 3, wherein the molecular sieve is copper
15 SAPO-34.
6. The emissions treatment system of claim 1, wherein the downstream carrier comprises a wall flow filter having a plurality of longitudinally extending passages formed by longitudinally extending walls bounding and defining said passages, wherein the passages comprise inlet
20 passages having an open inlet end and a closed outlet end, and outlet passages having a closed inlet end and an open outlet end, the wall flow filter being coated by the SCR catalyst in the range of about 10% to 100% of the axial length.
7. The emissions treatment system of claim 6, wherein the filter is coated with the SCR catalyst along the axial length in the range of 60 to 40% from an upstream end and with an oxidation catalyst along the axial length in the range of 40 to 60% from a downstream end.
- 25 8. The emissions treatment system of claim 1, wherein the ammonia-generating component comprises a lean NO_x trap (LNT) catalytic material disposed on an upstream carrier that is a flow through monolith.

9. The emissions treatment system of claim 8, wherein the undercoat washcoat layer comprises a support material, at least one precious metal, and at least one NO_x sorbent selected from the group consisting of oxides of magnesium, calcium, strontium, barium, lanthanum, cerium, praseodymium, neodymium, and combinations thereof wherein the undercoat washcoat layer is on the carrier; and

the top washcoat layer comprises a support material, at least one precious metal, and ceria in particulate form, the top washcoat layer being substantially free of alkaline earth components.

10. An emissions treatment system for an exhaust stream, comprising:

an ammonia-generating component that comprises a lean NO_x trap (LNT) catalytic material disposed on a carrier, the catalytic material comprising:

an undercoat washcoat layer comprising a support material, at least one precious metal, and at least one NO_x sorbent selected from the group consisting of alkaline earth elements, rare earth elements, and combinations thereof wherein the undercoat washcoat layer is on the carrier; and

a top washcoat layer comprising a support material, at least one precious metal, and ceria in particulate form, the top washcoat layer being substantially free of alkaline earth components; and

an SCR catalyst disposed downstream of the ammonia-generating component, wherein the SCR catalyst comprises a molecular sieve having the CHA crystal structure disposed on a carrier.

11. A method of converting NO_x in an exhaust gas stream from a diesel engine or lean burn gasoline engine to N₂ comprising: routing the exhaust gas stream through the emissions treatment system of any of the preceding claims.

12. The method of claim 11, comprising:

(a) contacting the exhaust gas stream comprising NO_x in a lean period with the ammonia-generating component that is an LNT to sorb NO_x from the exhaust gas stream;

(b) periodically altering the air/fuel ratio of the exhaust stream to provide a rich gaseous stream during a rich period;

(c) contacting the rich gaseous stream with the LNT to reduce a portion of the sorbed NO_x to NH₃ and sorbing NH₃ on the SCR catalyst; and

(d) subsequently reacting NH₃ sorbed on the SCR catalyst with NO_x in the exhaust gas with the SCR catalyst.

- 5 13. The method of claim 24, wherein step (d) occurs during a lean period of operation.
14. The emissions treatment system of claim 1, wherein the SCR catalyst is effective to suppress a spike in ammonia below a predetermined limit.
15. The emissions treatment system of claim 10, wherein the SCR catalyst is effective to suppress a spike in ammonia below a predetermined limit.

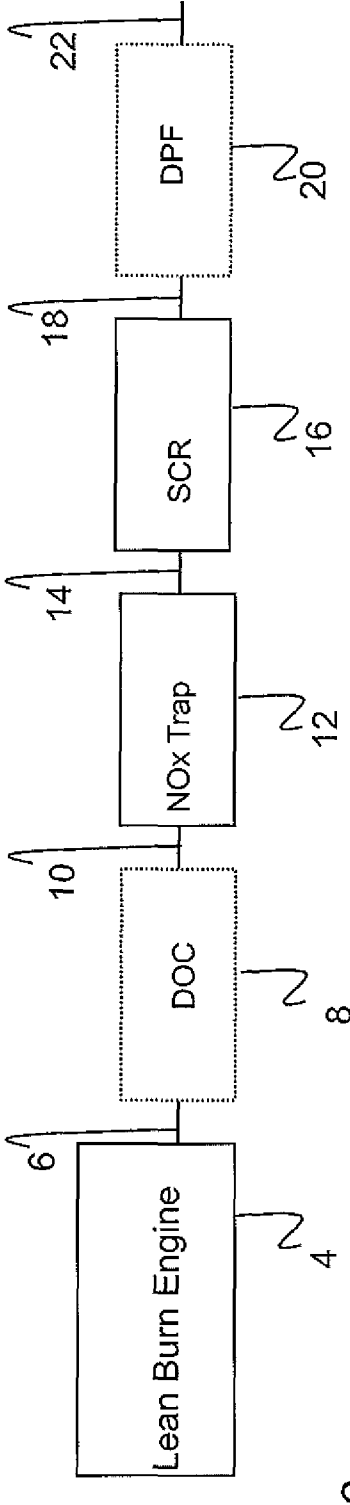


FIG. 1A

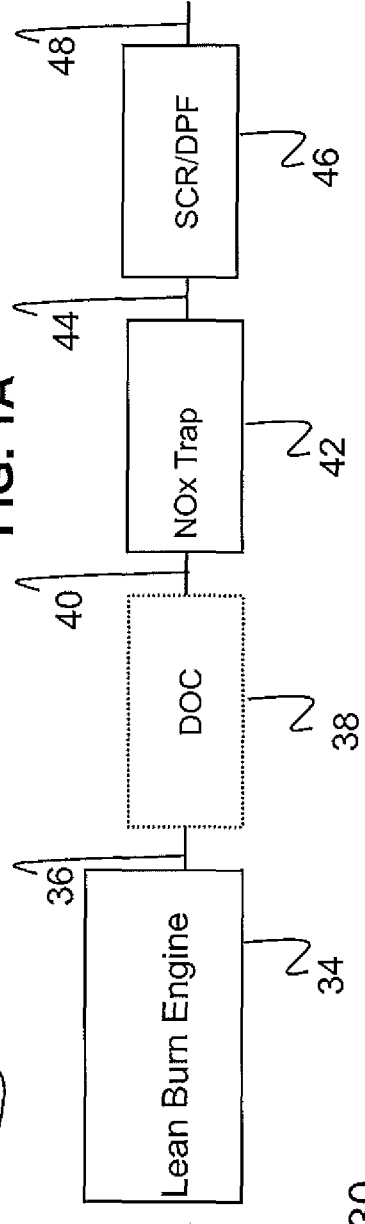


FIG. 1B

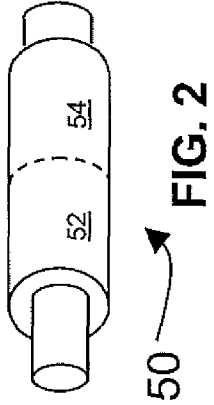


FIG. 2

2/5

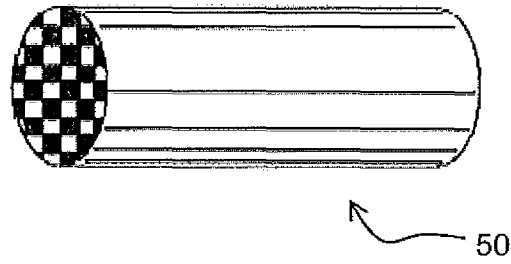


FIG. 3

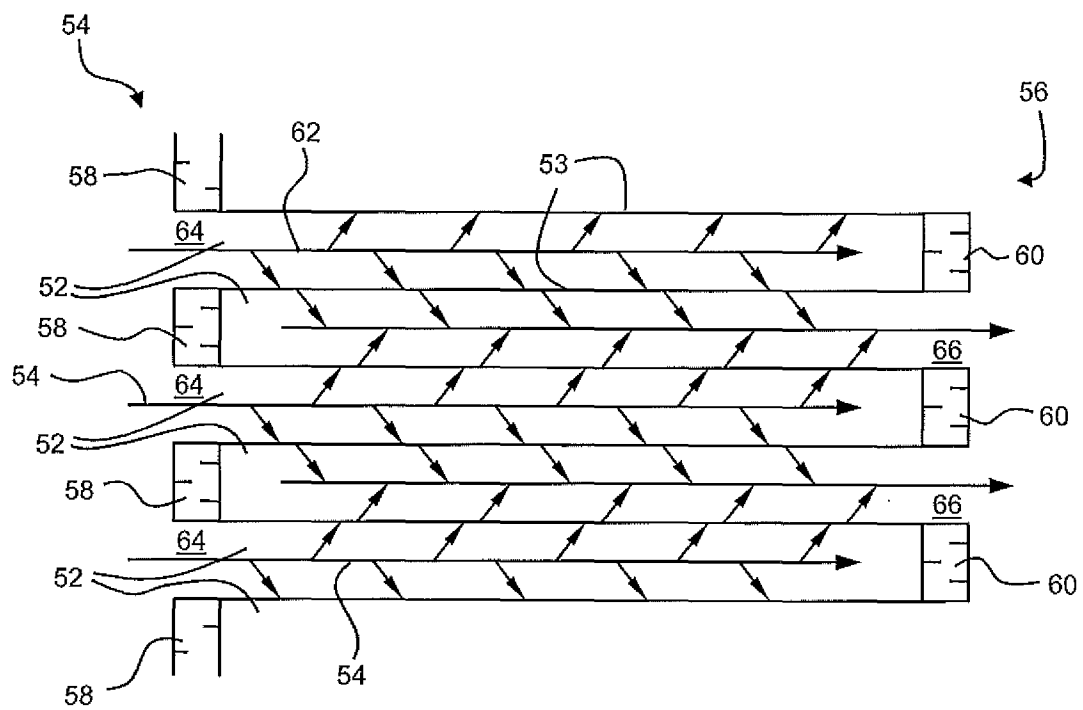


FIG. 4

3/5

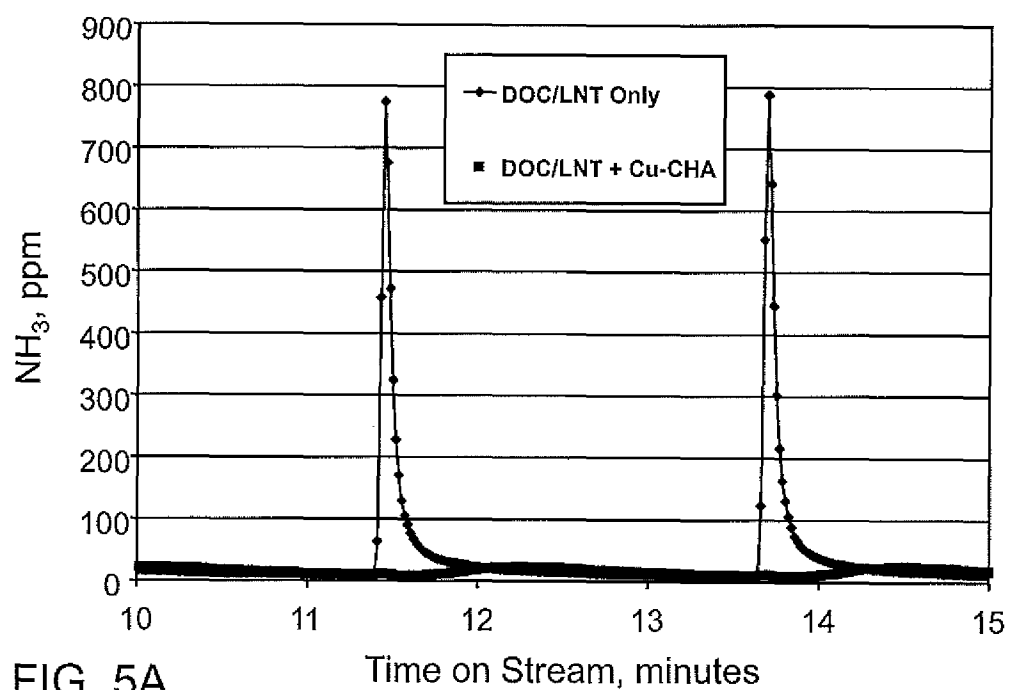


FIG. 5A

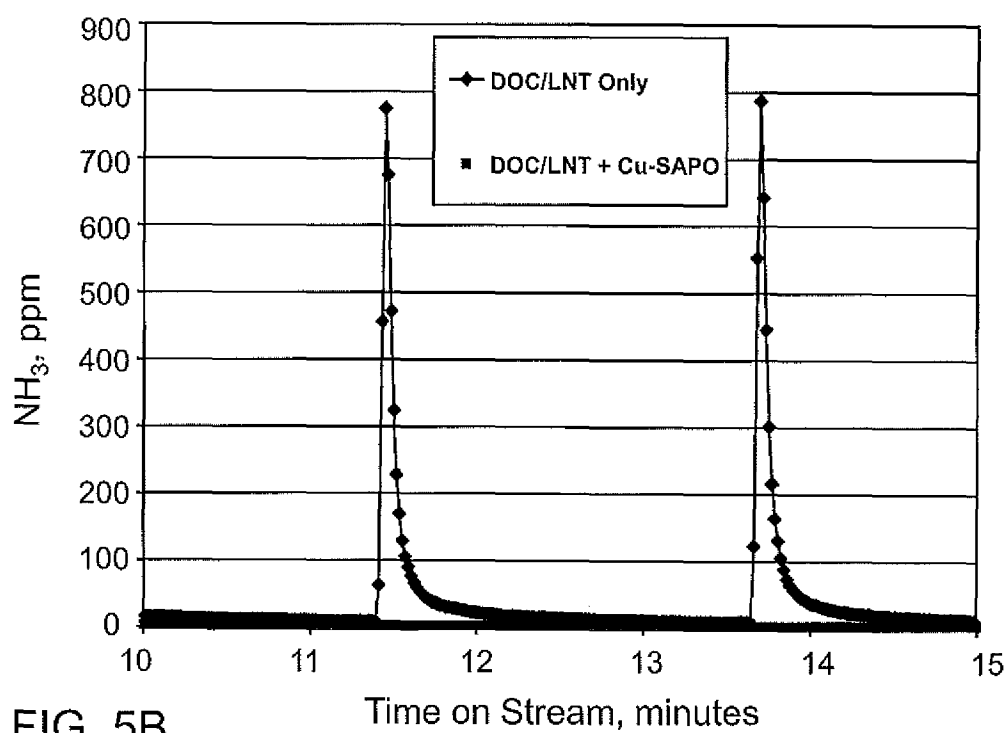


FIG. 5B

4/5

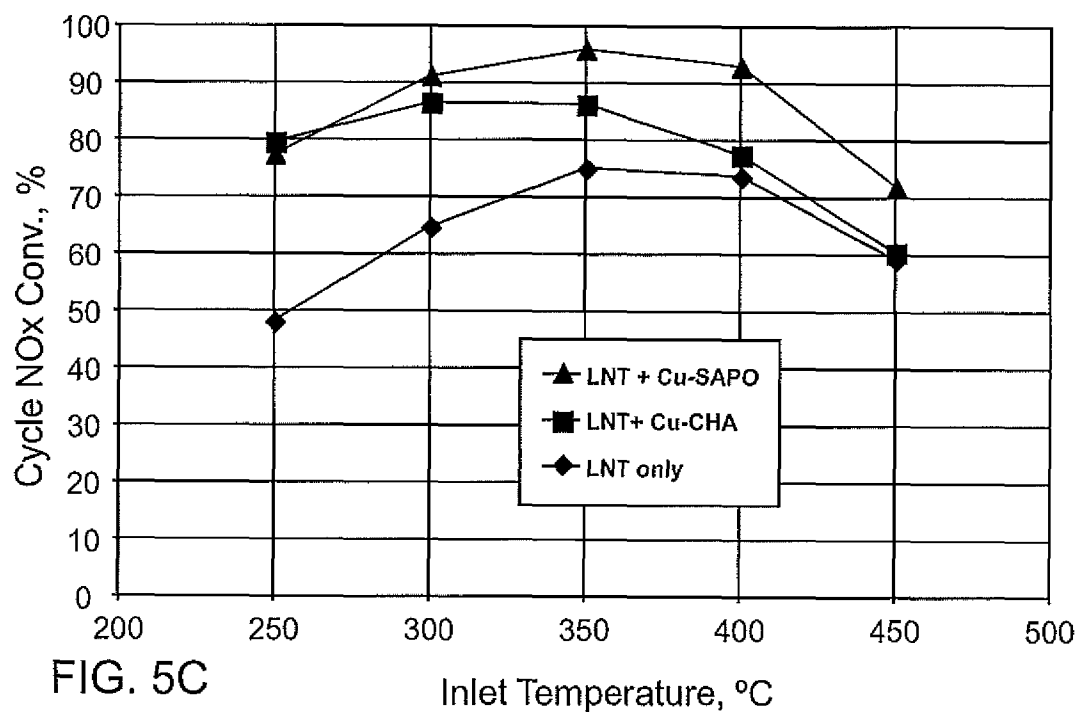


FIG. 5C

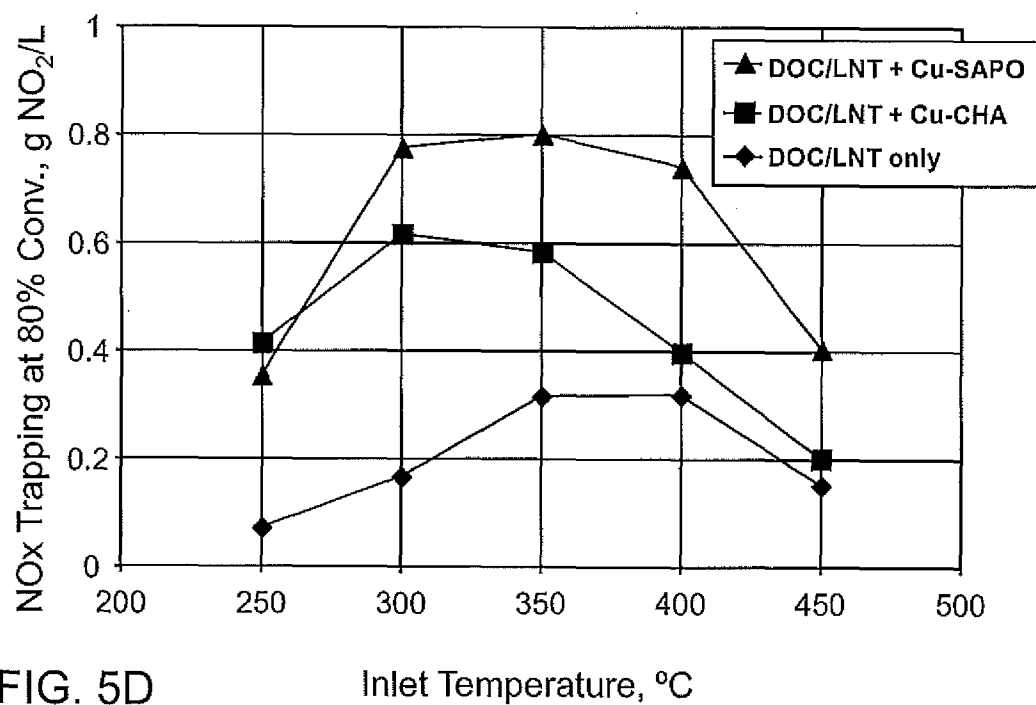


FIG. 5D

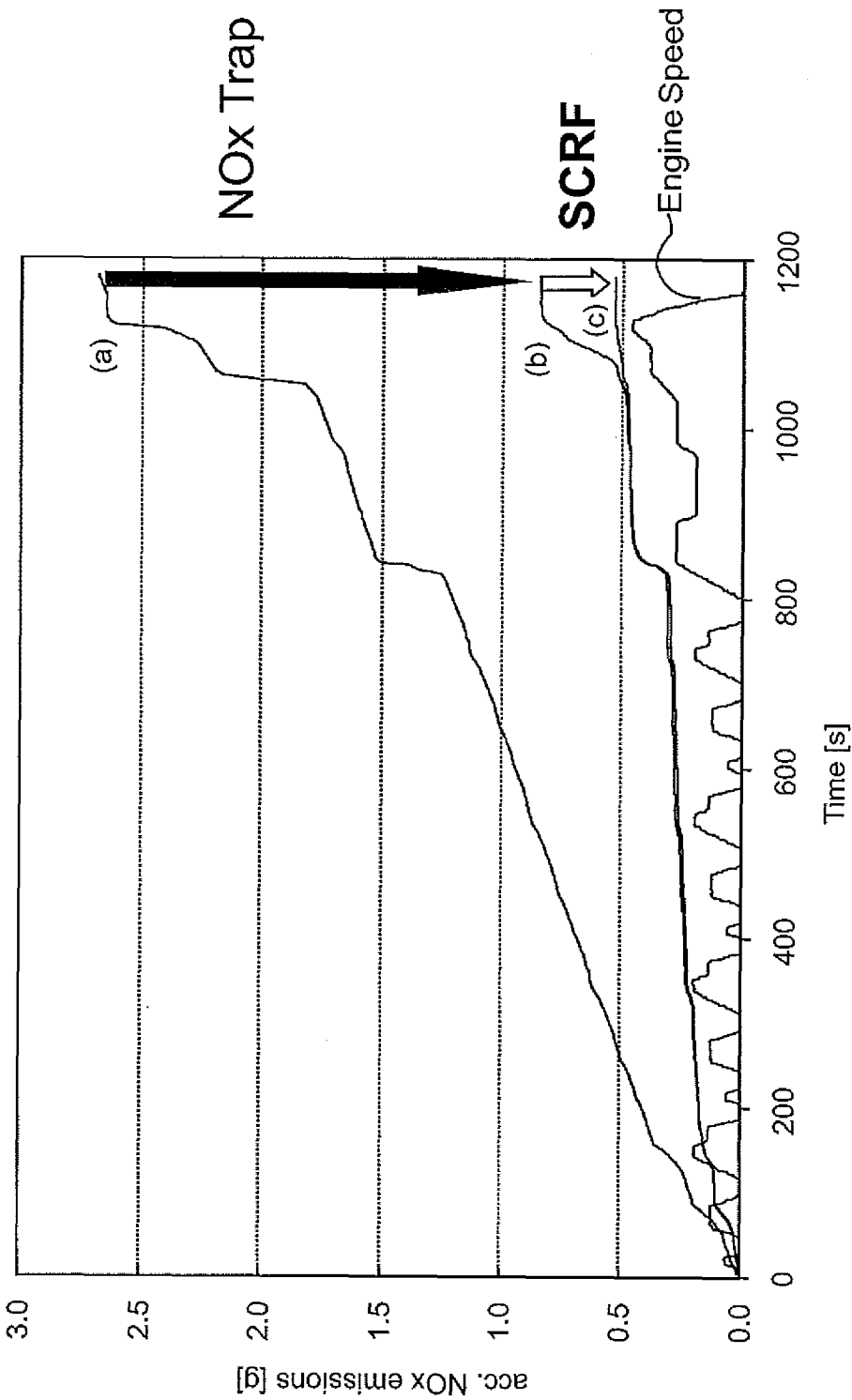


FIG. 6