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(58) Field of Search:
INT CL **B01J, F01N**
Other: **Online: WPI & EPODOC**

(54) Title of the Invention: **Method of treating nitrogen oxides and/or particulate matter in lean gas**
Abstract Title: **Exhaust system comprising a catalyst with a downstream filter and SCR catalyst**

(57) A method of treating nitrogen oxides NOx and particulate matter PM comprises the steps of catalytically converting nitrogen monoxide NO to nitrogen dioxide NO2 using a catalyst composition comprising a manganese oxide and at least one platinum group metal, converting NOx to nitrogen N2, by contacting a mixture of NO and NO2 with a nitrogenous reducing agent in the presence of a selective catalytic reduction SCR catalyst, and filtering PM to combust it in NO2. The catalyst composition may also comprise cerium oxide. An exhaust system is also claimed comprising a catalysed soot filter CSF with a portion of its substrate being catalysed and having an SCR downstream of it, where the catalyst on the substrate comprises a manganese oxide and at least one platinum group metal.

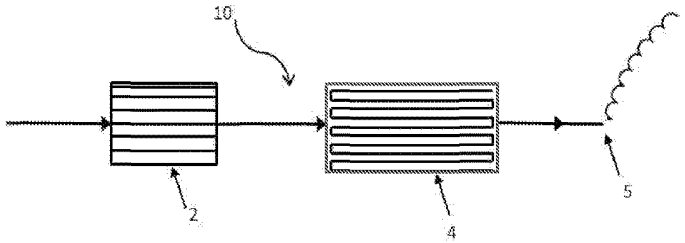

Figure 1

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At least one drawing originally filed was informal and the print reproduced here is taken from a later filed formal copy.

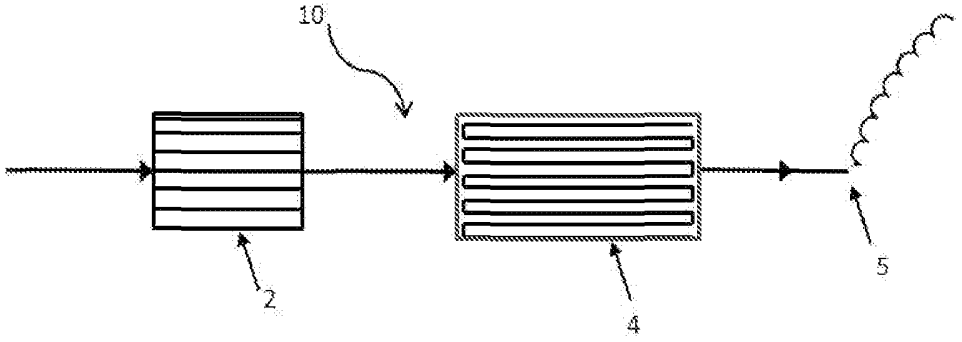

Figure 1

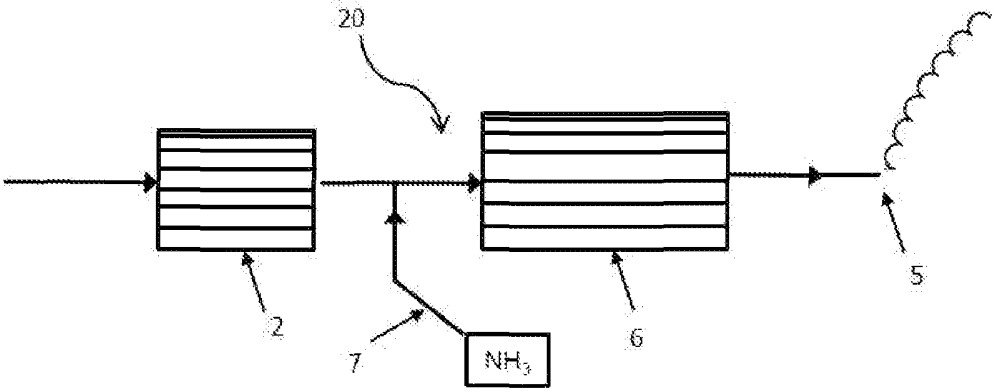

Figure 2

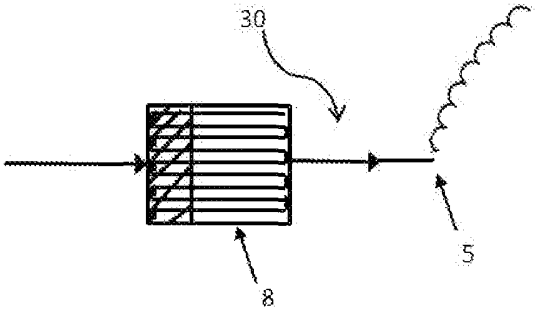

Figure 3

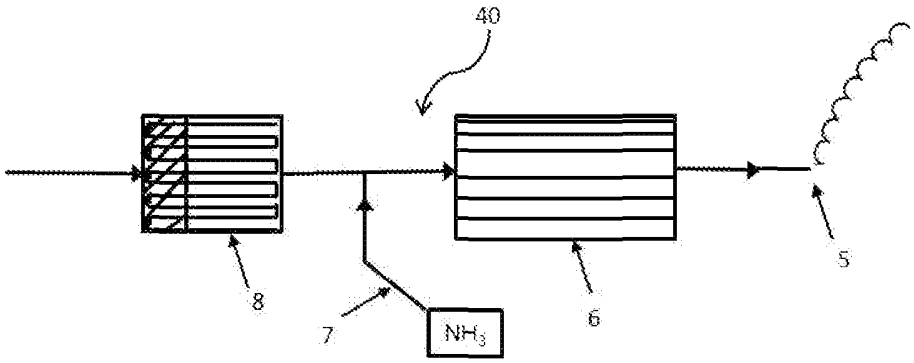

Figure 4

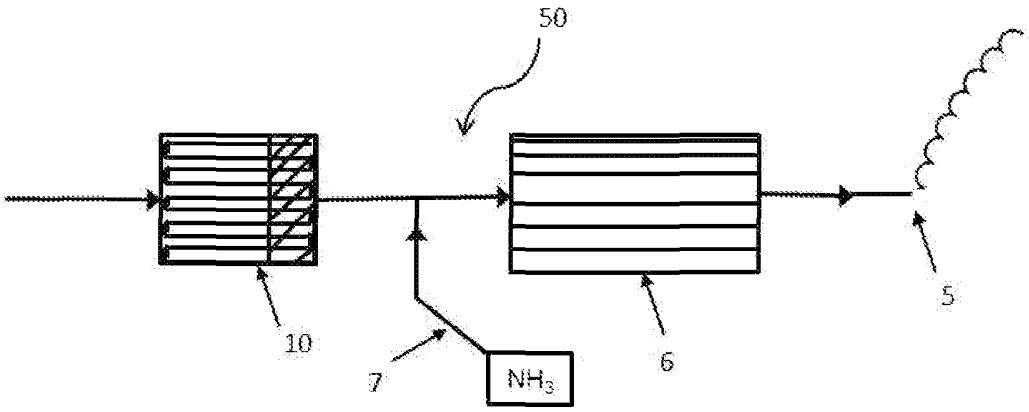

Figure 5

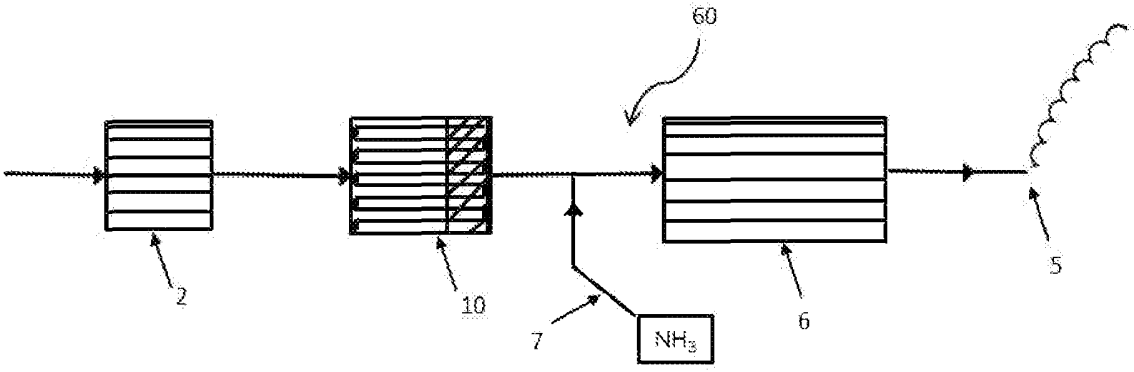

Figure 6

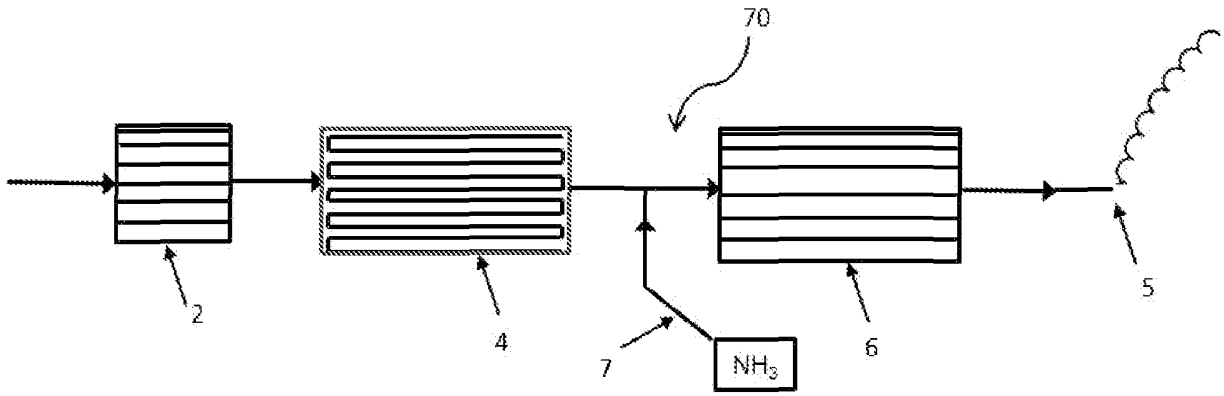

Figure 7

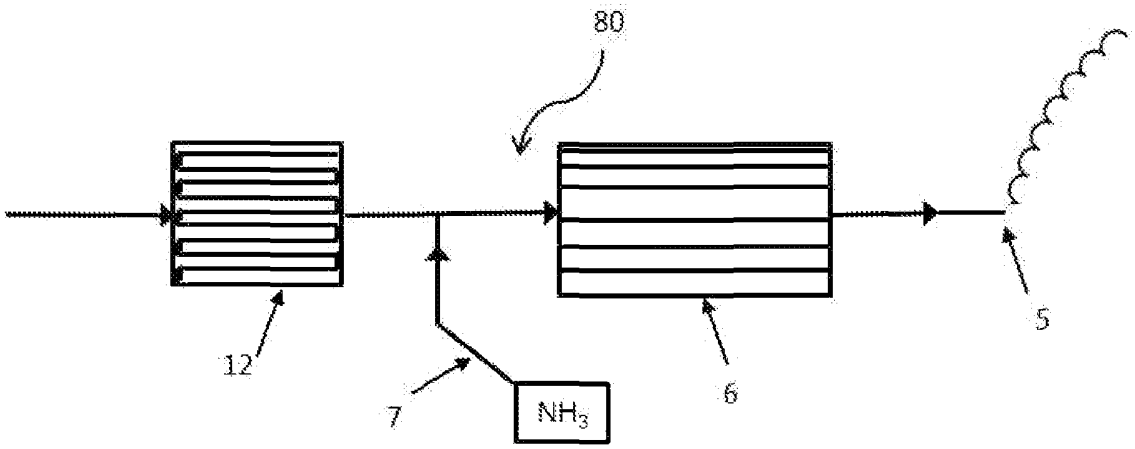

Figure 8

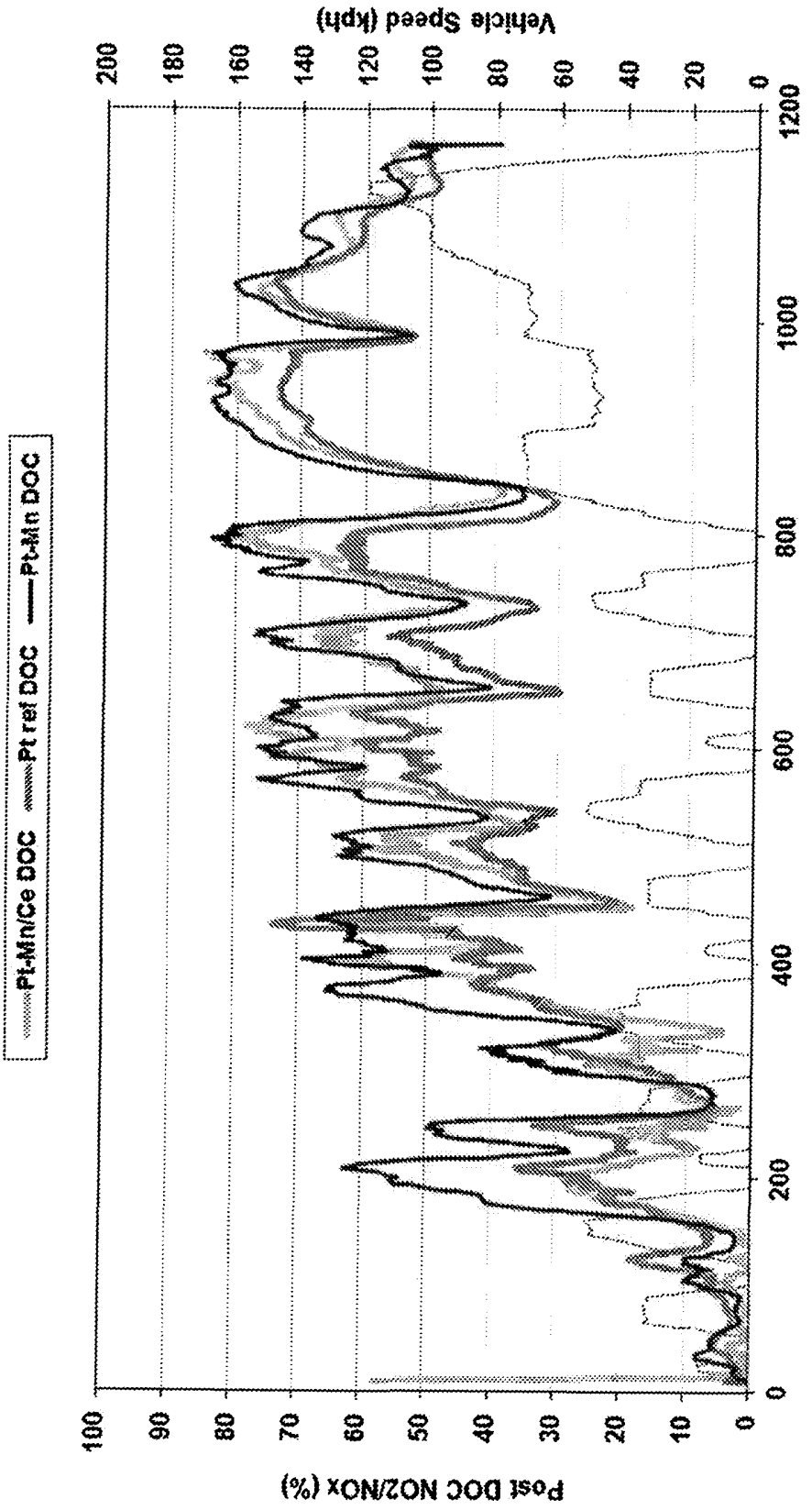

Figure 9

METHOD OF TREATING NITROGEN OXIDES AND/OR PARTICULATE MATTER IN LEAN GAS

The present invention relates to a method of treating nitrogen oxides (NO_x), particulate matter (PM) or both NO_x and PM in a lean gas containing NO_x and optionally also PM and to an exhaust system for carrying out the method. More particularly, the method includes a step of converting nitric oxide (NO) to nitrogen dioxide (NO_2) using a particular catalyst.

EP 341832 (the entire content of which is incorporated herein by reference) discloses a process for removing, by combustion, particulate deposited on a filter disposed in a diesel exhaust system, wherein exhaust gas containing NO is initially passed without filtering over a catalyst to convert the NO in the exhaust gas to NO_2 prior to filtering to remove particulate and wherein the exhaust gas containing NO_2 is then used to combust the particulate trapped on the filter, the amount of NO converted to NO_2 being sufficient to enable combustion of particulate trapped on filter to proceed at a temperature less than 400°C. The document mentions that suitable catalysts for converting NO to NO_2 include, for example, Pt, Pd, Ru, Rh or combinations thereof, platinum group metal oxides such as RhO_3 and the like and a $80g/ft^3$ Pt catalyst is used in the Examples.

US 2004/0065078 (the entire content of which is incorporated herein by reference) discloses a catalysed ceramic wall-flow filter homogeneously coated with a catalytic coating comprising at least one oxygen storage component (OSC) and at least one platinum group metal selected from the group consisting of platinum, palladium and rhodium. The oxygen storage component can be selected from the group consisting of cerium oxide, cerium/zirconium mixed oxide, manganese oxide, iron oxide, copper oxide, zinc oxide, lanthanum oxide, bismuth oxide, niobium oxide and tantalum oxide. In one example, the catalytic coating comprises 5.3 g/l platinum ($150g/ft^3$ Pt) and a 1:1 oxide mixture of cerium oxide and manganese oxide as the oxygen storage component.

WO 02/22241 (the entire content of which is incorporated herein by reference) discloses a NO_x-trap composition comprising: (a) at least one first NO_x storage component comprising at least one alkali metal supported on at least one first support material; and (b) a platinum oxidation catalyst and at least one second NO_x storage component not being an

alkali metal supported on at least one second support material. The at least one first NO_x storage component can be associated with at least one base metal oxidation catalyst, including manganese, chromium, cobalt or iron, or mixtures of any two or more thereof, and the at least one second NO_x storage component can be at least one rare earth and lanthanum, yttrium, cerium praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium or lutetium and a mixture of any two or more thereof are specifically mentioned. The support material can comprise alumina, ceria, zirconia or titania or a mixed oxide of any two or more thereof, or a mixture of any two or more of alumina, ceria, zirconia and titania.

WO 02/40151 (the entire content of which is incorporated herein by reference) discloses a three-way catalyst composition comprising a manganese-containing oxygen storage component (as an alternative to a ceria-based oxygen storage component), at least one optionally doped alumina and at least one platinum group metal.

We have now discovered that, very surprisingly, when a manganese oxide component is included in a catalyst composition for converting NO to NO_2, which catalyst composition also containing at least one platinum group metal, the catalyst composition is a more active catalyst for converting NO to NO_2 than a similar catalyst composition that does not include a manganese oxide component. This discovery has the particular advantage that it can enable expensive precious metals, such as platinum group metals (PGMs), to be thrifted from existing exhaust systems and it can be used in a number of novel exhaust system arrangements for lean-burn internal combustion engines, particularly those for vehicular use.

According to one aspect, the invention provides a method of treating nitrogen oxides (NO_x), particulate matter (PM) or both NO_x and PM in a lean gas containing NO_x and optionally also PM, which method comprising the steps of (i) catalytically converting nitrogen monoxide (NO) in the gas to nitrogen dioxide (NO_2); and one or both of step (ii) and step (iii), wherein step (ii) comprises converting NO_x in the gas to N_2 by contacting a mixture of NO and NO_2 in the gas with a nitrogenous reducing agent in the presence of a selective catalytic reduction catalyst; and step (iii) comprises filtering PM from the gas and combusting filtered PM in NO_2, wherein step (i) is done using a catalyst composition comprising a manganese oxide and at least one platinum group metal.

In a particular embodiment, the step (i) catalyst composition comprises a cerium oxide.

In a further embodiment comprising both steps (ii) and (iii), step (iii) precedes step (ii).

According to a further aspect, the invention provides an exhaust system for treating a lean gas containing nitrogen oxides (NO_x) and optionally also particulate matter (PM), which system comprising:

(a) a catalyst, carried on a substrate monolith, for converting nitrogen monoxide (NO) in the gas to nitrogen dioxide (NO_2) and a filter substrate for filtering PM from the gas disposed downstream of the substrate monolith carrying the NO conversion catalyst;

(b) a catalyst for converting NO in the gas to NO_2 carried on a flow-through substrate monolith, a catalyst for selectively catalysing the reduction of NOx to N2 using a nitrogenous reductant carried on a different substrate monolith from the flow-through substrate monolith carrying the NO conversion catalyst, which selective catalytic reduction (SCR) catalyst is located downstream from the flow-through substrate monolith carrying the NO conversion catalyst and means for providing a gas mixture comprising the lean gas and a nitrogenous reductant between the flow-through substrate monolith carrying the NO conversion catalyst and the substrate monolith carrying the SCR catalyst;

(c) a catalysed soot filter (CSF) comprising a filter substrate having a total length, which filter substrate comprising a catalyst for converting NO in the gas to NO_2 located in a contact zone of substantially uniform length comprising less than 80% (such as 10%, 15%, 20%, 45% or 75%) of the total filter substrate length, which contact zone being defined at one end by an inlet end of a filter substrate;

(d) a filter substrate having a total length, which filter substrate comprising a catalyst for converting NO in the gas to NO_2 located in a contact zone of substantially uniform length comprising less than 80% (such as 10%, 15%, 20%, 45% or 75%) of the filter substrate total length, which contact zone being defined at one end by an outlet end of the filter substrate, a SCR catalyst carried on a different substrate monolith from the filter substrate, which

different substrate monolith is located downstream of the filter substrate and means for providing a gas mixture comprising the lean gas and a nitrogenous reductant between the filter substrate and the SCR catalyst substrate monolith; or

(e) a catalysed soot filter (CSF) comprising a filter substrate, which filter substrate comprising a catalyst for converting NO in the gas to NO_2 homogeneously carried by an entire filter substrate length, a SCR catalyst carried on a different substrate monolith from the filter substrate, which different substrate monolith is disposed downstream of the filter substrate and means for providing a gas mixture comprising the lean gas and a nitrogenous reductant between the filter substrate and the SCR catalyst substrate monolith,

wherein the NO conversion catalyst comprises a manganese oxide and at least one platinum group metal.

The advantage of thrifting platinum group metals is particularly beneficial in systems that typically use PGMs in relatively large quantities. Such applications include a system marketed by Johnson Matthey as the "CCRT®", which is disclosed in EP 0341832. The CCRT® typically includes an oxidation catalyst comprising one or more PGMs for oxidising NO in exhaust gas to NO_2, which oxidation catalyst is disposed on a flow-through monolith substrate located upstream of a filtering substrate catalysed also with a catalyst comprising one or more PGMs. PGMs present in the filter can oxidise or re-oxidise NO to NO_2 for combusting PM held on the filter. Since the CCRT® uses NO_2 to combust PM, the CCRT® system benefits from additional performance from increased NO_2 generation when using manganese oxides as a component of NO conversion catalysts according to the invention.

Another application where PGM thrifting is desirable is in a system comprising an oxidation catalyst located upstream of a SCR catalyst, such as defined in system (b). The oxidation catalyst is for oxidising NO to NO_2 in order to promote a NO_x reduction reaction on the downstream SCR catalyst. As with the CCRT® application mentioned above, PGMs are typically used in the NO oxidation catalyst.

The systems according to the present invention are different from that which is disclosed in US 2004/0065078 in a number of significant respects. Firstly, the NO conversion catalyst of the present invention is active for NO oxidation in the absence of cerium oxide.

Secondly, the catalyst composition in US 2004/0065078 is carried by the total length of the filter substrate. Thirdly, there is no teaching or suggestion of combining the catalysed filter disclosed in US 2004/0065078 with suitable NO_x reduction devices. Fourthly, there is no teaching or suggestion in US 2004/0065078 that the presence of a manganese oxide component can improve the activity of a platinum group metal to convert NO to NO_2.

In embodiments of the exhaust system according to the invention including an SCR catalyst, the NO conversion catalyst is formulated so that a NO_2/NO ratio (of total NO_x comprising NO_2 and NO) is adjusted to the most beneficial such ratio for the particular SCR catalyst. In a particular embodiment, NO oxidation is promoted such that a mixture of approximately 1:1 NO:NO_2 of total NO_x at a desired exhaust gas temperature is fed into the substrate monolith carrying the SCR catalyst. This is because for some SCR catalysts, such as $V_2O_5/WO_3/TiO_2$, a particularly fast reaction for NO_x reduction is promoted where the feed gas includes a 1:1 mixture of NO and NO_2, according to reaction (2) hereinbelow relative to the less fast reactions where all NO_x is NO (reaction (1)) or all NO_x is NO_2 (relatively slow reaction (3)).

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \qquad \text{(1) Relatively fast reaction}$$

$$2NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O \qquad \text{(2) Relatively very fast reaction}$$

$$8NH_3 + 6NO_2 \rightarrow 7N_2 + 12H_2O \qquad \text{(3) Relatively slow reaction}$$

The filter substrate for use in systems according to the invention may be a ceramic or metal filter substrate including wall-flow substrates and partial filters, such as those disclosed in EP 1057519 or WO 01/080978.

In a particular embodiment of system (a), the filter substrate comprises a catalyst, comprising at least one PGM, for converting NO to NO_2, which catalyst may comprise a manganese oxide or may not include a manganese oxide. It will be appreciated that such an arrangement is a "CCRT®".

In further embodiments of system (a), the substrate monolith that carries the NO conversion catalyst is a partial filter (such as one of those disclosed in the paragraph immediately above) or a flow-through substrate monolith.

In one embodiment of system (c) according to the invention, the filter substrate is a wall-flow filter and only the inlet channels of the wall-flow filter carry the catalyst for converting NO in the gas to NO_2.

In an embodiment of exhaust system (d) according to the invention, the filter substrate is a wall-flow filter and only the outlet channels of the wall-flow filter carry the catalyst for converting NO in the gas to NO_2.

In another embodiment of exhaust system (c), the remainder of the filter substrate (optionally a wall-flow filter as in the above-mentioned embodiment) downstream of the inlet contact zone carries no catalyst or a catalyst for converting NO to NO_2 comprising at least one platinum group metal but containing no manganese oxide.

In other embodiments, exhaust systems (a) or (c) can comprise a SCR catalyst carried on a separate substrate monolith located downstream of the filter substrate and means for providing a gas mixture comprising the lean gas and a nitrogenous reductant between the filter substrate and the SCR catalyst substrate monolith. According to a particular embodiment of system (a) comprising a SCR catalyst downstream of the filter substrate, the filter substrate has a total length and the catalyst comprising a manganese oxide and at least one platinum group metal for converting NO in the gas to NO_2 is located in a contact zone of substantially uniform length comprising less than 45% of the total filter substrate length, which contact zone being defined at one end by an outlet end of a filter substrate.

In a further embodiment, exhaust system (c), (d) or (e) comprises a catalyst, carried on a substrate monolith disposed upstream of the filter substrate, for converting nitrogen monoxide (NO) in the gas to nitrogen dioxide (NO_2) to effect the process of EP 341832, described hereinabove. The catalyst can be a platinum group metal catalyst including manganese oxide, according to the invention, or a suitable platinum group metal catalyst without manganese oxide present. The substrate monolith used of the additional NO

conversion catalyst can be a flow-through monolith or a partial filter, such as one of those disclosed in EP 1057519 or WO 01/080978.

Where the exhaust system comprises a SCR catalyst carried on a substrate monolith, the substrate monolith can be a flow-through substrate monolith or a filter substrate, such as a partial filter, as disclosed in EP 1057519 or WO 01/080978.

The at least one platinum group metal for use in the NO conversion catalyst can be selected from the group consisting of platinum, palladium and rhodium, and may in particular consist of platinum or platinum and palladium. In embodiments, depending on whether the NO conversion catalyst is on a filter or a diesel oxidation catalyst, the total platinum group metal loading in the or each NO conversion catalyst can be from $1gft^{-3}$ to $240gft^{-3}$: a filter may have a lower PGM loading.

In particular embodiments according to systems (a) to (e) inclusive, the NO conversion catalyst comprises a cerium oxide.

At least some of the cerium oxide for use in the NO conversion catalyst can be cerium (II) oxide, but it may also be present as a mixed oxide or composite oxide with one or more other transition metal(s), preferably zirconium.

At least some of the manganese oxide for use in the NO conversion catalyst can be manganese dioxide, but other manganese oxides may be present such as Mn_3O_4. The manganese oxide loading in the NO conversion catalyst can be from 2-50wt% based on the total weight of the NO conversion catalyst, optionally 3-35wt% such as 10-20wt%.

The selective catalytic reduction catalyst for use in the invention can be any suitable catalyst for the intended purpose and include, without limitation, vanadia-based catalysts such as $V_2O_5/WO_3/TiO_2$ and zeolite-based catalysts exchanged with transition metals such as Fe and/or Cu, e.g. Cu/ZSM-5 or Fe-beta zeolite.

Nitrogenous reductant for use in the present invention includes ammonia *per se* or an ammonia precursor such as urea. In practice, introduction of nitrogenous reductant into the gas may be regulated by suitable valve and sensor means operated by a control means, e.g. a

microprocessor. Details of such arrangements are known to the skilled person and so will not be given here.

The "means for providing a gas mixture comprising the lean gas and a nitrogenous reductant" can comprise a suitable injector for injecting a source of nitrogenous reductant into the lean gas between, e.g. the flow-through substrate monolith carrying the NO conversion catalyst and the substrate monolith carrying the SCR catalyst in system (b); and between the filter substrate and the SCR catalyst substrate monolith in systems (d) and (e). However, it is also possible to inject such nitrogenous reductant into lean gas upstream of catalysed components, such as upstream of the NO conversion catalyst in system (b); or upstream of the filter substrate in systems (d) and (e), provided arrangements are adopted to reduce or avoid oxidation of nitrogenous reductant prior to contacting the SCR catalyst. Such arrangements include external (i.e. around a substrate monolith) and internal (i.e. within a substrate monolith) bypass structures. Suitable internal bypasses are disclosed in our WO 01/96717 (the entire content of which is incorporated herein by reference), including injecting a nitrogenous reductant over a region of a catalysed substrate monolith that has no catalyst capable of catalysing the oxidation of the nitrogenous reductant in lean gas; and injecting nitrogenous reductant over a region of catalysed substrate monolith wherein passage of lean gas is excluded.

According to a further aspect, the invention provides an apparatus comprising a lean-burn internal combustion engine and an exhaust system according to the invention. The lean-burn internal combustion engine is suitably a diesel engine, including HCCI-type diesel engines or a gasoline engine, including GDI-type engines. However, the invention may also be used in connection with engines powered by alternative fuels such as natural gas, liquid petroleum gas and gas-to-liquid fuels.

Whilst the method and system can be used in connection with treating combustion exhaust gases from stationary sources, e.g. power plants, in particular embodiments the invention relates to the treatment of vehicular exhaust gases, i.e. mobile applications.

In order that the invention may be more readily understood, embodiments whereof are provided with reference to the accompanying drawings, in which:

Figure 1 is a schematic diagram representing a first embodiment according to the invention;

Figure 2 is a schematic diagram representing a second embodiment according to the invention;

Figure 3 is a schematic diagram representing a third embodiment according to the invention;

Figure 4 is a schematic diagram representing a fourth embodiment according to the invention;

Figure 5 is a schematic diagram representing a fifth embodiment according to the invention;

Figure 6 is a schematic diagram representing a sixth embodiment according to the invention based on the embodiment shown in Figure 5;

Figure 7 is a schematic diagram representing a sixth embodiment according to the invention based on the embodiment shown in Figure 1;

Figure 8 is a schematic diagram representing a sixth embodiment according to the invention; and

Figure 9 is a graph showing the NO_2/NO_x ratio post-diesel oxidation catalyst on a 2.2l common rail diesel vehicle over the European MVEG-B cycle

Figure 1 shows an exhaust system 10 for a diesel engine comprising, in the flow direction of gas, a ceramic flow-through substrate monolith 2 carrying a catalyst for converting nitrogen monoxide (NO) in the gas to nitrogen dioxide (NO_2), which catalyst comprising a manganese oxide and at least one platinum group metal and optionally a cerium oxide. This arrangement is disclosed in EP 0341832 discussed hereinabove and is marketed by Johnson Matthey as the "CRT®". A ceramic wall-flow filter substrate 4 for filtering particulate matter from the gas is disposed downstream of substrate monolith 2. The filter

substrate 4 may in turn carry a suitable catalyst for converting nitrogen monoxide (NO) in the gas to nitrogen dioxide (NO_2), such as a platinum group metal-based catalyst, which may or may not also contain a manganese oxide component and optionally a cerium oxide component. This arrangement is marketed by Johnson Matthey as the "CCRT®". Exhaust gas exiting filter substrate 4 is exhausted to atmosphere at tailpipe 5.

Figure 7 shows an alternative exhaust system 70 based on the embodiment shown in Figure 1, with like features sharing the same reference numerals. Exhaust system 70 includes a selective catalytic reduction catalyst such as Fe/beta zeolite carried on a flow-through ceramic substrate 6. Means 7 such as a suitable injector for introducing a nitrogenous reductant (ammonia is illustrated) into the gas is located between the filter substrate 4 and the SCR catalyst substrate monolith 6. Such an arrangement is a variation on the system disclosed in EP 1054722 (the entire contents of which are incorporated herein by reference).

Figure 2 shows an exhaust system 20, wherein like features from the Figure 1 and 7 embodiments share the same reference numerals. Here, an NO conversion catalyst is formulated so that approximately 1:1 NO:NO_2 at a desired gas temperature passes into the SCR catalyst substrate monolith 6 at gas temperatures beneficial for NO_x reduction.

Figure 3 shows an alternative exhaust system embodiment 30 featuring a catalysed soot filter (CSF) 8. CSF 8 comprises a ceramic wall-flow filter substrate carrying a catalyst comprising a manganese oxide and at least one platinum group metal, and optionally a cerium oxide, for converting NO in the gas to NO_2 located in a contact zone of substantially uniform length comprising 20% the total filter substrate length (inlet channels), which contact zone being defined at one end by an inlet end of a filter substrate. In a further embodiment, the remaining 80% of the total length of the filter substrate (outlet channels) downstream of the contact zone can be coated with a platinum group metal-based catalyst which is devoid of manganese oxide. However, in the embodiment shown in Figure 3, the remaining 80% of the filter substrate downstream of the contact zone carries no catalyst.

An exhaust system embodiment 40 based on that shown in Figure 3 is at Figure 4, wherein like features from the previous Figures share the same reference numerals. In practice, the catalyst in the contact zone on CSF 8 (alternatively, the total catalyst volume on CSF 8, i.e. including any catalyst carried downstream of the inlet contact zone) is (or are) formulated to allow approximately 1:1 NO:NO_2 at a desired gas temperature to pass

downstream into the SCR catalyst substrate monolith 6 at gas temperatures beneficial for NO_x reduction.

In an alternative embodiment based on the embodiment shown in Figure 4 (not shown), a catalyst comprising a manganese oxide and at least one platinum group metal, and optionally a cerium oxide, for converting NO to NO_2 is located in a contact zone of substantially uniform length comprising 20% of the total filter substrate length, which contact zone being defined at one end by an outlet end of a filter substrate. Again, the purpose of this downstream catalyst contact zone is to convert sufficient NO to NO_2 at a desired temperature to provide the advantageous approximately 1:1 NO:NO_2 ratio, and so the catalyst in the downstream contact zone is formulated accordingly.

The system embodiment 50 shown in Figure 5 is based on the last embodiment discussed in connection with Figure 4, i.e. CSF 8 including a downstream catalyst contact zone is exchanged for a filter substrate 10 featuring a catalyst comprising a manganese oxide and at least one platinum group metal, and optionally a cerium oxide, for converting NO to NO_2 is located in a contact zone of substantially uniform length comprising 20% of the total filter substrate length (outlet channels), which contact zone being defined at one end by an outlet end of a filter substrate. As for the embodiment of Figure 4, the purpose of this downstream catalyst contact zone is to convert sufficient NO to NO_2 at a desired temperature to provide the advantageous approximately 1:1 NO:NO_2 ratio for NO_x conversion of the downstream SCR catalyst 6, and so the catalyst in the downstream contact zone is formulated accordingly. The filter substrate upstream of the downstream contact zone is catalyst-free.

The system embodiment 60 shown in Figure 6 is based in the system embodiment 50 shown in Figure 6 but features a separate flow-through monolith substrate 2 described in connection with Figure 1 hereinabove disposed upstream of the filter substrate 10.

Referring to Figure 8, CSF 12 in exhaust system 80 is homogeneously coated with a catalyst comprising a manganese oxide and at least one platinum group metal, and optionally a cerium oxide, for converting NO in the gas to nitrogen dioxide NO_2, but otherwise shares similar features to system 40 shown in Figure 4.

The following Example is provided by way of illustration only.

EXAMPLE

Three diesel oxidation catalysts (DOCs) were prepared by washcoating a ceramic 400 cells per square inch (62 cells per square centimetre) flow-through monolith at a loading on 100g/ft^3 Pt, wherein a reference catalyst the Pt was supported on an alumina based support. In two embodiments according to the invention, a first DOC contained 5wt% MnO_2 (balance Al_2O_3), and a second DOC contained the same quantity of MnO_2 in a MnO_2/Ce-ZrO_2 (mixed oxide)/alumina balance composite. The DOCs were tested in turn by fitting them in a close-coupled location (close to the engine exhaust manifold) in the exhaust system of a 2.2l common rail diesel vehicle, which was then run on a rolling road over the European MVEG-B cycle (dashed line in Figure 9, vehicle speed in right-hand axis)The ratio of NO_2 present in total NO_x in the exhaust gas downstream of the DOC was determined and is plotted in Figure 9.

It can be seen from Figure 9 that the DOCs containing Pt and MnO_2 (no Ce-ZrO_2) and Pt, MnO_2 and Ce-ZrO_2 are both more active than the reference catalyst. However, it can also be seen that the DOC containing Pt and MnO_2 (no Ce-ZrO_2) is significantly more active for NO oxidation than the DOC containing Pt, MnO_2 and Ce-ZrO_2.

CLAIMS:

1. A method of treating nitrogen oxides (NO_x), particulate matter (PM) or both NO_x and PM in a lean gas containing NO_x and optionally also PM, which method comprising the steps of (i) catalytically converting nitrogen monoxide (NO) in the gas to nitrogen dioxide (NO_2); and one or both of step (ii) and step (iii), wherein step (ii) comprises converting NO_x in the gas to N_2 by contacting a mixture of NO and NO_2 in the gas with a nitrogenous reducing agent in the presence of a selective catalytic reduction catalyst; and step (iii) comprises filtering PM from the gas and combusting filtered PM in NO_2, wherein step (i) is done using a catalyst composition comprising a manganese oxide and at least one platinum group metal.

2. A method according to claim 1, wherein the step (i) catalyst composition comprises a cerium oxide.

3. A method according to claim 1 or 2 comprising both steps (ii) and (iii), wherein step (iii) precedes step (ii).

4. An exhaust system for treating a lean gas containing nitrogen oxides (NO_x) and optionally also particulate matter (PM), which system comprising:

(a) a catalyst, carried on a substrate monolith, for converting nitrogen monoxide (NO) in the gas to nitrogen dioxide (NO_2) and a filter substrate for filtering PM from the gas disposed downstream of the substrate monolith carrying the NO conversion catalyst;

(b) a catalyst for converting NO in the gas to NO_2 carried on a flow-through substrate monolith, a catalyst for selectively catalysing the reduction of NOx to N2 using a nitrogenous reductant carried on a different substrate monolith from the flow-through substrate monolith carrying the NO conversion catalyst, which selective catalytic reduction (SCR) catalyst is located downstream from the flow-through substrate monolith carrying the NO conversion catalyst and means for providing a gas mixture comprising the lean gas and a nitrogenous reductant between the flow-through substrate monolith carrying the NO conversion catalyst and the substrate monolith carrying the SCR catalyst;

(c) a catalysed soot filter (CSF) comprising a filter substrate having a total length, which filter substrate comprising a catalyst for converting NO in the

gas to NO_2 located in a contact zone of substantially uniform length comprising less than 80% of the total filter substrate length, which contact zone being defined at one end by an inlet end of a filter substrate;
(d) a filter substrate having a total length, which filter substrate comprising a catalyst for converting NO in the gas to NO_2 located in a contact zone of substantially uniform length comprising less than 80% of the filter substrate total length, which contact zone being defined at one end by an outlet end of the filter substrate, a SCR catalyst carried on a different substrate monolith from the filter substrate, which different substrate monolith is located downstream of the filter substrate and means for providing a gas mixture comprising the lean gas and a nitrogenous reductant between the filter substrate and the SCR catalyst substrate monolith; or
(e) a catalysed soot filter (CSF) comprising a filter substrate, which filter substrate comprising a catalyst for converting NO in the gas to NO_2 homogeneously carried by an entire filter substrate length, a SCR catalyst carried on a different substrate monolith from the filter substrate, which different substrate monolith is disposed downstream of the filter substrate and means for providing a gas mixture comprising the lean gas and a nitrogenous reductant between the filter substrate and the SCR catalyst substrate monolith, wherein the NO conversion catalyst comprises a manganese oxide and at least one platinum group metal.

5. An exhaust system according to claim 4, system (a), wherein the filter substrate comprises a catalyst comprising at least one PGM for converting NO to NO_2, which catalyst optionally comprising a manganese oxide.

6. An exhaust system according to claim 4, system (c), wherein the filter substrate is a wall-flow filter and only the inlet channels of the wall-flow filter carry the catalyst for converting NO in the gas to NO_2.

7. An exhaust system according to claim 4, system (d), wherein the filter substrate is a wall-flow filter and only the outlet channels of the wall-flow filter carry the catalyst for converting NO in the gas to NO_2.

8. An exhaust system according to claim 4, 5 or 6, wherein system (a) or (c) comprises a SCR catalyst carried on a separate substrate monolith located downstream of the filter substrate and means for providing a gas mixture comprising the lean gas and a nitrogenous reductant between the filter substrate and the SCR catalyst substrate monolith.

9. An exhaust system according to claim 4, 6 or 8, wherein in system (c) the remainder of the filter substrate downstream of the inlet contact zone carries no catalyst or a catalyst for converting NO to NO_2 comprising at least one platinum group metal but containing no manganese oxide.

10. An exhaust system according to claim 4, 6, 8 or 9, wherein system (c), comprises a catalyst, carried on a substrate monolith disposed upstream of the filter substrate, for converting nitrogen monoxide (NO) in the gas to nitrogen dioxide (NO_2).

11. An exhaust system according to claim 4, wherein system (d) or (e) comprises a catalyst, carried on a substrate monolith disposed upstream of the filter substrate, for converting nitrogen monoxide (NO) in the gas to nitrogen dioxide (NO_2).

12. An exhaust system according to claim 10 or 11, wherein the catalyst for converting NO to NO_2 comprises a manganese oxide and at least one platinum group metal.

13. An exhaust system according to any of claims 4 to 12, wherein the SCR catalyst substrate monolith is a flow-through substrate monolith or a filter substrate.

14. An exhaust system according to any of claims 4 to 13, wherein the filter substrate is a wall-flow filter or a partial filter.

15. An exhaust system according to any of claims 4 to 14, wherein the at least one platinum group metal is selected from the group consisting of platinum, palladium and rhodium.

16. An exhaust system according to any of claims 4 to 15, wherein the platinum group metal consists of platinum or both platinum and palladium.

17. An exhaust system according to any of claims 4 to 16, wherein the total platinum group metal loading in the or each NO conversion catalyst is from $1gft^{-3}$ to $240gft^{-3}$.

18. An exhaust system according to any of claims 4 to 17, wherein the NO conversion catalyst comprises a cerium oxide.

19. An exhaust system according to claim 18, wherein at least some of the cerium oxide is present as cerium (II) oxide.

20. An exhaust system according to claim 18 or 19, wherein the cerium oxide is present as a mixed oxide or composite oxide with one or more other transition metal(s).

21. An exhaust system according to claim 20, wherein the other transition metal is zirconium.

22. An exhaust system according to any of claims 4 to 21, wherein at least some of the manganese oxide is present as manganese dioxide.

23. An exhaust system according to any of claims 4 to 22, wherein the manganese oxide loading in the NO conversion catalyst is from 2-50wt% based on the total weight of the NO conversion catalyst.

24. An apparatus comprising a lean-burn internal combustion engine and an exhaust system according to any of claims 4 to 23.

25. An apparatus according to claim 24, wherein the lean-burn internal combustion engine is a diesel engine or a gasoline engine.

26. A method of treating nitrogen oxides (NO_x), particulate matter (PM) or both NO_x and PM substantially as described herein with reference to the accompanying Examples.

27. An exhaust system for treating a gas containing nitrogen oxides (NO_x) and optionally also particulate matter (PM) substantially as described herein with reference to the accompanying drawings.

Application No: GB1009775.6 **Examiner:** Mr Robert Arnold

Claims searched: 1-25 **Date of search:** 11 October 2010

Patents Act 1977: Search Report under Section 17

Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance
X,Y	Claims 1 & 4 at least	US2009/173063 A (BOORSE ET AL) - See whole document, especially paragraph 37 and 47.
Y	Claim 1 at least	EP2060756 A (MAZDA MOTOR) - See whole document, especially paragraph 39.
Y	Claim 1 at least	US2009/100825 A (MITSUBISHI FUSO TRUCK & BUS) - See whole document, especially paragraphs 23 & 24.
Y	Claim 1 at least	WO2004/022935 A (JOHNSON MATTHEY PLC) - See whole document, especially page 14, paragraph 2.
Y	Claims 1 & 4 at least	EP2106841 A (HYUNDAI MOTOR CO LTD) - See whole document, especially paragraphs 37 & 39.
Y	Claims 1 & 4 at least	EP2161420 A (HYUNDAI MOTOR CO LTD) - See whole document, especially paragraphs 14 & 53.
Y	Claims 1 and 4 at least	US7052532 A (3M INNOVATIVE PROPERTIES CO) - See whole documents, especially paragraph 241 and figure 20.
Y	Claims 1 & 4 at least	US2004/065078 A (SCHAFER-SINDLINGER ET AL) - See whole document, especially claims 15 & 16.
Y	Claims 1 & 4 at least	US2004/067176 A (UMICORE AG & CO KG) See whole document, especially paragraphs 42 & 43.
A	-	WO01/12320 A (JOHNSON MATTHEY PLC) - See whole document, especially page 8 line 30 to page 9 line 28.
A	-	EP1657410 A (CATALER CORP) - See whole document, especially paragraphs 58 & 59.

Categories:

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
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Field of Search:

Search of GB, EP, WO & US patent documents classified in the following areas of the UKC[X] :

Worldwide search of patent documents classified in the following areas of the IPC

B01J; F01N

The following online and other databases have been used in the preparation of this search report

WPI & EPODOC

International Classification:

Subclass	Subgroup	Valid From
F01N	0003/035	01/01/2006
B01J	0023/56	01/01/2006
B01J	0023/656	01/01/2006
F01N	0003/023	01/01/2006
F01N	0003/20	01/01/2006