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

(72) **Inventor; and**
(75) **Inventor/Applicant** *(for US only)*: **WAN, Chung-Zong** [US/US]; 4 Scaletti Court, Somerset, NJ 08873 (US).

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

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(54) **Title**: NOX ADSORBER CATALYST WITH SUPERIOR LOW TEMPERATURE PERFORMANCE

(57) **Abstract**: The lean NOx trap catalyst composition of the present invention comprises distinct layers, or zone configuration or multi-brick arrangement. The top layer, front zone or front brick is free of any alkali or alkaline earth NOx trapping components. The under layer, rear zone or rear brick may contain any desirable NOx trapping component in contact with a precious metals group catalyst (e.g., Pt). Catalysts of this invention show wide temperature operation window with superior low temperature performance.

NOX ADSORBER CATALYST WITH SUPERIOR LOW TEMPERATURE PERFORMANCE

This patent application claims priority to pending patent applications US Serial No. 61/076,560 filed June 27, 2008 and US Serial No. 12/490,252 filed June 23, 2009 incorporated herein in its entirety.

FIELD OF THE INVENTION

The present invention is directed to a lean NOx trap system for NOx abatement, especially with NOx abatement in the exhaust gas of lean-burn internal combustion engines. More specifically, the present invention is concerned with a novel composition comprising a lean NOx trap catalyst, and to a method of using the same.

BACKGROUND OF THE INVENTION

Catalysts are employed in the exhaust systems of automotive vehicles to convert carbon monoxide, hydrocarbons, and nitrogen oxides (NOx) produced during engine operation into harmless gases. When the engine is operated in a stoichiometric or slightly rich air/fuel (A/F) ratio, catalysts containing palladium, platinum, and/or rhodium are able to efficiently convert all three gases simultaneously. That is, the carbon monoxide and hydrocarbons are oxidized to carbon dioxide and water and the NOx is reduced to nitrogen. Hence, such catalysts are often called "three-way" catalysts. It is desirable, however, to operate the engine in a "lean-burn" condition where the A/F ratio is greater than the 14.4-14.7 stoichiometric range, generally between 19 and 27, to realize a benefit in fuel economy. While such precious metal three-way catalysts are able to efficiently convert carbon monoxide and hydrocarbons during lean-burn (excess oxygen) operation, they are not efficient in converting the NOx under lean-burn conditions. Lean-burn, high air-to-fuel ratio, and diesel engines are certain to become more important in meeting the mandated fuel economy requirements of next-generation vehicles, the control of NOx emissions from the vehicles continues to post a challenge. Thus, development of an effective and durable catalyst for controlling NOx emissions under net oxidizing conditions accordingly is urgently needed.

Catalysts containing platinum and zeolite are known to be active for NOx reduction by hydrocarbons under lean conditions. However, this catalytic activity is significant only in a narrow temperature range around the light-off temperature of heavy hydrocarbon oxidation, typically between 180°C and 250°C. Above the light-off temperature, the lean-NOx catalysts quickly lose their catalytic activity because almost all hydrocarbon reductant completely oxidized and not available for NOx reduction. This narrow temperature window of the lean-NOx catalysts is considered to be one of the major technical obstacles, because it makes practical application of these catalysts difficult (for lean-burn gasoline or diesel engines). Base metal containing zeolite catalysts shows activity of NOx reduction by hydrocarbons at higher temperature, typically above 300°C. But they exhibit very little NOx conversion at lower temperatures. In addition, these catalysts deactivate irreversibly if a certain temperature is exceeded. Catalyst deactivation is also found to be accelerated by the presence of water vapor and sulfur containing compound. Thus, it is difficult to consider for commercial use.

Alternative is to employ selective catalytic reduction (SCR) technology using ammonia or urea as a reductant. Vanadium containing and certain zeolite containing catalysts are found to be quite efficient in selective reduction of NOx to N_2 in a lean exhaust. Commercial use of SCR technology has been developed for heavy duty diesel application. However, urea supply infra-structure and OBD requirement make SCR technology difficult to apply to all lean burn vehicles. Thus, the art continues to search NOx reduction technology using on-board fuel system.

One effective method to reduce NOx from the exhaust of lean-burn engines, such as gasoline direct injection and partial lean-burn engines, as well as from diesel engines, requires trapping and storing of NOx under lean burn engine operating conditions and reducing the trapped NOx under stoichiometric or rich engine operating conditions or lean engine operating with external fuel injected in the exhaust to induce rich conditions. The lean operating cycle is typically between 1 minute and 20 minutes and the rich operating cycle is typically short (1 to 10 seconds) to preserve as much fuel as possible. To enhance NOx conversion efficiency, the short and frequent regeneration is favored over long but less frequent regeneration. Thus, a lean NOx trap catalyst generally must provide a NOx trapping function and a three-way conversion function.

The lean-NOx-trap technology has been limited to use for low sulfur fuels because catalysts that are active for converting NO to NO_2 are also active in converting SO_2 to SO_3. Lean NOx trap catalysts have shown serious deactivation in the presence of SOx because, under oxidized conditions (exhaust containing excess oxygen), SOx adsorbs more strongly on NO_2 adsorption sites than NO_2, and the adsorbed SOx does not desorb under fuel-rich conditions in normal operating conditions. It is found that the surface adsorbed SOx can be removed at high temperature, typically greater than 600°C under rich (reducing) conditions. Periodic removal of sulfur accumulated on the catalyst tends to rejuvenate the performance and useful life of the lean NOx trap can be prolonged. In new generation of diesel powered vehicles (MY2007 and beyond), many have equipped with a diesel particulate filter (DPF) device to remove the harmful carbonaceous particles. The particulate filter periodic goes through a regeneration cycle, typically around 600°C to burn off the collected soot. In an exhaust aftertreatment system containing DPF and LNT, it is advantageous to incorporate a sulfur removal event during the regeneration of the particulate filter. Thus, a cost effective sulfur removal process can be easily achieved. In 2007 and beyond, diesel fuel sulfur has been mandated to lower to less than 15 ppm. The advance in engine design, exhaust aftertreatment device and low sulfur fuel makes the lean NOx trap technology attractive for the reduction of NOx emissions from a diesel engine.

Current lean NOx trap (LNT) systems contain alkali and alkaline earth (e.g., Ba) elements. The alkaline earth containing LNT systems show good and durable NOx conversion efficiency between 250° C and 450° C. However, the LNT exhibits limited NOx conversion below 250° C. It is believed that the presence of trapping components (e.g., Ba) in the LNT catalyst hinders the intrinsic activity of NO oxidation and NOx reduction over the precious metal elements at low temperatures (<250° C) especially after exposure to high temperature in excess of 750° C in a lean environment (containing excess oxygen). Since exhaust temperature of a diesel engine under low load and low speed conditions (e.g., FTP75 driving cycle) typically runs below 250° C, it is highly desirable that a lean NOx trap (LNT) catalyst system performs well at such conditions. The novel catalyst systems of the present invention overcome the deficiency of low temperature performance of current lean NOx trap systems.

SUMMARY OF THE INVENTION

The present invention is directed to a combined lean NOx trap and catalyst system (lean NOx trap/catalyst) for NOx abatement in lean burn engines, e.g., a diesel engine. The lean NOx trap/catalyst system of the present invention comprises at least two distinct catalyst washcoat layers for the treatment of exhaust gas emissions, such as unburned hydrocarbons (HC), carbon monoxides (CO) and nitrogen oxides (NOx). More particularly, the catalyst composition of the invention is designed to reduce pollutants, e.g., NOx, in automotive engine exhaust gas streams at temperatures from about 100° C to about 500° C.

The washcoat layers of the present invention may comprise at least one layer containing NOx trapping component such as alkaline earth elements and at least one layer containing ceria and substantially free of alkaline earth elements. Both layers are capable of adsorbing NOx during lean-burn conditions and reducing the trapped NOx during rich-burn conditions. In accordance with the present invention, multiple washcoat configurations can be used.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a perspective view of a honeycomb-type refractory carrier member which may comprise a NOx trap member or a NOx catalyst member in accordance with the present invention;

FIG. 2 is a partial cross-sectional view enlarged relative to FIG. 1 and taken along a plane parallel to the end faces of the carrier of FIG. 1, which shows an enlarged view of one of the gas flow passages shown in FIG. 1;

FIG. 3 is a schematic view showing a configuration of the first or undercoat washcoat layer and the second or top washcoat layer on a lean NOx trap/catalyst, in accordance with one embodiment of the present invention;

FIG. 4 is a schematic of an engine emission treatment system, in accordance with one embodiment of the present invention;

FIG. 5 is a schematic of an engine emission treatment system, in accordance with one embodiment of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to a method and a lean NOx trap/catalyst system treating gaseous emissions from a lean burn engine, e.g., a diesel engine. In particular, the present invention is directed to a novel lean NOx trapping/catalyst washcoat composition comprising at least two distinct washcoat layers containing NOx trapping components and catalyst components for the treatment of exhaust gas emissions, such as carbon monoxide (CO), unburned hydrocarbons (HCs) and nitrogen oxides (NOx). The lean NOx trap/catalyst system of the present invention may comprise distinct layers coated onto a single substrate member, a zone configuration or a multiple-brick arrangement wherein separate bricks within the system are coated with the distinct washcoat layers. At least one layer composition containing NOx trapping components comprising alkaline earth elements and at least another layer composition containing NOx trapping components comprising ceria and substantially free of alkaline earth elements. The catalyst compositions of this invention show wide temperature operation window with superior low temperature performance. The novel catalyst washcoat composition of the present invention is designed to reduce exhaust gas emissions in automotive engine exhaust gas streams at temperatures from about 100° C to about 500° C. Engine exhaust gas stream temperatures below about 350° C, below about 250° C, below about 200° C are also exemplified.

The catalyst composition of the present invention comprises a first or front zone or top washcoat layer and a second or rear zone or undercoat washcoat layer. The first of front zone or top washcoat layer is the first washcoat layer an exhaust gas stream from the engine comes into contact with. Whereas, the second or rear or undercoat washcoat layer is the second washcoat layer the exhaust gas stream comes into contact with (i.e., the exhaust gas stream comes into contact with the second washcoat layer after coming into contact with the first washcoat layer).

The first or top washcoat layer comprises one or more supported precious metal catalysts and ceria as a NOx trapping component or sulfur scavenger. Importantly, the first or top washcoat layer is free or devoid of any alkali or alkaline earth components, which are believed to hinder NO oxidation over the precious metal catalyst at low temperatures (typically <350° C). As such, the top washcoat layer is capable of oxidizing NOx at temperatures below 350° C. In fact, the inventors have surprisingly found that the top washcoat composition of the present invention is capable of oxidizing NOx at temperatures below 250° C, below 200° C and even below 150° C. Additionally, the top washcoat layer is capable of reducing unburned hydrocarbons and carbon monoxides at temperatures below 350° C. The second or undercoat layer comprises one or more NOx trapping components in intimate contact with one or more supported precious metal catalysts for the treatment of exhaust gas emissions. Preferably, the second or undercoat layer comprises one or more alkali or alkaline earth components as NOx trapping components.

In one embodiment, the lean NOx trap/catalyst of the present invention may comprise a novel 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 one or more supported precious metals for the treatment of exhaust gas emissions, and optionally may contain ceria, but is devoid of any alkali or alkaline earth components. The undercoat layer may contain one or more NOx trapping components or NOx adsorbents, which selectively and reversibly adsorb nitrogen oxides from exhaust gas streams. The undercoat washcoat layer may also contain one or more precious metal catalysts for the treatment of exhaust gas emissions. Under lean burn conditions, the undercoat washcoat layer of the present invention can simultaneously store nitrogen oxides (NOx) and catalyzes the conversion of hydrocarbons and carbon monoxide in exhaust gas streams and the top washcoat layer can catalyze the oxidation of nitrogen oxides (NOx). Under subsequent rich burn conditions excess stored NOx can be released and oxidized by the catalysts contained in both the top and undercoat washcoat layers.

The lean NOx trap/catalyst of this embodiment may be more readily appreciated by reference to **FIGS. 1** and **2**. **FIGS. 1** and **2** show a refractory carrier member **2**, in accordance with one embodiment of present invention. Referring to **FIG. 1**, the refractory carrier member **2** is a cylindrical shape having a cylindrical outer surface **4**, an upstream end face **6** and a downstream end face **8**, which is identical to end face **6**. Carrier member **2** has a plurality of fine, parallel gas flow passages **10** formed therein. As seen in **FIG. 2** flow passages **10** are formed by walls **12** and extend through carrier **2** from upstream end face **6** to downstream end face **8**, the passages **10** being unobstructed so as to permit the flow of a fluid, e.g., a gas stream, longitudinally through carrier **2** via gas flow passages **10** thereof. As more easily seen in **FIG. 2** walls **12** are so dimensioned and configured that gas flow passages **10** have a substantially regular polygonal shape, substantially square in the illustrated embodiment, but with rounded corners in accordance with U.S. Pat. No. 4,335,023, issued Jun. 15, 1982 to J. C. Dettling et al. A discrete layer undercoat layer **14**, which in the art and sometimes below is referred to as a "washcoat", is adhered or coated onto the walls **12** of the carrier member. As shown in **FIG. 2**, a second discrete washcoat layer or top layer **16** is coated over the undercoat washcoat layer **14**. In accordance with the present invention, the top washcoat layer **16** comprises one or more supported precious metal catalysts, ceria, and is devoid of any alkali or alkaline earth components. The undercoat washcoat layer **16** comprises one or more NOx trap materials in intimate contact with one or more supported precious metals.

As shown in **FIG. 2**, the carrier member include void spaces provided by the gas-flow passages **10**, and the cross-sectional area of these passages **10** and the thickness of the walls **12** defining the passages will vary from one type of carrier member to another. Similarly, the weight of washcoat applied to such carriers will vary from case to case. Consequently, in describing the quantity of washcoat or catalytic metal component or other component of the composition, it is convenient to use units of weight of component per unit volume of catalyst carrier. Therefore, the units grams per cubic inch ("g/in^3 ") and grams per cubic foot ("g/ft^3 ") are used herein to mean the weight of a component per volume of the carrier member, including the volume of void spaces of the carrier member.

During operation, exhaust gaseous emissions from a lean burn engine comprising hydrocarbons, carbon monoxide, nitrogen oxides, and sulfur oxides initially encounter the top washcoat layer **16**, and thereafter encounter the undercoat washcoat layer **14**.

Any suitable carrier or substrate may be employed, such as a monolithic carrier of the type having a plurality of fine, parallel gas flow passages extending therethrough from an inlet or an outlet face of the carrier, so that the passages are open to fluid flow therethrough. The passages, which are essentially straight 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 carrier are thin-walled channels which can be of any suitable cross-sectional shape and size such as trapezoidal, rectangular, square, sinusoidal, hexagonal, oval, circular. Such monolithic carriers may contain up to about 700 or more flow channels ("cells") per square inch of cross section, although far fewer may be used. For example, the carrier may have from about 60 to 600, more usually from about 200 to 400, cells per square inch ("cpsi").

The carrier may comprise a refractory ceramic or metal having a honeycomb structure. Suitable refractory ceramic materials include alumina, silica, titania and zirconia compounds, e.g., cordierite (which is preferred), cordierite-alpha alumina, silicon nitride, zircon mullite, spodumene, alumina-silica magnesia, zircon silicate, sillimanite, magnesium silicates, zircon petalite, alpha alumina and aluminosilicates. A metallic honeycomb may be made of a refractory metal such as stainless steel or other suitable iron-based corrosion-resistant alloys.

In yet another embodiment, the distinct washcoat layers of the present invention can be coated on a wall-flow substrate. **Figures 4** and **5** illustrate a wall-flow monolith **34**, which has a plurality of passages **42** and **45**. The passages can be described as the inlet passage **42** and outlet passage **45** and are tubularly enclosed by the internal walls **35** of the wall-flow monolith **34**. The wall-flow monolith **34** has an inlet end **44** and an outlet end **43**. Alternate passages are plugged at the inlet end **44** with inlet plugs **38**, and at the outlet end **40** with outlet plugs (not shown) to form opposing checkerboard patterns at the ends of the inlet **44** and outlet **43** ends. A gas stream enters through the unplugged channel inlet at the inlet end **44**, and flows through passage **42**. The gas flow is stopped by the outlet plug and diffuses through the internal walls **35** (which are porous) to the outlet passage **45** and exits the monolith. The gas cannot pass back to the inlet side of walls because of inlet plugs **38**.

Preferred wall-flow filters are composed of ceramic-like materials such as cordierite, α-alumina, silicon carbide, silicon nitride, zirconia, mullite, spodumene, alumina-silica-magnesia, zirconium silicate, or of refractory metals such as stainless steel. Preferred wall-flow filters are formed from cordierite and silicon carbide. Such materials are able to withstand the environment, and particularly high temperatures encountered in treating the exhaust gas streams.

Preferred wall-flow filters for use in the inventive system include thin porous walled honeycombs (monolith)s through which the fluid stream passes without causing too great an increase in backpressure or pressure across the article. Ceramic wall-flow substrates used in the system are preferably formed of a material having a porosity of from about 30 to about 75%, having a mean pore size of at least 5 microns (e.g., from 5 to 30 microns). More preferred are substrates having wall porosity, typically from about 40 to about 65%. When substrates with these porosities and these mean pore sizes are coated with the techniques described herein, adequate levels of the sub-micron catalyst washcoat composition can be coated onto the substrates to achieve excellent CO, HC and NOx conversion efficiency and allow these substrates to maintain adequate exhaust flow characteristics, i.e., acceptable backpressures. U.S. Patent No. 4,329,162 is herein incorporated by reference with respect to the disclosure of suitable wall-flow substrates.

The porous wall-flow filter used in this invention is catalyzed in that the wall of said element has thereon or contained therein one or more washcoat compositions in accordance with the present invention, as described herein. The washcoat may be coated on the inlet side of the element wall alone, the outlet side alone, within the pores of the wall itself, or the inlet and outlet sides and within the pores of the wall.

For the purposes of the present invention, when the catalyst composition of the invention is coated onto such a carrier, typically as a washcoat, the amounts of the various components are presented based on grams per volume. When the ingredients are applied as a thin coating to a carrier substrate, the amounts of ingredients are conventionally expressed as grams per cubic foot (g/ft^3) of the carrier for the precious metal component(s) and grams per cubic inch (g/in^3) of the carrier for the other ingredients (i.e., the composite and the support) as this measure accommodates different gas flow passage cell sizes in different monolithic carrier substrates.

The discrete top and undercoat layers of catalytic and/or trapping materials, conventionally referred to herein as "washcoats", are coated onto a suitable carrier with, preferably, the undercoat washcoat layer adhered to the carrier and the top washcoat layer overlying and adhering to the undercoat layer. With this arrangement, the gas being contacted with the catalyst, e.g., being flowed through the passageways of the catalytic material-coated carrier, will first contact the top coat and pass therethrough in order to contact the underlying undercoat. However, in an alternative configuration (discussed in more detail hereinbelow), the top coat need not overlie the undercoat coat but may be provided on an upstream (as sensed in the direction of gas flow through the catalyst composition) portion of the carrier, with the undercoat provided on a downstream portion of the carrier. Thus, to apply the washcoat in this configuration, an upstream longitudinal segment only of the carrier would be dipped into a slurry of the second coat catalytic material, and dried, and the unclipped downstream longitudinal segment of the carrier would then be dipped into a slurry of the first coat catalytic material and dried. In yet another alternative embodiment of the present invention (also discussed in more detail hereinbelow), the top washcoat composition may be coated as a single washcoat layer on an upstream carrier or brick which is placed in upstream of a downstream carrier or brick coated with the undercoat composition of the present invention as a single washcoat layer. In this configuration, an exhaust gas stream would first come into contact with the upstream carrier or brick, flow through the upstream carrier or brick, and subsequently come into contact with the downstream carrier or brick.

As previously stated, the top washcoat layer comprises a support, e.g., a refractory metal oxide support, one or more precious metal catalysts to catalyze the oxidation of hydrocarbons and carbon monoxide and the reduction of nitrogen oxides and ceria. In some embodiments, the use of ceria as a NOx trapping component and/or sulfur scavenger may be essential to provide for superior treatment of exhaust gas emissions at low temperatures. The ceria content in this embodiment may range from about 0.1 g/in^3 to about 3 g/in^3. In general, the precious metal component in the top washcoat layer is selected from the group consisting of platinum, palladium, rhodium, ruthenium, and iridium components. The undercoat washcoat layer comprises a support, e.g., a refractory metal oxide support, and a NOx trapping material. Typically, the NOx trapping material is ranges from about 0.1 g/in^3 to about 3 g/in^3. NOx trapping materials may including, but are not limited to, oxides, hydroxide, and/or carbonates of alkali metals (e.g., Li, Na, K, Rb, Cs, or Fr), alkaline earth metals (e.g., Ba, Be, Mg, Ca, or Sr), lanthanum group metals (e.g., La, Ce, etc.), compounds containing elements that form stable nitrates (e.g., alkali metal, alkaline earth metals, and/or rare earth metals), ceria or a combination of such elements. Preferably, the NOx trapping material is selected from the group consisting of oxides of calcium, strontium, and barium, potassium, sodium, lithium, and cesium, cerium, lanthanum, praseodymium, and neodymium. More preferably, the NOx trapping materials include barium oxide and strontium oxide. Either of the top or undercoat washcoat layers may additionally comprise a zirconium or cerium component. The undercoat washcoat catalyst/NOx trapping layer stores NOx during lean periods and releases and reduces stored NOx during rich periods. Additionally, under lean conditions, when temperatures are low, the top washcat catalyst layer catalyzes the oxidation of NOx contained in the exhaust gas stream.

The refractory metal oxide support includes materials such as activated compounds selected from the group consisting of alumina (which is preferred), silica, titania, silica-alumina, alumina-silicates, alumina-zirconia, alumina-chromia, alumina-ceria and mixtures thereof. Typically, the refractory metal oxide support will be present in the amount of about 0.1 to about 4.0 g/in^3 of carrier and will be present in the form of finely divided, high surface area particles having a particle size above 10-15 micrometers. Preferably, the activated alumina is thermally stabilized to retard undesirable alumina phase transformations from gamma to alpha at elevated temperatures by doping the activated alumina with a rare earth component such as lanthanum (preferred) or neodymium or mixtures thereof in an amount of about 0.02 to about 0.5 g/in^3 of carrier.

Typically, the refractive metal oxide support, e.g., activated alumina, is impregnated with an aqueous solution or dispersion of the precious metal component present as a compound or complex. The selected precious metal compound or complex should be one, which, upon calcination or use thereof, decomposes or otherwise converts to a catalytically active form, usually the metal or 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 catalyst, such compounds are converted into a catalytically active form of the platinum-group metal or a compound thereof.

The precious metal component of both the top and undercoat washcoat compositions comprises one or more catalytic metals selected from the group consisting of gold, silver and platinum group metals (i.e., precious metals). Platinum group metals include platinum, palladium, rhodium, ruthenium and iridium components and mixtures thereof. The precious metal component(s) are typically present in the amount of about 5 to about 500 g/ft^3 on the carrier. Precious metal contents from about 25 to 250 g/ft^3 and 60 to 150 g/ft^3 are also exemplified. The preferred precious metal components are platinum, rhodium or a mixture of platinum and rhodium metal components which are typically present in a platinum:rhodium ratio of about 0.1:1 to about 20:1, preferably 1:1 to 10:1.

A process which can be used to prepare the composite of the present invention starts with the preparation of a zirconium hydroxide sol. This sol can be prepared by precipitating zirconium sulfate with sodium hydroxide at high temperature reflux, typically from 90 to 100° C to make nanometer-size crystals (typically up to 100 nanometers). Impurities, e.g., sodium, sulfur, etc. can be washed out with an aqueous liquid. An acid, e.g., nitric acid, can be used to break up the aggregates to obtain the zirconium hydroxide sol and to reduce the pH of the liquid. At this stage, any cerium components in the form of salts such as nitrates may be added. The composite sol should be sufficiently acidic, e.g., a pH of 0.5 to 3, preferably, 0.5 to 2.0, at this point in order to keep the salts in solution. The pH can then be quickly increased, e.g., with ammonia, to precipitate the composite compounds. The formation of large aggregates is preferably avoided by controlling the pH. The precipitated composite can then be washed with an aqueous liquid such as deionized water and dried at suitable conditions in air in an oven at temperatures of up to 250° C, typically at 150° C, for as long as necessary, usually overnight. The precipitated composite can then be calcined in air at elevated temperatures to convert the composite to particulate oxide composite which comprises ceria, zirconia and samaria. The calcination process is typically carried out at a temperature of 450 to 750° C, preferably 550° C for 0.5 to 10 hours, preferably 2 hours. The resultant composite of ceria and zirconia may then be mixed with the precious metal component which has been preferably disposed, i.e., layered or coated, on the refractory metal oxide support.

The catalyst composition may be prepared by mixing the composite prepared as set forth above with the precious metal component and the refractory metal oxide support in the form of an aqueous slurry, comminuting the slurry (i.e., by ball milling), mixing the comminuted slurry with the carrier followed by drying and calcination. However, it is preferred that the composite be mixed with the precious metal component which has been previously disposed on the refractory metal oxide support.

The precious metal component(s) disposed on the refractory metal oxide support may be prepared in the following manner which involves the preparation of an aqueous slurry of the precious metal component(s) and the refractory metal oxide support. The method involves fixing the precious metal component(s) onto at least one support. The fixing step can be any of the suitable fixing steps known in the prior art such as chemical or thermal fixing. A preferred fixing step is to thermally fix the precious metal component(s) to the support. This is preferably conducted in air at a temperature of 50 to 500° C for about 0.5 to about 2 hours.

In another embodiment, the distinct washcoat layers of the present invention may be zone coated such that one washcoat layer is on the upstream end, and the other washcoat on the downstream end, of the carrier substrate. For example, an upstream washcoat layer can be coated over a portion of the upstream region of the substrate and a downstream washcoat layer can be coated over a downstream portion of the substrate. In this embodiment, the top washcoat layer of the present invention is coated over the upstream potion of the carrier substrate (i.e., the upstream washcoat layer) and the undercoat washcoat layer is coated over a downstream portion of the carrier substrate (i.e., the downstream washcoat layer). The upstream washcoat layer may comprise a supported precious metal catalyst, e.g., platinum supported on alumina and ceria. In accordance with the present invention it is essential that the upstream washcoat layer contains no alkali or alkaline earth components. The complete absence of alkali or alkaline earth components in the upstream washcoat layer prevents a deleterious interaction between the precious metal and the alkali or alkaline earth component under low temperature conditions. The downstream washcoat layer may comprise one or more NOx trapping components (e.g., BaO) in intimate contact with one or more supported precious metal catalysts.

The catalyst composition of this embodiment may be more easily understood by reference to **FIG. 3**. As shown in **FIG. 3** a novel catalyst composition **20** comprises a carrier member or substrate **22**, for example a honeycomb monolith, which contains two separate zone coated washcoated layers, an upstream washcoat layer **24** and a downstream washcoat layer **26**. The upstream layer **24** contains one or more supported precious metals, ceria and is devoid of any alkali or alkaline earth components. The downstream washcoat layer **26** may contain one or more NOx trapping components and one or more supported precious metal catalysts. Both the upstream washcoat layer **24** and downstream washcoat layer **26**, respectively, generally contain a precious metal loading of from about 5 to 500 g/ft^3. Loadings of precious metal from 25 to 250 g/ft^3 and 60 to 150 g/ft^3 are also exemplified.

In this embodiment, the upstream **24** and downstream **26** washcoat layers, respectively, are each zone coated only over a portion of the substrate **22**. However, the combination of the upstream **24** and downstream **26** washcoat layers, respectively, cover the entire length of the substrate **22**. The upstream washcoat layer **24** can be coated over at least 0.5 inches, and up to 5 inches, of the upstream portion of the substrate **22**. An upstream washcoat layer **24** having a length of at least about 1.0 inches, and up to 3.5 inches, or from at least 1.5 inches and up to 2.5 inches, from the upstream edge of the catalytic member, are also exemplified. With the downstream washcoat portion **26** covering the remaining downstream portion of the substrate **22**.

The length of the upstream washcoat layer **24** can also be described as a percentage of the length of the catalytic member from the upstream to downstream edge. Typically, the upstream washcoat layer **24** will comprise from about 5 to about 70% of the upstream length of the catalytic member. Also exemplified is an upstream washcoat layer **24** of up to about 20%, up to about 40%, and up to about 60% of the upstream length of the catalytic member **20**. With the downstream washcoat portion **26** covering the remaining downstream portion of the substrate **22**. Thus, the downstream washcoat portion **26** may comprise 95 to about 30% of the downstream portion **30** of the substrate **22**.

During operation, exhaust gases flow through the diesel oxidation catalytic member **20** from the upstream edge **25** to the down stream edge **27**. The precious metal catalysts contained in both the upstream **24** and downstream **26** washcoat layers, respectively, oxidize HC and CO pollutants contained in the exhaust gases.

In another embodiment, the lean NOx trap (LNT) system of the present invention can be included in an emission treatement system, wherein the lean NOx trap comprises one or more components or bricks in a multiple-component or multiple-brick system. In one embodiment, the top and undercoat washcoat compositions of the present invention may be coated onto a single carrier or substrate, as described hereinabove, wherein the coated substrate is one of multiple components in the emission treatment system. For example, the emission treatment system may further comprise, e.g., a diesel oxidation catalyst (DOC) and/or a particulate filter. In general any known diesel catalyst oxidation catalyst (DOC) and/or particulate filter in the prior art can be used. In some cases, the particulate filter may be catalyzed, as known in the art.

In yet another embodiment, the emission treatment system of the present invention may comprise a multiple-brick arrangement, wherein the top and undercoat washcoat compositions of the present invention are coated onto two separate carrier substrates or bricks in the emission treatment system. For example, the lean NOx trap (LNT) system of the present invention, i.e., the top and undercoat washcoat compositions, may comprise distinct layers coated onto separate substrates or bricks as distinct washcoat layers. Optionally, a particulate filter can be used in conjunction with the top and undercoat washcoated substrates. In one embodiment, either the top or undercoat washcoat composition of the present invention can be coated onto the particulate filter.

The emission treatment system of the present invention may be more readily appreciated by reference to **FIGS. 6** and 7, which depict schematic representations of two exemplary emission treatment systems, in accordance with the present invention. Referring to **FIG. 6**, a schematic representation of an emission treatment system **50** is illustrated. An exhaust gas stream containing gaseous pollutants (e.g., unburned hydrocarbons, carbon monoxide and NOx) and particulate matter is conveyed via line

53 from an engine **52** to an oxidation catalyst **54**. The oxidation catalyst **54** may be any known oxidation catalyst in the art, which can be used to treat exhaust gas emissions. For example, the oxidation catalyst **54** may be used to treat unburned gaseous and non-volatile hydrocarbons (i.e., the VOF) and carbon monoxides. In addition, a proportion of the NO of the NOx component may oxidized to NO_2 in the oxidation catalyst. The exhaust stream is subsequently conveyed via line **55** to a particulate filter **56**, which traps particulate matter and/or catalyst poisons present within the exhaust gas stream. The particulate filter may be coated with the top washcoat composition of the present invention. In another embodiment, the particulate filter may comprise a wall-flow substrate coated with the top washcoat layer of the present invention. In accordance with the present invention, the top washcoat layer comprises one or more supported precious metal catalysts, ceria, and is devoid of any alkali or alkaline earth components. As such, the top washcoat layer is capable of oxidizing NOx at temperatures below 350° C, below 250° C, and even below 150° C. Optionally, the particulate filter may be additionally catalyzed with a soot burning catalyst for regeneration of the particulate filter **56**. After removal of particulate matter, via the particulate filter **56**, the exhaust gas stream is conveyed via line **57** to a downstream NOx trapping component. The NOx trapping component **58** may be coated with the undercoat washcoat composition of the present invention. The undercoat washcoat layer comprises one or more NOx trap materials in intimate contact with one or more supported precious metals. In accordance with the present invention, under lean burn conditions, the undercoat washcoat layer of the present invention can simultaneously store nitrogen oxides (NOx) and catalyzes the conversion of hydrocarbons and carbon monoxide in exhaust gas streams and the top washcoat layer can catalyze the oxidation of nitrogen oxides (NOx). Under subsequent rich burn conditions excess stored NOx can be released and oxidized by the catalysts contained in both the top and undercoat washcoat layers.

Referring to **FIG. 7**, a schematic representation of an emission treatment system **60** is illustrated. An exhaust gas stream containing gaseous pollutants (e.g., unburned hydrocarbons, carbon monoxide and NOx) and particulate matter is conveyed via line **63** from an engine **62** to an oxidation catalyst **64**. The oxidation catalyst **64** may be any known oxidation catalyst in the art, which can be used to treat exhaust gas emissions. For example, the oxidation catalyst **64** may be used to treat unburned gaseous and non-volatile hydrocarbons (i.e., the VOF) and carbon monoxides. In addition, a proportion of the NO of the NOx component may oxidized to NO_2 in the oxidation catalyst. After treatment of the exhaust gas stream in the oxidation catalyst **64** the exhaust gas stream is conveyed via line **65** to a downstream NOx trapping component **66**. The NOx trapping component **66** may be coated with the undercoat washcoat composition of the present invention. The undercoat washcoat layer comprises one or more NOx trap materials in intimate contact with one or more supported precious metals. In accordance with the present invention, under lean burn conditions, the undercoat washcoat layer of the present invention can simultaneously store nitrogen oxides (NOx) and catalyzes the conversion of hydrocarbons and carbon monoxide in exhaust gas streams and the top washcoat layer can catalyze the oxidation of nitrogen oxides (NOx). Under subsequent rich burn conditions excess stored NOx can be released and oxidized by the catalysts contained in both the top and undercoat washcoat layers. The exhaust stream is subsequently conveyed via line **67** to a particulate filter **68**, which traps particulate matter and/or catalyst poisons present within the exhaust gas stream. The particulate filter may be coated with the top washcoat composition of the present invention. In another embodiment, the particulate filter may comprise a wall-flow substrate coated with the undercoat washcoat layer of the present invention. In accordance with the present invention, the top washcoat layer comprises one or more supported precious metal catalysts, ceria, and is devoid of any alkali or alkaline earth components. As such, the top washcoat layer is capable of oxidizing NOx at temperatures below 350° C, below 250° C, and even below 150° C. Optionally, the particulate filter may be additionally catalyzed with a soot burning catalyst for regeneration of the particulate filter **68**.

Example

This example exemplifies a two-layer coating formulation useful for the treatment of exhaust gases, in accordance with one embodiment of the present invention. This two-layer formulation comprises an undercoat layer and a top washcoat layer, were coated onto a substrate carrier, the top washcoat layer being coated over the undercoat washcoat layer. The undercoat washcoat layer contained 0.6 g/in^3 (15 g/ft^3) of platinum and 0.6 g/in^3 (2 g/ft^3) of palladium impregnated a support composition comprising 0.25 g/in^3 BaO, 0.05 g/in^3 ZrO_2, 0.10 g/in^3 Ceria and

0.10 g/in Sr. The total washcoat composition of the top washcoat layer comprises about 1.7 g/in^3. The coated carrier was then calcined at 530° C for 2 hours.

The top washcoat layer was applied to the surface of the undercoat layer. The top washcoat layer comprises 1.2 g/in3 (70 g/ft3) Pt/SBA150, 0.8 g/in3 (8 g/ft3) and 0.6 g/in3 Rh/HAS-5. The resultant carrier was then calcined at 430° C for 2 hours.

CLAIMS

What is claimed is:

1. A combined lean NOx trap/catalyst system for treatment of exhaust gas emissions, comprising:
    a. a carrier substrate;
    b. an undercoat washcoat layer comprising a support material, one or more precious metals and one or more NOx trapping components, wherein said undercoat layer is coated on said carrier substrate; and
    c. a top washcoat layer comprising a support material, one or more precious metals, and ceria, said top washcoat layer being devoid of alkali or alkaline earth components, and wherein said top washcoat layer is coated on said carrier substrate.

2. The lean NOx trap/catalyst of claim 1, wherein said undercoat washcoat layer is coated over the entire axial length of said substrate and said top washcoat layer is coated over said undercoat washcoat layer.

3. The lean NOx trap/catalyst of claim 1, wherein said top washcoat layer is coated over an upstream portion of said substrate and said undercoat washcoat layer is coated over a downstream portion of said substrate.

4. The lean NOx trap/catalyst of claim 3, wherein said top washcoat layer is coated over about 5 to about 70% of the upstream length of said substrate and wherein said undercoat washcoat layer is coated over the remaining downstream portion of the substrate.

5. The NOx trap/catalyst of claim 1, wherein said support material is a refractory oxide support.

6. The NOx trap/catalyst of claim 1, wherein said NOx trapping component in said undercoat washcoat layer comprises an oxide, hydroxide, and/or

carbonates of alkali earth metals, alkaline earth metals, lanthanum group metals, ceria or a combination thereof.

7. The NOx trap/catalyst of claim 6, wherein said NOx trapping component is an oxide of an alkali or alkaline earth metal.

8. An exhaust gas treatment system for treating exhaust gas emissions from a lean burn engine comprising:
    a. a multiple-brick arrangement comprising at least two bricks;
    b. wherein said first brick contains a washcoat layer comprising a support material, one or more precious metals, ceria and is devoid of any alkali or alkaline earth components; and
    c. wherein said second brick contains a support material, one or more precious metals and one or more NOx trapping components.

9. The exhaust gas treatment system of claim 8, wherein said first brick is located upstream of said second brick.

10. The exhaust gas treatment system of claim 8, wherein said second brick is located upstream of said first brick.

Fig. 1

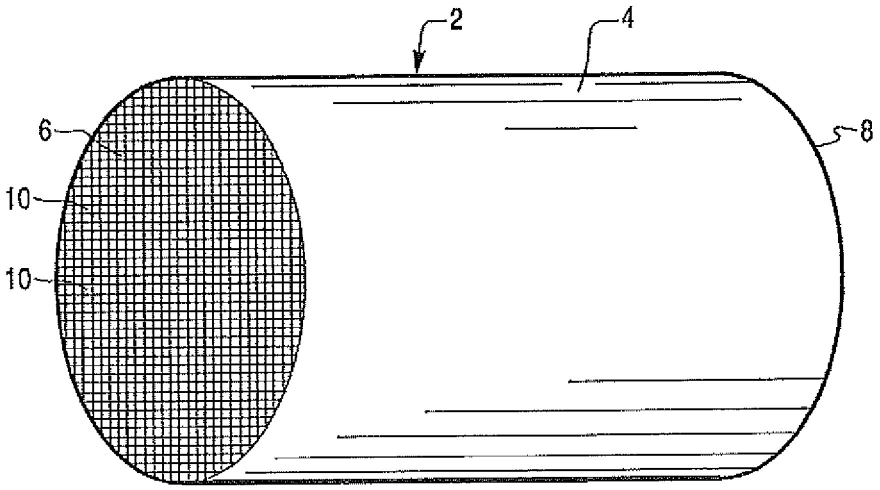


Fig. 2

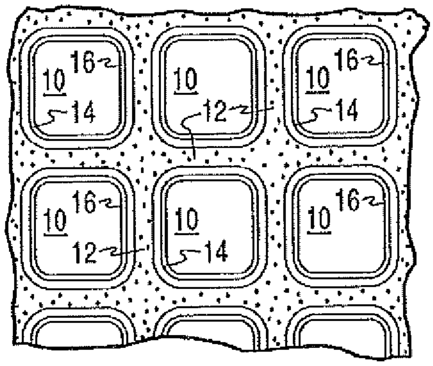


Fig. 3

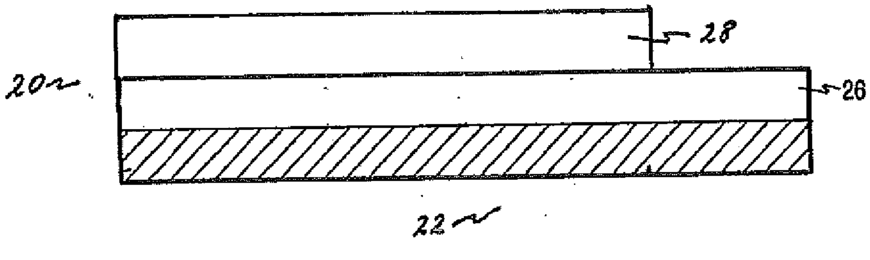


Fig. 4

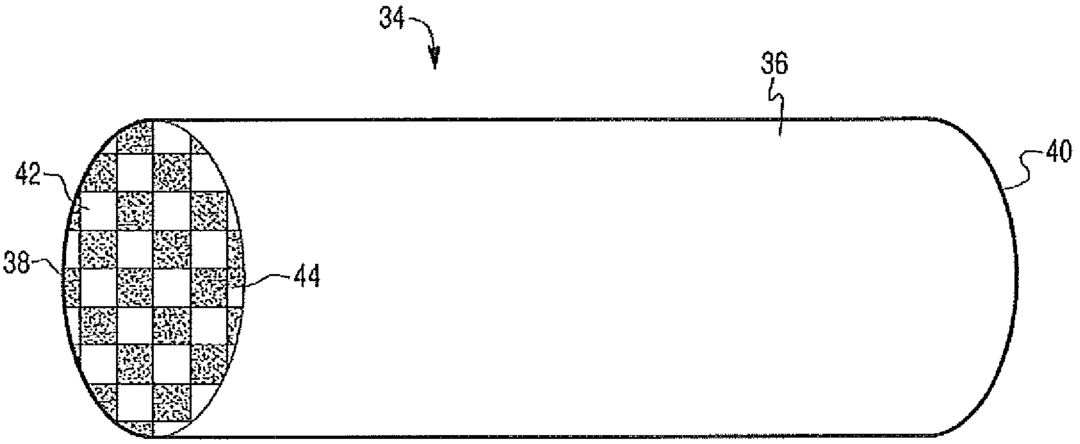


Fig. 5

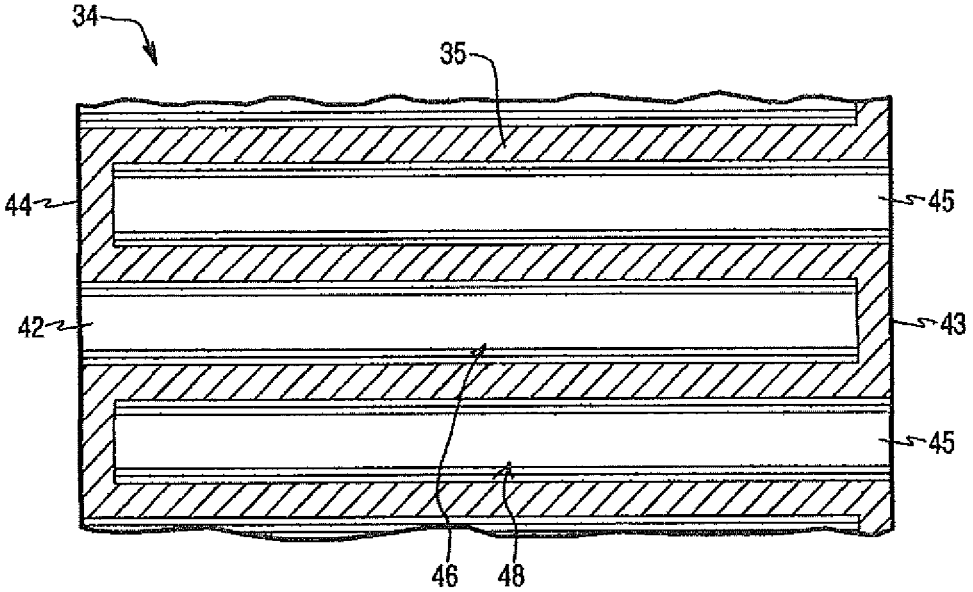
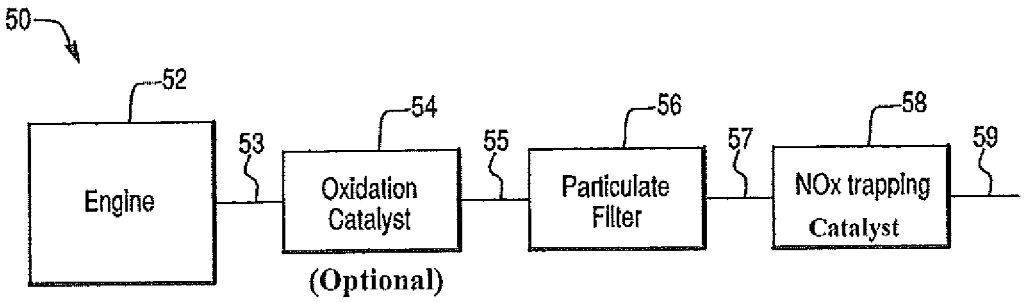


Fig. 6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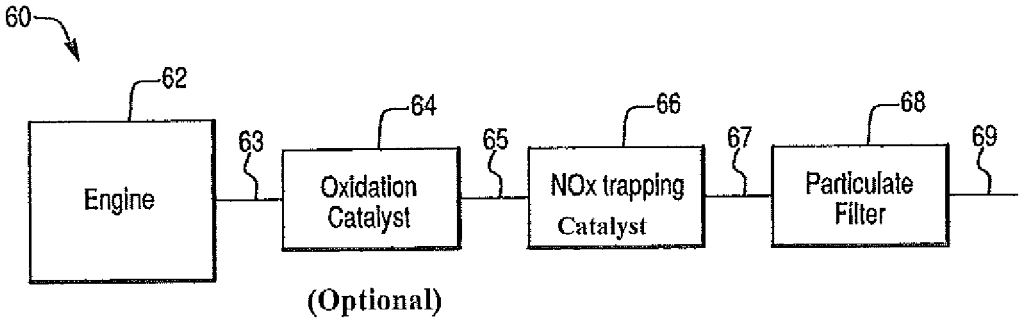
52
Engine
53
54
Oxidation Catalyst
(Optional)
55
56
Particulate Filter
57
58
NOx trapping Catalyst
59

Fig. 7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Engine
63
64
Oxidation Catalyst
(Optional)
65
66
NOx trapping Catalyst
67
68
Particulate Filter
69

Fig. 8

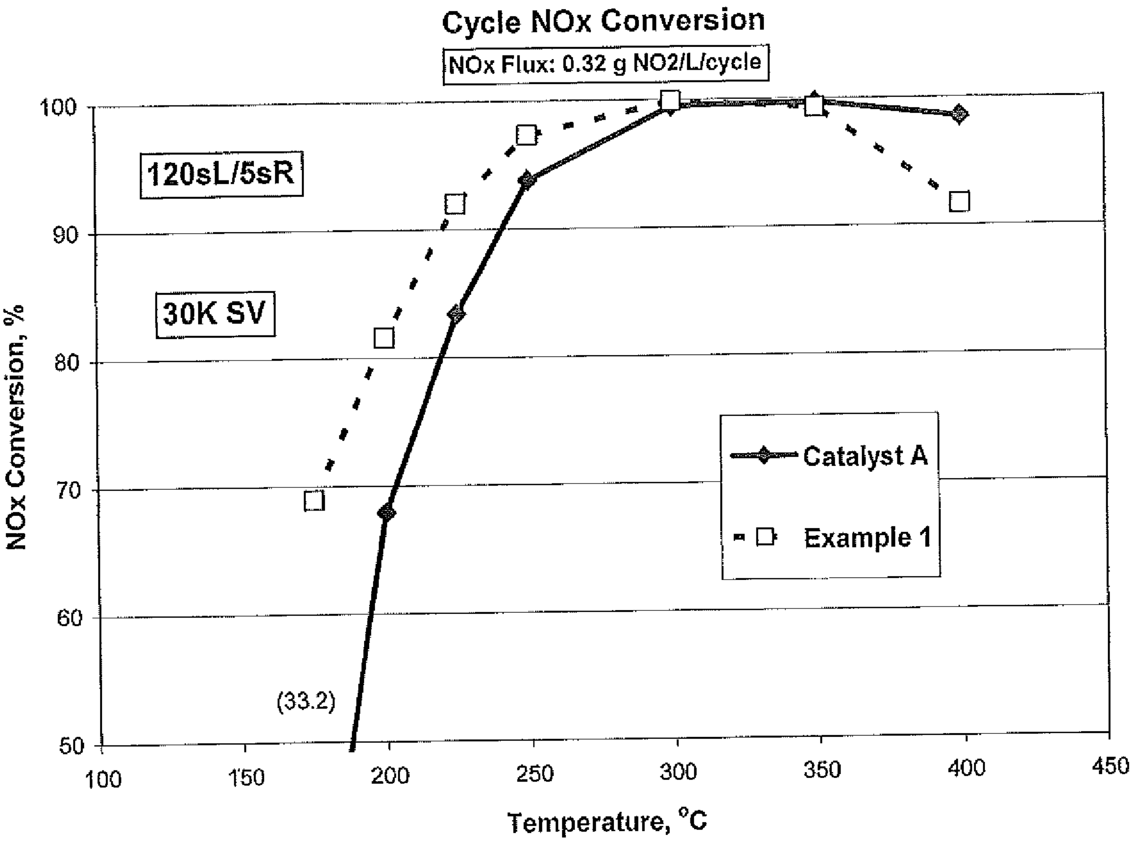
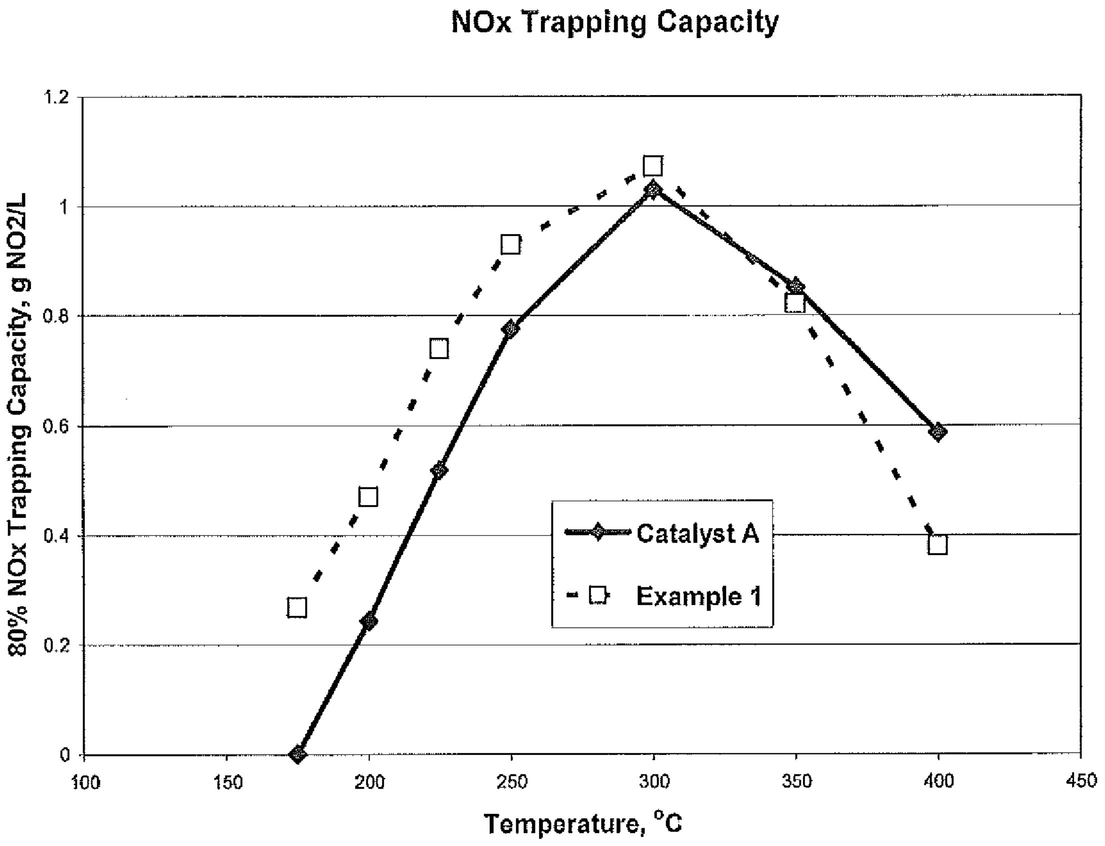

Cycle NOx Conversion
NOx Flux: 0.32 g NO2/L/cycle
120sL/5sR
30K SV
NOx Conversion, %
100
90
80
70
60
50
(33.2)
Catalyst A
Example 1
100
150
200
250
300
350
400
450
Temperature, °C

Fig. 9


NOx Trapping Capacity
80% NOx Trapping Capacity, g NO2/L
1.2
1
0.8
0.6
0.4
0.2
0
100
150
200
250
300
350
400
450
Temperature, °C
Catalyst A
Example 1

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2009/048565

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01D53/94 B01J21/04 B01J23/63 B01J35/00 B01J37/02
F01N3/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01D B01J F01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 2 342 056 A (TOYOTA MOTOR CO LTD [JP]) 5 April 2000 (2000-04-05) page 1, lines 9-15 page 6, lines 27-37 page 17, lines 13-21 page 25, lines 9-25 page 27, line 35 - page 30, line 4 page 31, line 8 - page 32, line 7 figures 3,4,7 claims 1-3,5,7 ----- -/--	1-10

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search 22 October 2009	Date of mailing of the international search report 19/11/2009
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Fax: (+31–70) 340–3016	Authorized officer Hackenberg, Stefan

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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X	EP 0 885 650 A (DEGUSSA [DE] UMICORE AG & CO KG [DE]) 23 December 1998 (1998-12-23) page 2, lines 3-36,57,58 page 3, lines 9-16 page 4, lines 32-51 page 5, line 24 - page 6, line 27 examples 1,5 claims 1-4,6 -----	1,2,5-7
X	EP 1 243 766 A (NISSAN MOTOR [JP]) 25 September 2002 (2002-09-25) paragraphs [0001], [0009], [0018], [0025] - [0029], [0038], [0039], [0045], [0074] figure 2 claims 1,2,9 -----	3-10
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Information on patent family members

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