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ABSTRACT (NOT MORE THAN 150 WORDS)

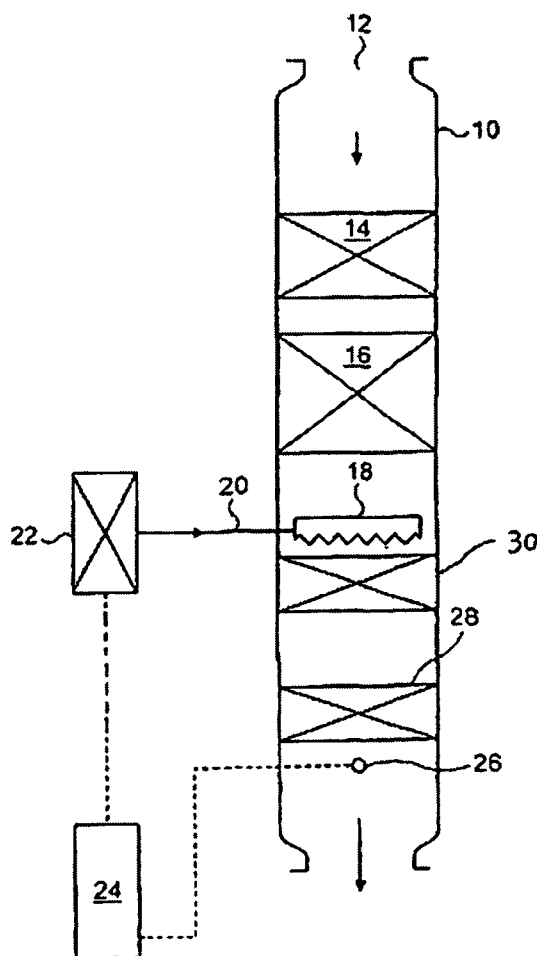
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The figure of the drawing to which the abstract refers is attached.

ABSTRACT

An exhaust system (10) for a lean-burn internal combustion engine comprises a nitrogen oxide (NO_x) absorbent (28), a catalyst (30) for catalysing the selective catalytic reduction (SCR) of NO_x with a NO_x specific reactant, first means (18, 22) for introducing a NO_x specific reactant or a precursor thereof into an exhaust gas upstream of the SCR catalyst (30) and means (24) for controlling the introduction of the NO_x -specific reactant or precursor thereof into the exhaust gas via the first introducing means (18, 22), wherein the SCR catalyst (30) is disposed upstream of the NO_x absorbent (28) and optionally with the NO_x absorbent, wherein the control means (24) is arranged to introduce the NO_x -specific reactant or the precursor thereof to exhaust gas via the first introducing means (18, 22) only when the SCR catalyst (30) is active, whereby exhaustion of NO_x -specific reactant to atmosphere is substantially prevented.



EXHAUST SYSTEM FOR LEAN BURN IC ENGINES

The present invention relates to an exhaust system for a lean-burn internal combustion engine, which exhaust system comprising a NO_x trap and a catalyst for catalysing the reduction of NO_x with a NO_x specific reactant, e.g. NH₃.

By "NO_x specific reactant" herein, we mean a reducing agent that, in most conditions, preferentially reduces NO_x instead of other components of a gaseous mixture. Examples of NO_x-specific reactants include nitrogenous compounds such as nitrogen hydrides, e.g. ammonia (NH₃) or hydrazine, or an NH₃ precursor.

By "NH₃ precursor" we mean one or more compounds from which NH₃ can be derived, e.g. by hydrolysis. These include urea (CO(NH₂)₂) as an aqueous solution or as a solid or ammonium carbamate (NH₂COONH₄). If the urea is used as an aqueous solution, a eutectic mixture, e.g. a 32.5% NH₃ (aq), is preferred. Additives can be included in the aqueous solutions to reduce the crystallisation temperature.

Urea hydrolyses at temperatures above 160°C according to equation (1) to liberate NH₃ itself. It also thermally decomposes at this temperature and above according to equations (2) and (3) resulting in reduction of NO_x.



The NH₃ can be in anhydrous form or as an aqueous solution, for example.

The application of NH₃ SCR technology to treat NO_x emissions from IC engines, particularly lean-burn IC engines, is well known. Several chemical reactions occur in the NH₃ SCR system, all of which represent desirable reactions which reduce NO_x to elemental nitrogen. The dominant reaction mechanism is represented in equation (4).



Competing, non-selective reactions with oxygen can produce secondary emissions or may unproductively consume NH_3 . One such non-selective reaction is the complete oxidation of NH_3 , represented in equation (5).



Presently, urea is the preferred source of NH_3 for mobile applications because it is less toxic than NH_3 , it is easy to transport and handle, is inexpensive and commonly available.

Early methods of using urea as a source of NH_3 in exhaust systems involved injecting urea directly into the exhaust gas, optionally over an in-line hydrolysis catalyst (see EP-A-0487886 (incorporated herein by reference)). However, not all urea is hydrolysed in such arrangements, particularly at lower temperatures.

Incomplete hydrolysis of urea can lead to increased PM emissions on tests for meeting the relevant emission test cycle because partially hydrolysed urea solids or droplets will be trapped by the filter paper used in the legislative test for PM and counted as PM mass. Furthermore, the release of certain products of incomplete urea hydrolysis, such as cyanuric acid, is environmentally undesirable. Another method is to use a pre-injection hydrolysis reactor (see US-A-5,968,464 (incorporated herein by reference)) held at a temperature above that at which urea hydrolyses.

It will be appreciated that at lower temperatures, below about 100-200°C, NH_3 can also react with NO_2 to produce explosive ammonium nitrate (NH_4NO_3) according to equation (6):



For the avoidance of doubt, the present invention does not embrace such reactions or the promotion of conditions which bring them about. For example, the reaction can be avoided by ensuring that the temperature does not fall below about 200°C or by supplying into a gas stream less than the precise amount of NH_3 necessary for the stoichiometric reaction with NO_x (1 to 1 mole ratio). For cold start applications, measures to prevent water from contacting the catalyst

can be adopted. These can include disposing a water trap, e.g. a zeolite, upstream of the catalyst to reduce the amount of water vapour contacting the catalyst until it is heated sufficiently. A water trap can also be positioned downstream of the catalyst, to prevent atmospheric humid air from travelling up the exhaust pipe. An electric heater can also be employed to drive off moisture from the catalyst pre-cold start. Such arrangements are described in our EP 0747581, (incorporated herein by reference).

In order to meet existing and future emission legislation, generally a vehicular exhaust system includes one or more components, such as catalysts. One of the legislated exhaust gas components is NO_x . During normal operation, the exhaust gas produced by a lean-burn internal combustion engine, for example, includes an excess of oxygen and oxidising species. It is very difficult to reduce NO_x to N_2 in an oxidising or lean atmosphere. In order to treat NO_x in lean exhaust gases, a component has been developed that absorbs NO_x during normal lean-burn operation of the engine. This component is commonly called a NO_x -trap and generally it includes: (i) an oxidation catalyst (e.g. platinum) to oxidise NO in the exhaust gas to NO_2 in the oxidising atmosphere; (ii) a NO_x storage component to store the NO_2 e.g. as the nitrate. The NO_x storage component is generally a basic compound of an alkali metal or an alkaline-earth, such as barium oxide; and (iii) a reduction catalyst, such as rhodium. It is possible, however, to use a NO_x trap formulation in certain circumstances which comprises only the NO_x storage component, or the NO_x storage component and one or other of the oxidation and reduction catalyst.

Intermittently, the engine is run rich, e.g. by adjusting the moment of fuel injection into one or more cylinders, or by injecting a reducing agent, e.g. a hydrocarbon fuel, into the exhaust gas, in order to remove the stored NO_x and reduce it to N_2 . This also regenerates the absorber for another store-regenerate cycle.

Another approach for removing NO_x from a gas stream is by selective catalytic reduction (SCR), which comprises adding e.g. NH_3 to the gas and passing the mixture over a catalyst effective to react the NO_x and NH_3 to nitrogen. Another approach is described in our WO 00/21647 (incorporated herein by reference) wherein NO_x from a diesel engine exhaust gas is removed by absorbing it in a solid absorbent. The absorbent is regenerated by the action of a NO_x -specific reactant.

Either such process requires careful control to avoid over- or under-supply of e.g. NH_3 , leading respectively to emission of NH_3 or NO_x . NH_3 is an irritant and has an unpleasant odour and, accordingly, it is undesirable to slip NH_3 to atmosphere. In practice this would mean positioning an oxidation "clean-up" catalyst downstream of the SCR catalyst or NO_x -trap to oxidise slipped NH_3 to NO_x . Therefore, slipping NO_x *per se*, by providing inadequate levels of NH_3 , or NH_3 would have the effect of reducing the overall effectiveness of the exhaust system to limit emissions.

One problem associated with NH_3 SCR technology is to maintain good NO_x conversion when the exhaust gas temperature is relatively low, e.g. during extended idling or following cold-start. NO_x conversion can be achieved using NH_3 at temperatures as low as 150°C using Pt-based catalysts, but the preferred delivery form of NH_3 , aqueous urea solution, does not decompose significantly below 200°C . Pt-based catalysts generate nitrous oxide (NO) according to equation (5) at above about 225°C .

Changes in engine test cycles have been introduced in the present Euro III standard and will govern Euro IV type approval of new vehicles. In particular, the new test cycles include the European Stationary Cycle (ESC); the European Transient Cycle (ETC); and a test for smoke opacity on the European Load Response (ELR) test. These cycles and tests include significant periods at low temperature. To attain type approval, a new vehicle will have to pass both the ETC and ESC/ELR tests.

It is stated in our WO 00/21647 that "If the [NH_3 SCR] catalyst system is associated with the [NO_x] absorbent, that is the absorber is 'catalysed', the catalytic material may be for example co-precipitated or co-impregnated or co-deposited with NO_x absorbent or present as one or more sandwiched layers or as fine (e.g. 10-500 microns) particles on or in a layer of absorbent or among particles of absorbent".

Elsewhere in WO 00/21647 we state that the point of injection of a NO_x specific reactant can be downstream of the filter, i.e. upstream of the NO_x absorbent and "in this event the temperature is typically in the range $150\text{-}300^\circ\text{C}$ ".

We have looked at putting barium (a NO_x absorbent) on a cerium and iron-containing SCR catalyst, and the SCR function was significantly reduced, although the ability of the composition to absorb and desorb NO_x was unimpaired. In our WO 02/068099 we demonstrate the principle of using NH₃ (or urea) injection over a NO_x trap catalyst to reduce stored NO_x during lean running conditions. This arrangement is particularly useful for diesel applications. In WO 02/068099 we state: "Whichever [NO_x storage] compounds are used, there may be present also one or more catalytic agents, such as precious metals, effective to promote reactions of NO_x-specific reactant [including NH₃] with nitroxy salt. Such catalysts are also known as SCR catalysts and can include iron/zeolite or V₂O₅/TiO₂. Where the NO_x absorbent and SCR catalyst are associated, in one embodiment they are segregated. By 'segregated' we mean that they should, at least, be supported on separate supports and can therefore be disposed in separate layers above and/or below the other component or in the same layer. Alternatively, they can be coated on distinct areas of the same substrate 'brick' or on separate substrates disposed within the same system."

We have now found that it is possible to use a NO_x absorbent disposed downstream of a SCR catalyst to prevent NH₃ slip from an SCR catalyst and NO_x and NH₃ slip from the system as a whole. We have also found that it is possible to regenerate a NO_x absorbent in a manner set out in our WO 02/068099 by intentionally slipping a controlled amount of NH₃ past an SCR catalyst when the catalyst is above a pre-determined temperature.

According to a first aspect, the invention provides an exhaust system for a lean-burn internal combustion engine, which system comprising a nitrogen oxide (NO_x) absorbent, a catalyst for catalysing the selective catalytic reduction (SCR) of NO_x with a NO_x-specific reactant, first means for introducing a NO_x-specific reactant or a precursor thereof into an exhaust gas upstream of the SCR catalyst and means for controlling the introduction of the NO_x-specific reactant or precursor thereof into the exhaust gas via the first introducing means, wherein the SCR catalyst is disposed upstream of the NO_x absorbent and optionally with the NO_x absorbent, wherein the control means is arranged to introduce the NO_x-specific reactant or the precursor thereof to the first introducing means only when the SCR catalyst is active, whereby exhaustion of NO_x-specific reactant to atmosphere is substantially prevented.

In one embodiment, the activity of the SCR catalyst is determined by its temperature. In a further embodiment, the NO_x-specific reactant or the precursor thereof is introduced when the SCR catalyst is above a first pre-determined temperature.

5 In another embodiment, the NO_x absorbent is supported on a first substrate and the SCR catalyst is supported on a second substrate.

In another embodiment, the control means is arranged also to interrupt the supply of the NO_x-specific reactant or the precursor thereof to the exhaust gas when the SCR catalyst is hot
10 enough to oxidise NO_x-specific reactant to NO.

In one embodiment, the supply of NO_x-specific reactant or the precursor thereof is interrupted when the SCR catalyst is above a second pre-determined temperature.

15 According to a particular embodiment, the exhaust system comprises a second means for introducing the NO_x specific reactant or the precursor thereof, which second introducing means is disposed upstream of the NO_x absorbent and downstream of the SCR catalyst. Desirably, the control means is arranged also to supply the NO_x-specific reactant or the precursor thereof to the exhaust gas only when the NO_x absorbent is above a temperature at which NO_x regeneration is
20 effective and, optionally, to interrupt the supply of the NO_x-specific reactant or the precursor thereof to the exhaust gas when the NO_x absorbent is above a temperature at which NO_x storage is effectively limited.

In one embodiment, the temperature at which NO_x regeneration is effective is a third pre-determined temperature. By "NO_x regeneration is effective" herein, we mean, dependent on
25 conditions such as exhaust gas mass flow and lambda composition of the exhaust gas, temperatures of the NO_x absorbent above which it is possible to employ a practical NO_x absorbent regeneration strategy. For example, if in practice at a particular temperature, a second generation event would be required ten seconds after a first regeneration event in order to
30 recover NO_x absorbent capacity, such a strategy would be ineffective in that it would lead to increased fuel penalty and driveability issues.

In another embodiment, the temperature at which NO_x storage is effectively thermally limited is a fourth pre-determined temperature. By "effectively thermally limited" herein, we mean a temperature at which NO_x conversion using the NO_x absorbent is too low for practical application. This is because NO_x storage on the NO_x absorbent is reduced on account of the nitrate of the NO_x absorbent being thermally unstable.

We have observed that when a NO_x-specific reactant is introduced into an exhaust gas upstream of the SCR catalyst, certain reactants, such as NH₃, can become adsorbed to the SCR catalyst. Suitable control methods can make allowances for this and in certain arrangements the adsorption phenomenon can be useful, e.g. for supplying low levels of NO_x-specific reactant to the SCR catalyst below the SCR catalyst light off temperature to effect NO_x conversion. However, the adsorption can complicate control of supply of NO_x-specific reactant to the downstream NO_x absorbent to effect the process described in our WO 02/068099. Accordingly, in one embodiment, a second, separate NO_x-specific reactant introducing means is provided downstream of the SCR catalyst and the NO_x-specific reactant or precursor thereof is introduced via only this second introducing means when the SCR catalyst is below its light-off temperature. ("Light-off" is the temperature of a catalyst at which 50% conversion of a particular reaction is achieved.)

The first and second pre-determined temperatures will depend on the nature of the SCR catalyst (see below), and on other factors such as the composition and temperature range of the exhaust gases to be treated. However, generally the first predetermined temperature will be in the range from 100-600°C, preferably 150-500°C and most preferably 200-450°C and the second pre-determined temperature will be from 450-900°C, preferably 550-800°C and most preferably 650-700°C.

Like the SCR catalyst, the third and fourth pre-determined temperatures will depend on the nature of the NO_x absorbent (see below), and on other factors such as the composition and temperature range of the exhaust gases to be treated. However, generally the third pre-determined temperature will be from 75-200°C, preferably 100-175°C and most preferably 125-600°C and the fourth pre-determined temperature will be from 350-600°C, preferably 400-550°C and most preferably 450-500°C.

In another embodiment, the first pre-determined temperature can be the same as the third pre-determined temperature.

According to another embodiment, the exhaust system comprises a second SCR catalyst
5 disposed downstream of the NO_x absorbent.

According to a particular embodiment, the exhaust system comprises a catalyst for oxidising NO in the exhaust gas to NO₂ and a filter for collecting particulate matter in the exhaust gas for combustion in the NO₂ at up to 400°C. Such an arrangement is described in our
10 EP 0341832 or US-A-4,902,487 (the entire contents of which are incorporated herein by reference) and sold by Johnson Matthey plc as the CRT[®].

In one such embodiment, shown in Figure 1, the SCR catalyst is downstream of the filter. In a further embodiment, the SCR catalyst is carried by the filter. In another embodiment, both
15 the SCR catalyst and the NO_x absorbent are disposed on the filter.

In embodiments featuring the CRT[®], the NO_x-specific reactant can be injected upstream of the SCR catalyst, such as downstream of the filter as shown in Figure 1, between the CRT[®] oxidation catalyst and the filter or even upstream of the CRT[®] oxidation catalyst.
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This last arrangement can be useful to increase NO_x in the exhaust system for combusting particulate matter on the filter, as described in our WO 00/74823, the entire contents of which is incorporated herein by reference.

Control of the system is effected by the control means. In preferred embodiments, the
25 control means receives input from sensors positioned at appropriate points in the exhaust system to detect certain conditions therein. These can include the temperature of the NO_x absorbent and/or the SCR catalyst, and the NO_x composition of the exhaust gas. In order to control the system to prevent slip of NO_x specific reactant, suitable sensors can be used. These can be
30 positioned downstream of the SCR catalyst and/or downstream of the NO_x absorbent. In addition, or in the alternative, the control means can control the system in response to pre-determined settings in an engine speed/load map or in response to exhaust gas temperature.

Supply of NO_x-specific reactant can be continuous, semi-continuous, or periodic. In any case, the control means can be arranged to supply the NO_x-specific reactant or the precursor thereof intermittently at "spike" concentration, which can be useful for example in the method of regenerating the NO_x absorbent. Where supply of the NO_x-specific reactant or precursor thereof is periodic, each such period between supply events can be selected from between 1 second and 10 minutes.

According to a further aspect, the invention provides a lean-burn internal combustion engine including an exhaust system according to any preceding claim. According to one embodiment, the lean-burn engine is a diesel engine or a gasoline engine. We particularly prefer engines that can be run on fuel of less than 10 ppm sulfur.

According to a further aspect, the invention provides a process for treating NO_x in an exhaust gas from a lean-burn internal combustion engine, which engine including an exhaust system comprising a nitrogen oxide (NO_x) absorbent and a catalyst for catalysing the selective catalytic reduction (SCR) of NO_x with a NO_x-specific reactant wherein the SCR catalyst is disposed upstream of the NO_x absorbent and optionally with the NO_x absorbent, which process comprising, when the SCR catalyst is inactive, contacting the NO_x absorbent with insufficient NO_x-specific reactant to completely reduce the total NO_x stored on the NO_x absorbent, thereby to regenerate it, and, when the SCR catalyst is active, contacting it with sufficient NO_x-specific reactant to reduce NO_x in the exhaust gas to N₂, whereby exhaustion of NO_x-specific reactant to atmosphere is substantially prevented.

According to one embodiment, SCR catalyst activity is determined by its temperature relative to a first pre-determined temperature.

In another embodiment of the process, the NO_x-specific reactant for contacting the NO_x absorbent when the SCR catalyst is active does not contact said catalyst, for the reasons relating to adsorption of the NO_x-specific reactant to the SCR catalyst as explained above. That is, the NO_x-specific reactant can be introduced into the exhaust gas at a point downstream of the SCR catalyst.

In another embodiment, when said SCR catalyst is active, sufficient NO_x-specific reactant contacts the SCR catalyst to reduce NO_x in the exhaust gas to N₂ and slips past the SCR catalyst to contact the NO_x absorbent thereby to reduce stored NO_x, which process is controlled so that the slipped NO_x specific reactant is insufficient to completely reduce the total NO_x stored.

5 In this embodiment, the NO_x-specific reactant can be introduced into the exhaust gas upstream of the SCR catalyst and optionally downstream thereof also, as desired.

In the process according to the invention, the first pre-determined temperature can be from 100-600°C, preferably 150-500°C and most preferably 200-450°C, for example.

10 Process features for controlling NO_x absorbent regeneration may be similar to those set out in our WO 02/068099 and can include the features that at the end of regeneration, the NO_x absorbent contains 5 to 50% of the content of NO_x present at the start of regeneration; that regeneration is started when the absorbent contains 5 to 50% of the NO_x content at which NO_x slip takes place; that regeneration is controlled to stop at one of the following points: when NO_x-specific reactant is detected at a point part-way along the length of a substrate carrying the NO_x absorbent; in a system having two substrates carrying the solid absorbent in series, when NO_x-specific reactant is detected at a point between the substrates; when a level of NO_x content prescribed on the basis of pre-determined data in an engine speed/load map has been reached; 15 when a level of NO_x content established iteratively from an initial observation of NO_x-specific reactant slip has been reached; and that the NO_x-specific reactant is produced *in situ* from a precursor thereof, wherein the NO_x-specific reactant can be liberated from the precursor by a catalytic reaction.

25 The NO_x absorbent and any catalyst are suitably supported on a ceramic or metal honeycomb or foam substrate, the ceramic comprising one or more of alumina, silica, titania, cordierite, ceria, zirconia, zeolite or other, generally oxidic, material or a mixture or mixed oxide of any two or more thereof. Silicon carbide is another possible substrate material. The honeycomb or foam substrate preferably carries a washcoat and, in one or more layers thereon, 30 the active absorptive and/or catalytic material. The honeycomb has typically at least 50, for example 50-400, cells per square inch (cpsi) (7.8 – 62.0 cells cm⁻²), possibly more, e.g. up to 800 cpsi (124 cells cm⁻²), or up to 1200 cpsi (186 cells cm⁻²) if composed structurally of metal.

Generally the range 200-800 cpsi ($31 - 124 \text{ cells cm}^{-2}$) is preferred for the substrate comprising nitroxy salt or absorbent and any catalyst.

The NO_x absorbent may be selected from compounds of alkali metals, alkaline earth metals, rare earth metals, such as lanthanides, and transition metals, capable of forming nitroxy salt (nitrates and/or nitrites) of adequate stability in absorbing conditions and of reacting with NO_x -specific reactant in regenerating conditions. The "conditions" can include temperature of the gas and its redox state as expressed for example by its lambda; and/or adsorptive materials such as zeolites, carbons and high-area oxides.

Suitable alkali metals for use as NO_x absorbents can be at least one of potassium, or caesium; alkaline earth metals can be at least one of magnesium, calcium, strontium and barium; and lanthanides can be at least one of lanthanum, praseodymium, neodymium and cerium.

Absorbent compounds may be present (before NO_x absorption) as composite oxides, e.g. of alkaline earth metal and copper such as Ba-Cu-O or MnO_2 -BaCuO₂, possibly with added Ce oxide, or Y-Ba-Cu-O and Y-Sr-Co-O. (The oxides are referred to for simplicity, but in practice hydroxides, carbonates and carboxylates such as acetates are present, depending on the temperature and gas composition).

The NO_x absorbent can be associated with one or more platinum group metals (PGM) in order to effect certain processes useful to the procedure of storing NO_x thereon, or reducing released NO_x to N_2 . Such PGMs can be platinum, palladium and rhodium. In one embodiment, the NO_x trap PGM consists platinum alone (since any reduction function can be performed downstream), whereas in another embodiment it can include both platinum and rhodium.

The SCR catalysts for use in the present invention can be any known to the person skilled in the art, and, as mentioned above, choice of the SCR catalyst can depend on the conditions in which the catalyst will be required to work.

For example, Pt-based SCR catalysts can catalyse the reduction of NO_x with NH_3 at between about 175°C and about 250°C . Above 250°C the oxidation of NH_3 to NO predominates, thus losing its selectivity. Medium temperature vanadium-based catalysts e.g. $\text{V}_2\text{O}_5/\text{TiO}_2$ operate

in the temperature range between about 260°C and about 450°C. Again beyond this higher temperature, selectivity is lost and NO is produced. If the exposure temperature of the V₂O₅/TiO₂ catalyst exceeds a certain level, the active, high surface area anatase phase of TiO₂ irreversibly converts to rutile with a surface area of less than 10 m²/g. Normally this conversion takes place
5 above about 550°C, but catalysts may include stabilisers to increase their thermal durability. Some V₂O₅/TiO₂ catalysts have been reported to be thermally stable up to about 700°C. In certain situations, it can be useful to include at least one of tungsten and molybdenum with base metal-containing SCR catalysts.

10 Zeolites can operate in the temperature range of about 350°C to about 600°C. Zeolites suitable for use in catalysts according to the present invention include ZSM-5, mordenite, gamma-zeolite or beta-zeolite. They can comprise at least one metal or be metallised with at least one metal, which metal can be selected from one or more of Cu, Ce, Fe or Pt, and they can be ion-exchanged or impregnated.

15 Zeolites are characterised by their crystalline structure and SiO₂:Al₂O₃ ratio. For example, common mordenites have a ratio of about 10. When NO_x is present in the exhaust gas, zeolite-based SCR catalysts do not oxidise NH₃ to NO_x. Therefore, unlike Pt or V₂O₅ catalysts, their selectivity towards NO_x conversion continually increases with temperature. However,
20 zeolite-based catalysts can have stability problems when exposed to high temperatures in the presence of water vapour. At exposure temperatures above 600°C, in a high water content process stream, zeolites tend to deactivate by de-alumination whereby Al³⁺ ion in the SiO₂-Al₂O₃ framework migrates out of the structure. This leads to permanent deactivation and, in extreme cases, collapse of the crystalline structure.

25 Of course, zeolites are preferred where adsorption of NH₃ on a catalyst is required, see WO 99/55446.

30 Non-zeolite supports for any of metal-based SCR catalysts can include at least one of alumina, titania, silica, silica-alumina, ceria, zirconia, or a mixture or a mixed oxide of any two or more thereof.

As defined herein a "solid absorbent", "absorbent" and "absorbent material", "storage

component” are used interchangeably; By “NO_x absorbent” herein we refer to the optionally supported alkali metal, alkaline earth metal, rare-earth metal or transition metal *per se*, i.e. without additional catalytic metal; By “NO_x trap”, we refer to a substrate comprising the NO_x absorbent and any additional catalytic material e.g. PGM.

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The exhaust systems for the present invention are for IC engines and in particular to lean-burn IC engines. These can include gasoline lean-burn engines, such as gasoline direct injection (GDI) engines. It can also include diesel engines. In particular, diesel engines can include heavy-duty diesel engines (as defined in Europe by European Directives 88/77/EEC and 1999/96/EC).

10 In the USA, heavy-duty vehicles are defined by gross vehicle weight rating (GVWR) 8,500 lbs in the US Federal jurisdiction and above 14,000 lbs in California (model year 1995 and later). The heavy-duty diesel category is subdivided into light heavy-duty diesel engines: <8,500 lbs<LHDDE<19,500 lbs (14,000 lbs<LHDDE<19,500 in California, 1995+); medium heavy-duty diesel engines: 19,500 lbs<MHDDE<33,000 lbs; and heavy heavy-duty diesel engines
15 (including urban buses): HHDDE>33,000 lbs. Diesel engines can also be light-duty diesel engines as defined in Europe by European Directive 70/220/EEC, as amended by 93/59/EC and 98/69/EC. In the USA passenger vehicles, light light-duty trucks (LLDT), below 6000 lbs GVWR and heavy light-duty trucks (HLDT), above 6000 lbs are included in the light-duty diesel category.

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In order that the invention may be more fully understood, the following embodiment and Example are provided by way of illustration only and with reference to the accompanying drawings, in which:

25 Figure 1 is a schematic sectional view of an exhaust treatment system for lean-burn internal combustion engine;

Figure 2 is a graph comparing NH₃ slip in an exhaust system comprising SCR catalysts alone with that in an exhaust system comprising SCR and NO_x trap catalysts; and

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Figure 3 is a graph showing the gradual loss of NO_x conversion after NH₃ is turned off in an exhaust system comprising SCR and NO_x trap catalysts.

Referring to Figure 1, the system illustrated consists of single "can" 10, which is connected at 12 to the exhaust from a diesel engine (not shown) fuelled with diesel oil of under 10 ppm sulfur content. At the inlet end of can 10 is catalyst 14, which is a low temperature light-off oxidation catalyst supported on a 400 cells/in² (62.0 cells cm⁻²) ceramic honeycomb monolith. Catalyst 14 is designed to be capable of meeting emission regulations in relation to CO and HC for the engine and vehicle and also converts the NO in the starting gas to NO₂ at temperatures of up to 400°C at an efficiency of up to 70% or more.

The gas leaving catalyst 14 passes into soot filter 16, which is of the ceramic wall flow type and collects PM over 50nm. The NO₂ and surplus oxygen in the gas oxidise the soot at temperatures around 250°C as described in EP-A-0341832. The gas leaving filter 16 is passed over sparging spray injector 18, from which it receives intermittent supplies of NH₃ or NH₃ precursor via line 20 from high-pressure pump 22 under the control of computer 24. The gas leaving injector 18 passes into an SCR catalyst 30 comprising V₂O₅/TiO₂. Computer 24 receives data on engine running time and fuel used, on inlet gas temperature and composition and also, from sensor 26, on any slipped NO_x or NH₃. It is programmed in particular to recalculate the NH₃ feed time to a shorter period and/or at a lower rate if NH₃ is detected in gas leaving NO_x trap 28.

To facilitate replacement of NO_x trap 28, the can portion containing it may be linked to the main upper and lower portion of can 10 by flanges (not shown). If provision for SO_x absorption is to be made, bed 28 may be in two parts, one upstream of the other, the upstream part being the SO_x absorber. When the SO_x-absorbing part is due for replacement, it can be replaced by a fresh SO_x absorber and the can portion re-inserted with the unreplaced NO_x trap in the upstream position.

In the operation of the system two phases alternate. In the absorption phase the gas contains no NH₃ and the NO_x content of the absorber slowly increases as the NO_x reacts with the absorbent to give solid nitroxy salt. The absorption phase can occur when the SCR catalyst is below its light-off temperature for catalysing the reaction of NH₃ and NO_x, or when NO_x not converted over the SCR catalyst when the SCR catalyst is above said light-off temperature is present in the exhaust gas leaving the SCR catalyst. At the end of this phase the regeneration phase takes place, in which NH₃ is injected until part, suitably 50-90%, or possibly 5-50%, of the

nitroxy salt has been reacted. During regeneration the system slips substantially no NH_3 downstream of NO_x trap 28.

The regeneration phase can occur when the SCR catalyst is below or above its light-off temperature for catalysing the reaction of NH_3 and NO_x . When below SCR catalyst light-off temperature, the NH_3 or NH_3 precursor is metered so that substantially all of the NH_3 is consumed by the stored NO_x . When the SCR catalyst has lit off, NH_3 or NH_3 precursor is metered so that an above stoichiometric amount of NH_3 is present relative to NO_x over the SCR catalyst so that the SCR catalyst slips sufficient NH_3 to regenerate the NO_x trap. Stopping NH_3 slip past the SCR catalyst ends the regeneration phase, so that the absorption phase re-starts with absorption of residual NO_x from its end-level attained in the regeneration phase. Alternatively, no provision for intentional NH_3 slip is made, and the NO_x trap is regenerated "passively" by NH_3 slipped from the SCR catalyst. If the regeneration phase were continued for longer, for example up to complete decomposition of the nitroxy salt, the NH_3 content of the gas leaving absorber 28 would rise to its level at the start of regeneration, thus emitting NH_3 to atmosphere unless a clean-up catalyst were provided as in conventional continuous SCR.

Example

A cordierite monolith (5.66 inch diameter (14.4 cm), 6 inch (15.24 cm) long, 400 cells per square inch ($62.0 \text{ cells cm}^{-2}$) with 6 thousandths of an inch (0.15 mm) thick walls) was coated with a washcoat consisting of gamma alumina (surface area $120 \text{ m}^2 \text{ g}^{-1}$) in water made by slurring sufficient solid in de-ionised water to give a solids content of 45%. The slurry was poured onto the face and down the channels of the ceramic monolith. Excess slurry was removed from the channels by compressed air. The water was then removed from the washcoat by drying in a hot air flow (150°C). The dry coated monolith was then calcined at 500°C for an hour. The total washcoat loading on the coated monolith was 2.5 g in^{-3} (152.6 g l^{-1}). The coated monolith was then immersed in a platinum tetra-ammine solution for five minutes, removed, and excess solution removed by suction. The monolith was then dried in a hot air flow (150°C) and calcined at 500°C for an hour. The concentration of solution was chosen to give a platinum loading of 100 g ft^{-3} (3.53 g l^{-1}) was achieved on the monolith. Next the monolith was impregnated with an aqueous barium acetate solution. The monolith was immersed in the solution for five minutes, removed, and excess solution removed by suction. The monolith was dried in a hot air flow

(150°C) and calcined at 500°C for an hour. The concentration of solution was chosen such that a final barium loading of 800 g ft⁻³ (28.24 g l⁻¹) was achieved on the monolith.

Using analogous methods, SCR catalysts were prepared (on 5.66 inch (14.4 cm) diameter, 6 inch long (15.24 cm), 400 cells per square inch (62.0 cells cm⁻²) with 6/1000th inch (0.15 mm) thick walls), a commercially available V₂O₅/TiO₂ catalyst available from Johnson Matthey plc.

The final monoliths were mounted in a stainless steel can using standard procedures, and fitted in the exhaust gas system of 2.2 litre, 4 cylinder turbo-charged diesel engine. The engine was coupled to a dynamometer in the conventional manner. The engine and dynamometer were computer controlled to allow a range of different engine operating conditions to be selected. Exhaust emissions of HC, CO, NO_x, O₂, and CO₂ pre- and post-catalyst were measured with commercial gas analysers in the conventional way. NH₃ was measured using a tuned infra-red laser (AltOptronic), and N₂O was measured with a Unor (Germany) Instrument.

The engine was operated at 1200 rpm with a dynamometer load of 44 Nm, that resulted in a catalyst inlet exhaust gas temperature of 210°C. The catalyst inlet NO_x concentration was 120 ppm, and the engine was run steadily at this condition. NH₃ gas was injected into the exhaust upstream of the catalyst in a 10 minute long pulse, before being turned off for a further 10 minutes. This alternation was continued 5 times. The NH₃ gas level during the injection period was 120 ppm.

The experiment was conducted with two SCR catalysts alone in the exhaust as a baseline, and repeated with the NO_x trapping formulation behind the two SCR catalysts.

Baseline tests:

At this temperature/flow-rate/NH₃ injection level, a significant amount of NH₃ slip is possible from the SCR catalysts. This was desired in order to let NH₃ reaching the NO_x trapping catalyst (when present) in order to effect the method described in WO 02/068099 (the entire contents of which is incorporated herein by reference).

NH₃ slip gradually increased during the duration of the injection, it is believed, due to NH₃ storage within the SCR catalysts. After 10 minutes of injection, 53 ppm NH₃ slip occurred (shown Figure 1 for a typical 10 minute injection cycle). It was noted that with a period of > 10 minutes for NH₃ injection, more NH₃ slip occurred until a steady slip of 73 ppm NH₃ was reached. NO_x conversion due to the SCR reaction was 20% at these operating conditions.

Combined SCR and NO_x trapping catalyst tests:

When the NO_x trapping catalyst is present in the exhaust, significantly lower NH₃ slip occurs (see Figure 2), with a maximum of 20 ppm NH₃ slip occurring after 10 minutes of NH₃ injection. This indicates that the NO_x trapping catalyst can be used to prevent NH₃ slip in an SCR system.

Further, as demonstrated in WO 02/068099, this NO_x trap formulation can store NO_x at 210°C, and regenerate when exposed to NH₃. In the current example, 80% of the engine out NO_x is slipping through the SCR catalysts, as they are not active enough for the SCR reaction under these conditions. Some of this NO_x can be stored on the NO_x trapping catalyst, and this NO_x can be regenerated with the NH₃ slip.

Figure 3 shows the NO_x conversion after NH₃ injection. Clearly, when NH₃ is turned off, there is a gradual decrease in NO_x conversion caused by a combination of NO_x storage and, we believe, SCR reaction with stored NH₃ as we describe in WO 03/054364 (incorporated herein by reference). This effect was repeated multiple times.

CLAIMS:

1. An exhaust system for a lean-burn internal combustion engine, which system comprising a nitrogen oxide (NO_x) absorbent, a catalyst for catalysing the selective catalytic reduction (SCR) of NO_x with a NO_x -specific reactant, first means for introducing a NO_x -specific reactant or a precursor thereof into an exhaust gas upstream of the SCR catalyst and means for controlling the introduction of the NO_x -specific reactant or precursor thereof into the exhaust gas via the first introducing means, wherein the SCR catalyst is disposed upstream of the NO_x absorbent and optionally with the NO_x absorbent, wherein the control means is arranged to introduce the NO_x -specific reactant or the precursor thereof to exhaust gas via the first introducing means only when the SCR catalyst is active, whereby exhaustion of NO_x -specific reactant to atmosphere is substantially prevented.
2. An exhaust system according to claim 1, wherein the SCR catalyst activity is determined by its temperature.
3. An exhaust system according to claim 2, wherein the control means introduces the NO_x -specific reactant or the precursor thereof, when the SCR catalyst is above a first pre-determined temperature.
4. An exhaust system according to claim 1, 2 or 3, wherein the control means is arranged to interrupt the supply of the NO_x -specific reactant or the precursor thereof to the exhaust gas when the SCR catalyst is hot enough to oxidise NO_x -specific reactant to NO .
5. An exhaust system according to claim 1, wherein the supply of NO_x -specific reactant or the precursor thereof is interrupted when the SCR catalyst is above a second pre-determined temperature.
6. An exhaust system according to any of claims 1 to 5, comprising a second means for introducing the NO_x -specific reactant or the precursor thereof, which second introducing means is disposed upstream of the NO_x absorbent and downstream of the SCR catalyst.

7. An exhaust system according to claim 6, wherein the control means is arranged to supply the NO_x-specific reactant or the precursor thereof to the exhaust gas only when the NO_x absorbent is above a temperature at which NO_x regeneration is effective.
- 5 8. An exhaust system according to claim 7, wherein the temperature at which NO_x regeneration is effective is a third pre-determined temperature.
9. An exhaust system according to claim 7 or 8, wherein the control means is arranged to interrupt the supply of the NO_x-specific reactant or the precursor thereof to the exhaust
10 gas when the NO_x absorbent is above a temperature at which NO_x storage is effectively thermally limited.
10. An exhaust system according to claim 9, wherein the temperature at which NO_x storage is effectively thermally limited is a fourth pre-determined temperature.
15
11. An exhaust system according to claim 3, wherein the first pre-determined temperature is from 100-600°C, preferably 150-500°C and most preferably 200-450°C.
12. An exhaust system according to claim 5, wherein the second pre-determined temperature
20 is from 450-900°C, preferably 550-800°C and most preferably 650-700°C.
13. An exhaust system according to claim 8 or 11, wherein the third pre-determined temperature is from 75-200°C, preferably 100-175°C and most preferably 125-600°C.
- 25 14. An exhaust system according to any claim 13, wherein the first pre-determined temperature is the same as the third pre-determined temperature.
15. An exhaust system according to claim 10, wherein the fourth pre-determined temperature is from 350-600°C, preferably 400-550°C and most preferably 450-500°C.
30
16. An exhaust system according to any preceding claim comprising a catalyst for oxidising NO in the exhaust gas to NO₂ and a filter for collecting particulate matter in the exhaust gas for combustion in the NO₂ at up to 400°C.

17. An exhaust system according to claim 16, wherein the filter is upstream of the SCR catalyst.
- 5 18. An exhaust system according to claim 16, wherein the SCR catalyst is disposed on the filter.
19. An exhaust system according to claim 16 or 18, wherein the NO_x absorbent is disposed on the filter.
- 10 20. An exhaust system according to any preceding claim, further comprising a second SCR catalyst disposed downstream of the NO_x absorbent.
- 15 21. An exhaust system according to any preceding claim, including at least one sensor for detecting a concentration of the NO_x-specific reactant or the precursor thereof in the exhaust gas positioned downstream of the SCR catalyst.
- 20 22. An exhaust system according to any preceding claim, including at least one sensor for detecting a concentration of the NO_x specific reactant or the precursor thereof in the exhaust gas positioned downstream of the NO_x absorbent.
- 25 23. An exhaust system according to claim 21 or 22, wherein the control means regulates the supply of the NO_x-specific reactant or the precursor thereof in response to the detected concentration of the NO_x-specific reactant or the precursor thereof in the exhaust gas, thereby to reduce slip of the NO_x-specific reactant or the precursor thereof.
- 30 24. An exhaust system according to any preceding claim, wherein the control means regulates the supply of the NO_x-specific reactant or the precursor thereof in response to exhaust gas temperature.
25. An exhaust system according to any preceding claim, wherein the control means regulates the supply of the NO_x-specific reactant or the precursor thereof in response to pre-determined setting in an engine speed/load map.

26. An exhaust system according to any preceding claim, wherein the control means is arranged to supply the NO_x-specific reactant or the precursor thereof intermittently and at "spike" concentration.
- 5 27. An exhaust system according to claim 26, wherein each period between supply of the NO_x specific reactant or precursor thereof is selected from the range from 1 second to 10 minutes.
- 10 28. A lean-burn internal combustion engine including an exhaust system according to any preceding claim.
29. An engine according to claim 28, wherein it is a diesel engine or a gasoline engine.
- 15 30. A process for treating NO_x in an exhaust gas from a lean-burn internal combustion engine, which engine including an exhaust system comprising a nitrogen oxide (NO_x) absorbent and a catalyst for catalysing the selective catalytic reduction (SCR) of NO_x with a NO_x-specific reactant wherein the SCR catalyst is disposed upstream of the NO_x absorbent and optionally with the NO_x absorbent, which process comprising, when the
- 20 SCR catalyst is inactive, contacting the NO_x absorbent with insufficient NO_x-specific reactant to completely reduce the total NO_x stored on the NO_x absorbent, thereby to regenerate it, and, when the SCR catalyst is active, contacting it with sufficient NO_x-specific reactant to reduce NO_x in the exhaust gas to N₂, whereby exhaustion of NO_x-specific reactant to atmosphere is substantially prevented.
- 25 31. A process according to claim 30, wherein SCR catalyst activity is determined by its temperature relative to a first predetermined temperature.
32. A process according to claim 30 or 31, wherein the NO_x-specific reactant for contacting the NO_x absorbent when the SCR catalyst is inactive does not contact said catalyst.
- 30 33. A process according to claim 30, 31 or 32, wherein, when said SCR catalyst is active, sufficient NO_x-specific reactant contacts the SCR catalyst to reduce NO_x in the exhaust

gas to N_2 and slips past the SCR catalyst to contact the NO_x absorbent thereby to reduce stored NO_x , which process is controlled so that the slipped NO_x -specific reactant is insufficient to completely reduce the total NO_x stored.

- 5 34. An exhaust system according to claim 31, wherein the first pre-determined temperature is from 100-600°C, preferably 150-500°C and most preferably 200-450°C.
- 10 35. A process according to any of claims 30 to 34, wherein at the end of regeneration, the NO_x absorbent contains 5 to 50% of the content of NO_x present at the start of regeneration.
36. A process according to any of claims 30 to 35, wherein regeneration is started when the absorbent contains 5 to 50% of the NO_x content at which NO_x slip takes place.
- 15 37. A process according to any of claims 30 to 36, wherein regeneration is controlled to stop at one of the following points:
when NO_x -specific reactant is detected at a point part-way along the length of a substrate carrying the NO_x absorbent;
in a system having two substrates carrying the solid absorbent in series, when NO_x -
20 specific reactant is detected at a point between the substrates;
when a level of NO_x content prescribed on the basis of pre-determined data in an engine speed/load map has been reached;
when a level of NO_x content established iteratively from an initial observation of NO_x -
specific reactant slip has been reached.
- 25 38. A process according to any of claims 30 to 37, wherein the time period of absorption and/or regeneration is in the range of from 1 second to 10 minutes.
- 30 39. A process according to any of claims 30 to 38, wherein the NO_x absorbent is supported on a first substrate and the SCR catalyst is supported on a second substrate.
40. A process according to any of claims 30 to 39, wherein the NO_x specific reactant is produced *in situ* from a precursor thereof.

41. A process according to claim 40, further including a step of catalytically reacting the precursor to provide NO_x specific reactant.
- 5 42. A process according to any of claims 30 to 41, wherein the starting gas is the exhaust of a lean-burn, especially diesel, internal combustion engine.

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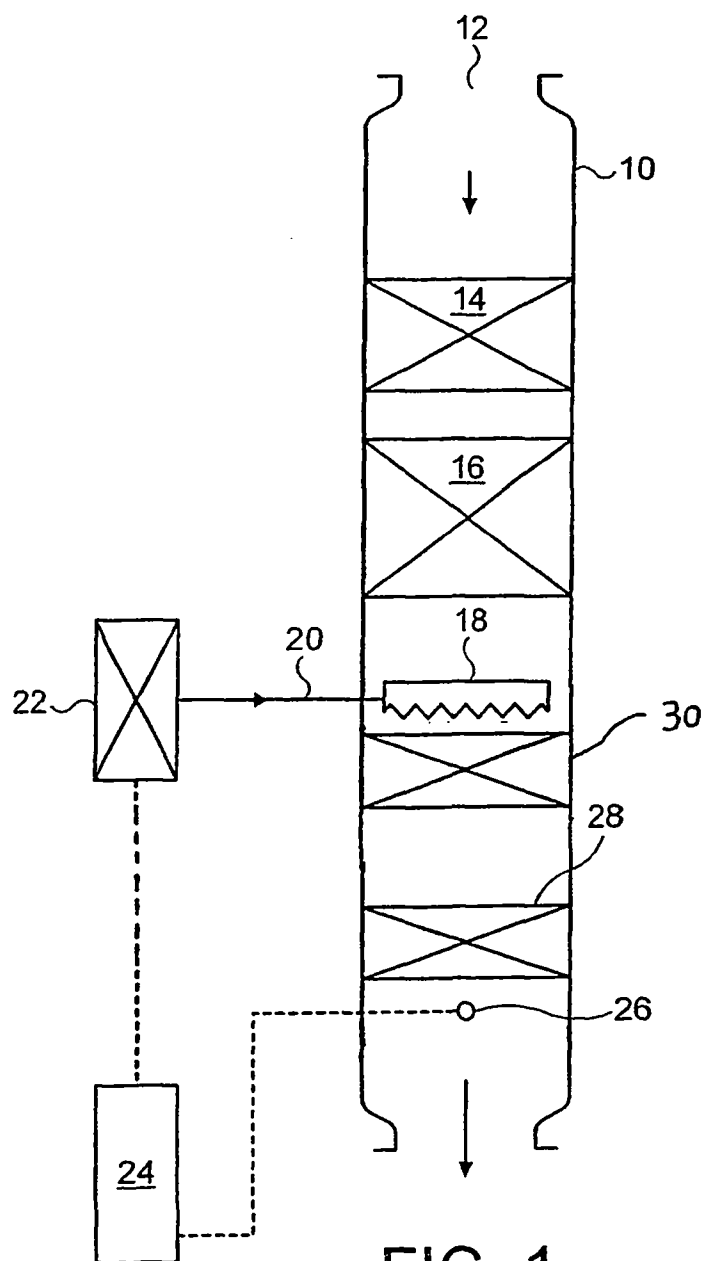


FIG. 1

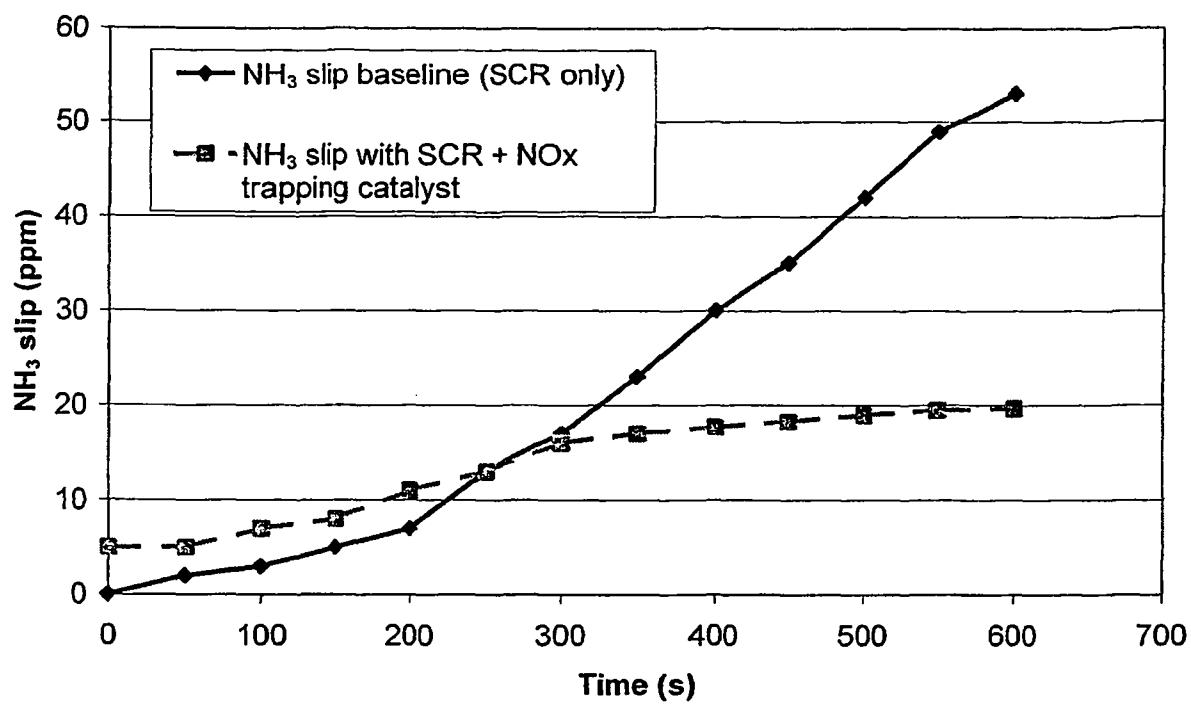
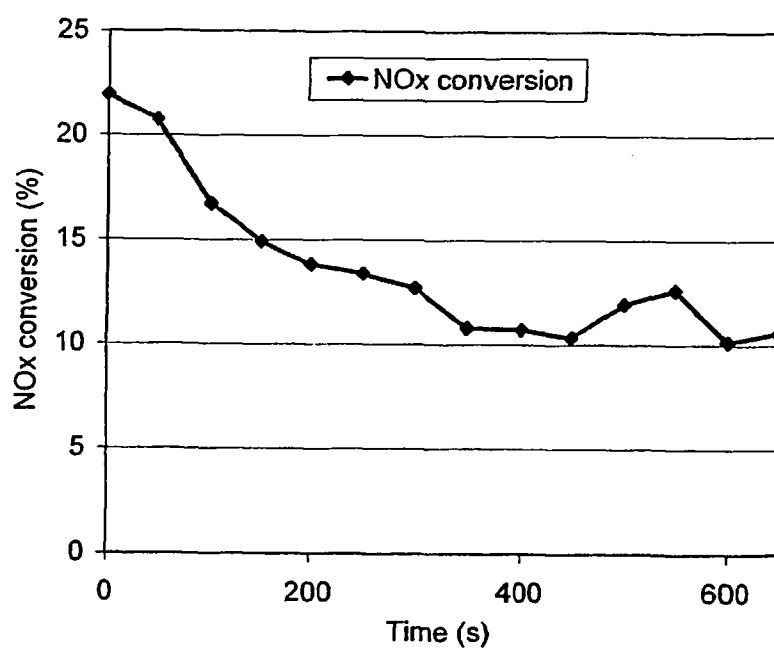


Figure 2

**Figure 3**