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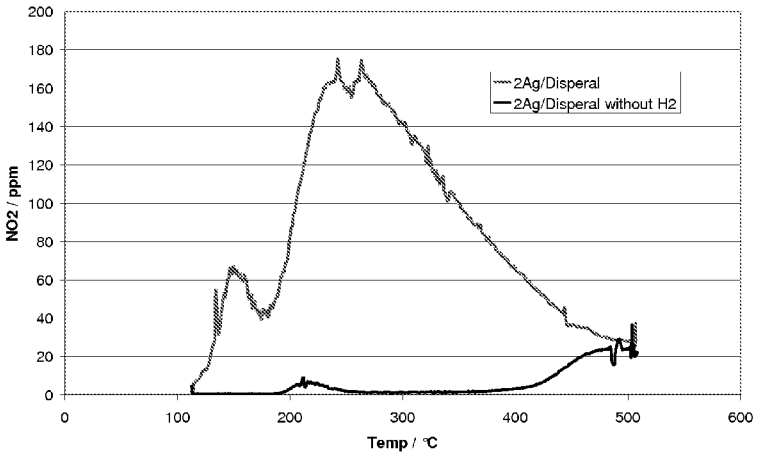
(54) **Title**: SYSTEM AND METHOD FOR GENERATING NO2

Figure 1 **NO2 formation over Ag/Al2O3 catalysts**



(57) **Abstract**: An exhaust system for an internal combustion engine comprises a catalyst chamber, a silver catalyst positioned within the catalyst chamber and means to supply a quantity of hydrogen to the catalyst chamber, wherein the silver catalyst is disposed in one of the following arrangements: (i) the silver catalyst is deposited on a soot filter or as a component of a Catalytic Soot Filter; (ii) the silver catalyst is disposed upstream of a soot filter; and/or (iii) the silver catalyst is disposed upstream of a selective catalytic reduction catalyst, and wherein $N0_2$ is generated by contacting the silver catalyst with hydrogen.

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SYSTEM AND METHOD FOR GENERATING NO_2

The present invention concerns improvements in catalytic processes, and more particularly concerns improvements in the oxidation of nitric oxide (also known as nitrogen monoxide or "NO").

It is known that NO present in a gas stream such as an exhaust gas from an internal combustion engine can be oxidised to NO_2 by passing the exhaust gas stream over a platinum catalyst. This Pt-catalysed reaction has been used in a number of systems used commercially for exhaust gas aftertreatment. In particular, the first successful apparatus for removing combustion soot from diesel exhausts, the CRT® system developed and licensed by Johnson Matthey, uses NO_2 for the low temperature oxidation of soot. (The principle of the CRT® system is disclosed in EP 341832, the entire contents of which are incorporated herein by reference). The NO_2 required is formed by passing the lean exhaust gas from the diesel engine, which contains excess oxygen and NO, over a Pt catalyst. That is commercial CRT® system comprises a platinum-based oxidation catalyst coated on a flow-through monolith substrate and downstream thereof a soot filter, preferably a wall-flow filter. The filter can be catalysed with a catalyst for reducing the combustion temperature of trapped soot, in which case the catalysed filter is often referred to as a Catalysed Soot Filter (CSF).

Although there were suggestions prior to the CRT® system to catalyse a filter in an effort to reduce the soot combustion temperature, it seems what may be termed "the CRT® reaction", i.e. $NO_2 + C$ (i.e. soot) $\rightarrow NO + CO$, was not discovered or appreciated because of the high sulphur content in fuel at the time. Subsequently, the CRT® reaction has been adapted and utilised extensively in recent years to provide a variety of approaches and systems for exhaust gas aftertreatment. One example of this approach is in the CSF (Catalysed Soot Filter), which has been found effective to remove particulate from the exhaust gases from light duty diesel engines. That is, a catalytic Pt coating is applied to a wall-flow filter which is disposed in the exhaust gas line. The filter surface generally has further catalysts to promote the soot oxidation reaction. The CSF tends to operate by accumulating soot when the vehicle is operated at low speeds, such as in an urban environment. The exhaust gas temperatures under low loads/low speeds are too low effectively to generate NO_2 or to cause the oxidation

of soot by the CRT ® reaction. The CSF may be regenerated to remove the accumulation of soot by running the engine at higher speeds and/or under higher load or by engine management to create higher temperatures within the CSF.

Whilst the CSF is effective, essentially it requires coatings containing expensive Pt for the purpose of generating NO_2.

Another exhaust gas aftertreatment is SCR (Selective Catalytic Reduction). Several commercial applications use ammonia, generated from a urea solution, to reduce NOx (nitrogen oxides) to nitrogen (N_2). An alternative SCR system that has the attraction that no separate on-board storage of urea reductant is required, is HC-SCR (HydroCarbon Selective Catalytic Reduction) in which hydrocarbon, which is already present on-board in the form of fuel, has been found to have the ability to chemically reduce NOx. The necessary hydrocarbon may be supplied to the gas stream entering the SCR catalyst in a number of ways, including by post-combustion injection into the cylinders, and by injection of fuel into the exhaust gas stream. Several SCR catalysts have been studied for HC-SCR, including catalysts based on silver, such as Ag on alumina.

One exhaust system which combines the commercial CRT® system and a SCR catalyst is disclosed in EP 1054722, the entire contents of which is incorporated herein by reference, wherein the CRT® device is disposed upstream of a means for injecting reductant into the exhaust gas and the SCR catalyst (in that order). The system described in EP 1054722 is known by the registered trademark "SCRT®". From EP 1054722 and other publications it is known that an approximately 1:1 NO_2:NO mixture in gas entering a SCR catalyst beneficially improves the rate of NO_x reduction, compared to the same process practised on an exhaust gas wherein NO_x is present entirely as NO or particularly wherein NO_x is present entirely as NO_2. In order to take advantage of this phenomenon, EP 1054722 discloses the oxidation of NO to NO_2 thereby to provide a mixture of NO and NO_2 at the SCR catalyst inlet.

There is a need for alternative catalysts and methods for generating NO_2 for improving downstream processes, desirably including the reduction or elimination of Pt in the catalyst.

Accordingly, the present invention provides a process for the generation of NO_2 by oxidation of NO in the presence of a catalyst, comprising the step of passing NO in the presence of a gaseous oxidising agent over a silver catalyst, in the presence of a quantity of hydrogen, wherein:

(i) the silver catalyst is deposited on a soot filter or as a component of a Catalytic Soot Filter;

(ii) the silver catalyst is disposed upstream of a soot filter; and/or

(iii) the silver catalyst is disposed upstream of a selective catalytic reduction catalyst.

The invention also provides an exhaust system for an internal combustion engine, which system comprising a catalyst chamber, a silver catalyst positioned within the catalyst chamber and means to supply a quantity of hydrogen to the catalyst chamber, wherein the silver catalyst is disposed in one of the following arrangements:

(i) the silver catalyst is deposited on a soot filter or as a component of a Catalytic Soot Filter;

(ii) the silver catalyst is disposed upstream of a soot filter; and/or

(iii)the silver catalyst is disposed upstream of a selective catalytic reduction catalyst,

and wherein NO_2 is generated by contacting the silver catalyst with hydrogen.

In one embodiment, therefore, the system of feature (iii) comprises means for injecting a nitrogenous reductant between the silver catalyst and the SCR catalyst and a source of nitrogenous reductant.

It will be appreciated that the combination of all of features (i), (ii) and (iii) results in a system having the system "architecture" of the EP 1504722, whereas the combination of features (i) and (ii), for example, provides the commercial CRT® embodiment, wherein the filter, e.g. a wall-flow filter, is also catalysed.

It will be recognised that to supply a particularly active reducing agent in the form of hydrogen to assist in an oxidation reaction is counter-intuitive, and that the results are surprising.

Desirably, the silver catalyst is silver on an alumina support. Our initial studies indicate that the silver is desirably present as dispersed silver particles or Ag_2O clusters, but in the preferred catalysts, the particles are too small to be seen by Transmission Electron Microscopy. Larger silver particles are not particularly active. Most desirably, the alumina is in the form of boehmite or gamma alumina. Preferably, the silver is present in an amount below 10% by weight of the alumina, more preferably below 5wt%, and most preferably an amount of approximately 2wt%. Suitable silver catalysts may be prepared in known manner. Suitable alumina supports are commercially available, such as "Disperal®" (Sasol) and "SCF140" (Condea).

The mixture of NO and gaseous oxidising agent is conveniently an exhaust stream from an internal combustion engine. If the quantity of oxidising agent is too low for the desired quantity of reaction, for example the exhaust stream is from a stoichiometric engine, supplementary air may be added. Conveniently, the gas mixture is from a lean burn engine such as a diesel engine.

Early studies indicate that the quantity of hydrogen suitable for the present invention is in the region of 200-5000ppm of the total gas present in the catalyst chamber, such as 500-3000ppm or 750-2000ppm, but is conveniently around 1000ppm. The hydrogen may conveniently be supplied to the gas stream before it enters the catalyst chamber, although other ways of injecting or admixing the hydrogen may be considered. It will be noted that such quantities of hydrogen are relatively small and even where present the exhaust gas remains lean overall.

The formation of NO_2 in the present invention is, as with every catalytic reaction, temperature sensitive, although the method may be used over a usefully broad temperature range of approximately 150°C to 450°C. Desirably, the method operates at 200°C to 400°C, especially in the range 220°C to 300°C.

The present invention offers a useful control over the generation of NO_2, because NO_2 is produced in the present invention mainly or exclusively when hydrogen is supplied to the catalyst chamber. Existing Pt catalysts can generate

relatively high tailpipe NO_2 levels, which may present the engine/vehicle designer with difficulties in meeting required levels of regulated emissions. So, for example, the California Air Resources Board (CARB) has proposed that a maximum of 20% of tailpipe NO_x of the relevant drive cycle is emitted as NO_2. NO_2 is toxic and can cause headaches, dizziness and nausea in low doses. It also has an objectionable "swimming pool"-type chlorine smell.

The means for supplying the hydrogen in the present invention may therefore provide for continuous hydrogen supply, but in at least some applications, the means may desirably provide for intermittent supply, e.g. by a pre-programmed control means, desirably in response to engine operating conditions which are known to be associated with increased soot formation, or in response to sensed accumulation of soot on a filter by feedback control, e.g. again controlled by pre-programmed means. This may be achieved using known technology.

Initial applications of the invention are expected to be related to the CRT® reaction. Thus, the silver catalyst may be incorporated in a CSF, to replace all or a proportion of the Pt catalyst normally present. The CSF is generally of single "brick" design, that is to say, a single filter substrate which is coated with all necessary catalytic coatings, including zoned or homogeneous arrangements. Alternative designs, such as the conventional CRT® system, or a SCRT® system, in which a filter (which may itself be catalysed to reduce the soot oxidation temperature) is separate from the NO_2 generating catalyst, may also benefit from the present invention, i.e. in order from upstream to downstream, the exhaust system comprises an oxidation catalyst, a filter e.g. a wall-flow filter, an injector for ammonia or a precursor thereof, such as urea and a SCR catalyst (see EP 1054722, the entire contents of which is incorporated herein by reference).

The invention is expected to be applied initially to so-called LDD (light duty diesel) engines, which are used widely in personal automobiles and light commercial applications. It is expected to be subsequently applied to heavy duty diesel (HDD) applications, such as trucks, buses and stationary sources. The invention should not be considered as limited to diesel applications, however, and gasoline engine or other applications may be developed in the future.

The required hydrogen may be supplied from a variety of sources. It may be convenient, for example, to produce hydrogen by fuel reforming or by exhaust gas reforming. The on-board reforming of fuel or exhaust gas is currently under active development by commercial and academic teams. The reformate gas may, in certain cases, be used directly without purification or separation, in the present invention.

It is conventional to deposit an emission control catalyst on a flow-through substrate or on a filter. Conventional catalyst substrates and filters may be used to support the silver catalyst in the present invention, and conventional deposition techniques may be used.

Whilst the present invention requires a silver catalyst as an essential requirement, the catalyst may include other components which assist or do not significantly degrade the performance of the silver catalyst.

The present invention will now be illustrated with reference to tests carried out using a synthetic diesel exhaust, and to the sole accompanying Figure, which is a graph wherein NO_2 formation is plotted as a function of temperature using a synthetic diesel exhaust gas with and without hydrogen and a Ag/Al_2O_3 catalyst.

In a laboratory rig, 0.4g of catalyst is held in a catalyst chamber with a test gas supply at a flow rate of 2 litre/min. The gas leaving the catalyst chamber is analysed using conventional equipment. Catalyst bed temperatures are measured at the bed inlet. The catalyst bed is heated by preheating the feed gas.

A model, (i.e. synthetic) LDD exhaust gas containing 12% O_2, 1000ppm CO, 300ppm NO, 300ppm C_3H_6, 4.5% H_2O, 4.5% CO_2, balance nitrogen is passed over the catalyst bed at various catalyst temperatures, and the quantity of NO_2 in the outlet gas is measured. The results are shown in Figure 1, for the same catalyst of 2wt% Ag deposited on Disperal alumina, both with the standard gas and for the standard gas with 1000ppm H_2 added.

It can be seen from Figure 1 that without H_2, negligible NO_2 is produced until at about 450°C, approximately 20ppm is produced. However, the addition of H_2 has an immediate and dramatic effect, peaking at approximately 160ppm at a temperature of approximately 250°C.

Subsequent tests have been carried out by varying the loading of silver from 2 to 8wt%, and by varying the catalyst support. The best results have been observed with over 200 ppm peak NO_2 output at approximately 225°C, using 2wt% silver on SCF140 gamma alumina.

CLAIMS:

1. An exhaust system for an internal combustion engine, which system comprising a catalyst chamber, a silver catalyst positioned within the catalyst chamber and means to supply a quantity of hydrogen to the catalyst chamber, wherein the silver catalyst is disposed in one of the following arrangements:

(i) the silver catalyst is deposited on a soot filter or as a component of a Catalytic Soot Filter;

(ii) the silver catalyst is disposed upstream of a soot filter; and/or

(iii) the silver catalyst is disposed upstream of a selective catalytic reduction catalyst,

and wherein NO_2 is generated by contacting the silver catalyst with hydrogen.

2. A system according to claim 1, feature (iii), comprising means for injecting a nitrogenous reductant between the silver catalyst and the SCR catalyst and a source of nitrogenous reductant.

3. A system according to claim 1 or 2, wherein the silver catalyst is silver deposited on alumina.

4. A system according to claim 3, wherein the alumina is gamma-alumina or boehmite.

5. A system according to claim 3 or 4, wherein the silver catalyst comprises silver in an amount of below 5% by weight.

6. A system according to any preceding claim, wherein the means to supply hydrogen comprises a reformer for fuel or for exhaust gas.

7. A system according to any preceding claim, wherein the means for supplying hydrogen is controlled, when in use, to supply hydrogen intermittently.

8. A system according to claim 7, wherein the intermittent supply of hydrogen is controlled, when in use, in response to engine operating conditions or in response to sensed accumulation of soot on a filter.

9. A process for the generation of NO_2 by oxidation of NO in the presence of a catalyst, comprising the step of passing NO in the presence of a gaseous oxidising agent over a silver catalyst, in the presence of a quantity of hydrogen, wherein

(i) the silver catalyst is deposited on a soot filter or as a component of a Catalytic Soot Filter;

(ii) the silver catalyst is disposed upstream of a soot filter; and/or

(iii) the silver catalyst is disposed upstream of a selective catalytic reduction catalyst.

10. A process according to claim 9, wherein the NO in the presence of a gaseous oxidising agent comprises the exhaust gas from an internal combustion engine.

11. A process according to claim 9 or 10, wherein the hydrogen is present in an amount in the region of 200-5000 ppm of the total gas present.

12. A process according to claim 9, 10 or 11, wherein the catalyst temperature is from 200 to 400° C.

13. A process according to claim 9, 10, 11 or 12, wherein the supply of hydrogen is intermittent.

14. A process according to claim 13, wherein the intermittent supply of hydrogen is in response to engine operating conditions or to sensed accumulation of soot on a filter.

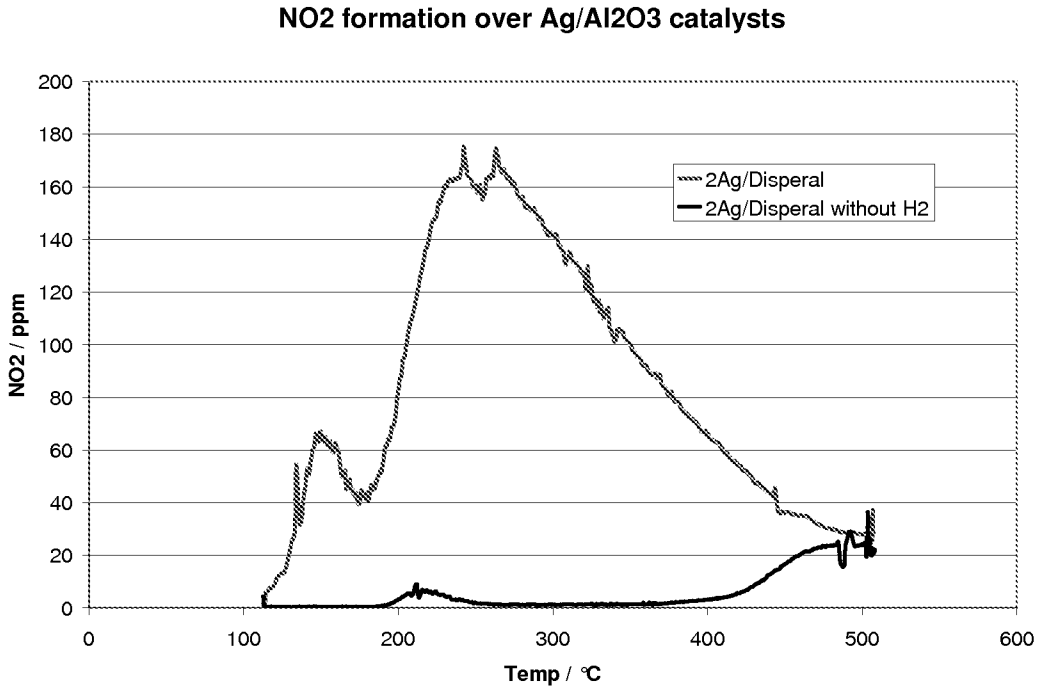
NO2 formation over Ag/Al2O3 catalysts
NO2 / ppm
Temp / ℃
2Ag/Disperal
2Ag/Disperal without H2
0
20
40
60
80
100
120
140
160
180
200
0
100
200
300
400
500
600

Figure 1

INTERNATIONAL SEARCH REPORT

International application No
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A. CLASSIFICATION OF SUBJECT MATTER
INV. B01D53/94 B01J23/50 F01N3/20 F01N3/10
ADD.

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 practicable, search terms used)
EPO-Internal, WPI Data

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
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