ABSTRACT

A system for NOx reduction in combustion gases, especially from diesel engines, incorporates an oxidation catalyst to convert at least a portion of NO to NO2, particulate filter, a source of reductant such as NH3 and an SCR catalyst and methods for operating such a system are disclosed. Considerable improvements in NOx conversion and soot reduction are observed even at relatively low operating temperatures.
Fig. 3

Temperature (°C)

NOx Conversion (%)
Fig. 4

- CO: 67.09
- HC: 66.77
- Particulates: 69.57
- NOx: 81.06

Conversion (%)
CATALYTIC REDUCTION OF NOX

CROSS REFERENCE TO RELATED APPLICATIONS


SUMMARY OF THE INVENTION

[0002] The present invention concerns improvements in selective catalytic reduction of NOx in waste gas streams such as diesel engine exhausts or other lean exhaust gases such as from gasoline direct injection (GDI).

BACKGROUND OF THE INVENTION

[0003] The technique named SCR (Selective Catalytic Reduction) is well established for industrial plant combustion gases, and may be broadly described as passing a hot exhaust gas over a catalyst in the presence of a nitrogenous reductant, especially ammonia or urea. This is effective to reduce the NOx content of the exhaust gases by about 20-25% at about 250°C, or possibly rather higher using a platinum catalyst, although platinum catalysts tend to oxidise NH3 to NOX during higher temperature operation. We believe that SCR systems have been proposed for NOX reduction for vehicle exhausts, especially large or heavy duty diesel engines, but this does require on-board storage of such reductants, and is not believed to have met with commercial acceptability at this time.

[0004] We believe that if there could be a significant improvement in performance of SCR systems, they would find wider usage and may be introduced into vehicular applications. It is an aim of the present invention to improve significantly the conversion of NOX in a SCR system, and to improve the control of other pollutants using a SCR system.

BRIEF DESCRIPTION OF THE DRAWINGS

[0005] FIG. 1 is a graph plotting percentage NOX conversion against temperature resulting from Test 1.

[0006] FIG. 2 is a graph plotting percentage NOX conversion against temperature resulting from Test 2.

[0007] FIG. 3 is a graph plotting percentage NOX conversion against temperature resulting from Test 3.

[0008] FIG. 4 is a bar graph showing percentage conversion of pollutants [NOx, particulates, hydrocarbons (HC) and carbon monoxide (CO)] resulting from Test 4.

DETAILED DESCRIPTION OF THE INVENTION

[0009] Accordingly, the present invention provides an improved SCR catalyst system, comprising in combination and in order, an oxidation catalyst effective to convert NO to NO2, a particulate filter, a source of reductant fluid and downstream of said source, an SCR catalyst.

[0010] The invention further provides an improved method of reducing NOx in gas streams containing NO and particulates comprising passing such gas stream over an oxidation catalyst under conditions effective to convert at least a portion of NO in the gas stream to NO2 removing at least a portion of said particulates, adding reductant fluid to the gas stream containing enhanced NOx to form a gas mixture, and passing the gas mixture over an SCR catalyst.

[0011] Although the present invention provides, at least in its preferred embodiments, the opportunity to reduce very significantly the NOx emissions from the lean (high in oxygen) exhaust gases from diesel and similar engines, it is to be noted that the invention also permits very good reductions in the levels of other regulated pollutants, especially hydrocarbons and particulates.

[0012] The invention is believed to have particular application to the exhausts from heavy duty diesel engines, especially vehicle engines, e.g., truck or bus engines, but is not to be regarded as being limited thereto. Other applications might be LDD (light duty diesel), GDI, CNCG (compressed natural gas) engines, ships or stationary sources. For simplicity, however, the majority of this description concerns such vehicle engines.

[0013] We have surprisingly found that a “pre-oxidising” step, which is not generally considered necessary because of the low content of CO and unburnt fuel in diesel exhausts, is particularly effective in increasing the conversion of NOX to NO2 by the SCR system. We also believe that minimising the levels of hydrocarbons in the gases may assist in the conversion of NO to NOX. This may be achieved catalytically and/or by engine design or management. Desirably, the NOX/NO ratio is adjusted according to the present invention to the most beneficial such ratio for the particular SCR catalyst and CO and hydrocarbons are oxidized prior to the SCR catalyst. Thus, our preliminary results indicate that for a transition metal/zeolite SCR catalyst it is desirable to convert all NO to NOX whereas for a rare earth-based SCR catalyst, a high ratio is desirable providing there is some NOX and for other transition metal-based catalysts gas mixtures are notably better than either substantially only NO or NOX. Even more surprisingly, the incorporation of a particulate filter permits still higher conversions of NOX.

[0014] The oxidation catalyst may be any suitable catalyst, and is generally available to those skilled in art. For example, a Pt catalyst deposited upon a ceramic or metal through-flow honeycomb support is particularly suitable. Suitable catalysts are, e.g., Pt/Al2O3 catalysts, containing 1-150 Pt/Pt (0.035-5.3 g Pt/litre) catalyst volume depending on the NOX/NO ratio required. Such catalysts may contain other components providing there is a beneficial effect or at least no significant adverse effect.

[0015] The source of reductant fluid conveniently uses existing technology to inject fluid into the gas stream. For example, in the tests for the present invention, a mass controller was used to control supply of compressed NH3, which was injected through an annular injector ring mounted in the exhaust pipe. The injector ring had a plurality of injection ports arranged around its periphery. A conventional diesel
fuel injection system including pump and injector nozzle has been used to inject urea by the present applicants. A stream of compressed air was also injected around the nozzle; this provided good mixing and cooling.

[0016] The reductant fluid is suitably NH₃, but other reductant fluids including urea, ammonium carbamate and hydrocarbons including diesel fuel may also be considered. Diesel fuel is, of course, carried on board a diesel-powered vehicle, but diesel fuel itself is a less selective reductant than NH₃ and is presently not preferred.

[0017] Suitable SCR catalysts are available in the art and include Cu-based and vanadia-based catalysts. A preferred catalyst at present is a V₂O₅/WO₃/TiO₂ catalyst, supported on a honeycomb through-flow support. Although such a catalyst has shown good performance in the tests described hereafter and is commercially available, we have found that sustained high temperature operation can cause catalyst deactivation. Heavy duty diesel engines, which are almost exclusively turbocharged, can produce exhaust gases at greater than 500°C under conditions of high load and/or high speed, and such temperatures are sufficient to cause catalyst deactivation.

[0018] One embodiment of the invention, therefore, cooling means is provided upstream of the SCR catalyst. Cooling means may suitably be activated by sensing high catalyst temperatures or by other, less direct, means, such as determining conditions likely to lead to high catalyst temperatures. Suitable cooling means include water injection upstream of the SCR catalyst, or air injection, for example utilizing the engine turbocharger to provide a stream of fresh intake air by-passing the engine. We have observed a loss of activity of the catalyst, however, using water injection, and air injection by modifying the turbocharger leads to higher space velocity over the catalyst which tends to reduce NO conversion. Preferably, the preferred SCR catalyst is maintained at a temperature from 160°C to 450°C.

[0019] We believe that in its presently preferred embodiments, the present invention may depend upon an incomplete conversion of NO to NO₂. Desirably, therefore, the oxidation catalyst, or the oxidation catalyst together with the particulate trap if used, yields a gas stream entering the SCR catalyst having a ratio of NO to NO₂ of from about 4:1 to about 1:3 by volume, for the commercial vanadia-type catalyst. As mentioned above, other SCR catalysts perform better with different NO/NO₂ ratios. We do not believe that it has previously been suggested to adjust the NO/NO₂ ratio in order to improve NO reduction.

[0020] The present invention incorporates a particulate trap downstream of the oxidation catalyst. We discovered that soot-type particulates may be removed from a particulate trap by “combustion” at relatively low temperatures in the presence of NO₂. In effect, the incorporation of such a particulate trap serves to clean the exhaust gas of particulates without causing accumulation, with resultant blockage or back-pressure problems, whilst simultaneously reducing a proportion of the NOR. Suitable particulate traps are generally available, and are desirably of the type known as wall-flow filters, generally manufactured from ceramic, but other designs of particulate trap, including woven knitted or non-woven heat-resistant fabrics, may be used.

[0021] It may be desirable to incorporate a clean-up catalysis downstream of the SCR catalyst, to remove any NH₃ or derivatives thereof which could pass through unreacted or as by-products. Suitable clean-up catalysts are available to the skilled person.

[0022] A particularly interesting possibility arising from the present invention has especial application to light duty diesel engines (car and utility vehicles) and permits a significant reduction in volume and weight of the exhaust gas after treatment system, in a suitable engineered system.

EXAMPLES

[0023] Several tests have been carried out in making the present invention. These are described below, and are supported by results shown in graphical form in the attached drawings.

[0024] A commercial 10 litre turbocharged heavy duty diesel engine on a test-bed was used for all the tests described herein.

Test 1 — (Comparative)

[0025] A conventional SCR system using a commercial V₂O₅/WO₃/TiO₂ catalyst, was adapted and fitted to the exhaust system of the engine. NH₃ was injected upstream of the SCR catalyst at varying ratios. The NH₃ was supplied from a cylinder of compressed gas and a conventional mass flow controller used to control the flow of NH₃ gas to an experimental injection ring. The injection ring was a 10 cm diameter annular ring provided with 20 small injection ports arranged to inject gas in the direction of the exhaust gas flow. NOx conversions were determined by fitting a NOx analyser before and after the SCR catalyst and are plotted against exhaust gas temperature in FIG. 1. Temperatures were altered by maintaining the engine speed constant and altering the torque applied.

[0026] A number of tests were run at different quantities of NH₃ injection, from 60% to 100% of theoretical, calculated at 1:1 NH₃/NO and 4:3 NH₃/NO₂. It can readily be seen that at low temperatures, corresponding to light load, conversions are about 25%, and the highest conversions require stoichiometric (100%) addition of NH₃ at catalyst temperatures of from 325 to 400°C, and reach about 90%. However, we have determined that at greater than about 70% of stoichiometric NH₃ injection, NH₃ slips through the SCR catalyst unreacted, and can cause further pollution problems.

Test 2 — (Comparative)

[0027] The test rig was modified by inserting into the exhaust pipe upstream of the NH₃ injection, a commercial platinum oxidation catalyst of 10.5 inch diameter and 6 inch length (26.67 cm diameter and 15.24 cm length) containing 10 g Pt/Rh (0.35 g/litre) of catalyst volume. Identical tests were run, and it was observed from the results plotted in FIG. 2, that even at 225°C, the conversion of NOx has increased from 25% to >60%. The greatest conversions were in excess of 95%. No slippage of NH₃ was observed in the test nor in the following test.

Test 3

[0028] The test rig was modified further, by inserting a particulate trap before the NH₃ injection point, and the tests run again under the same conditions at 100% NH₃ injection and a space velocity in the range 40,000 to 70,000 hr⁻¹ over the SCR catalyst. The results are plotted and shown in FIG. 3. Surprisingly, there is a dramatic improvement in NOx conversion, to above 90% at 225°C, and reaching 100% at 350°C. Additionally, of course, the particulates, which are the most visible pollutant from diesel engines, are also controlled.
Test 4

[0029] An R49 test with 80% NH₃ injection was carried out over a V₂O₅/WO₃/TiO₂ SCR catalyst. This gave 67% particulate, 85% HC, and 87% NOx conversion; the results are plotted in FIG. 4.

[0030] Additionally tests have been carried out with a different diesel engine, and the excellent results illustrated in Tests 3 and 4 above have been confirmed.

[0031] The results have been confirmed also for a non-valanadum SCR catalyst.

We claim:

1. A method for treating a diesel engine exhaust gas stream for introduction to an SCR catalyst, comprising:
   passing the exhaust gas stream over an oxidation catalyst and a particulate trap under conditions effective to convert NO to NO₂ in the exhaust gas stream to NO₂ such that there is sufficient NO₂ to combust a substantial portion of the particulates from the gas stream in the particulate trap; and
   whereby the resulting gas stream has a ratio of NO to NO₂ of about 4:1 to 1:3 when the exhaust gas exits the particulate trap.

2. The method of claim 1, wherein the exhaust gas stream is between 225°C and 425°C.

3. The method of claim 1, wherein the gas stream is between 225°C and 350°C.

4. The method of claim 1, wherein the gas stream is between 250°C and 425°C.

5. The method of claim 2, wherein the diesel engine is a heavy duty diesel engine configured for mobile use.

6. The method of claim 5, wherein the heavy duty diesel engine is turbocharged.

7. The method of claim 6, further comprising injecting a metered dose of urea reductant into the exhaust gas stream after the exhaust gas stream exits the particulate trap and before the exhaust gas stream enters the SCR catalyst system.

8. The method of claim 7, wherein the oxidation catalyst comprises a Pt catalyst deposited upon a through-flow honeycomb support.

9. The method of claim 8, wherein the SCR catalyst comprises a transitional metal/zeolite catalyst.

10. The method of claim 9, further comprising passing the exhaust gas over a clean-up catalyst to remove NH₃ from the exhaust gas.

11. The method of claim 10, wherein the oxidation catalyst and particulate trap are sized and configured such that under the majority of normal on-road operational conditions of the heavy duty diesel engine the exhaust gas stream has a ratio of NO to NO₂ of about 4:1 to 1:3 when the exhaust gas exits the particulate trap.

12. The method of claim 11, further comprising adjusting the amount of urea injected into the exhaust gas stream based at least in part upon the NO:NO₂ ratio of the NOₓ in the exhaust gas stream.

13. The method of claim 12, wherein under the majority of normal on-road operational conditions of the heavy duty diesel truck engine the exhaust gas stream has at least 90% less NOₓ as it exits the SCR catalyst than the exhaust gas stream contained before it entered the oxidation catalyst.

14. A method for treating a diesel engine exhaust gas stream, comprising:
   passing the exhaust gas stream over an oxidation catalyst under conditions effective to convert a sufficient amount of NO in the gas stream to NO₂ such that there is sufficient NO₂ to:
   (i) combust, when operated at a temperature between 225°C and 425°C, a substantial portion of particulates from the gas stream in a particulate trap; and
   (ii) reduce a substantial portion of NOₓ exiting the particulate trap in an SCR catalyst.

15. The method of claim 14, wherein the diesel engine is a heavy duty diesel truck engine configured for mobile use.

16. The method of claim 15, wherein the heavy duty diesel truck engine is turbocharged.

17. The method of claim 16, further comprising injecting a metered dose of urea reductant into the exhaust gas stream after the exhaust gas stream exits the particulate trap and before the exhaust gas stream enters the SCR catalyst system.

18. The method of claim 17, further comprising adjusting the amount of urea injected into the exhaust gas stream based at least in part upon the NO:NO₂ ratio of the NOₓ in the exhaust gas stream.

19. The method of claim 18, wherein the SCR catalyst comprises a transitional metal/zeolite catalyst.

20. The method of claim 19, further comprising passing the exhaust gas over a clean-up catalyst to remove NH₃ from the exhaust gas.

21. The method of claim 20, wherein the oxidation catalyst and particulate trap are sized and configured to provide an exhaust gas stream with a ratio of NO to NO₂ of about 4:1 to 1:3 at the exit of the particulate trap when the exhaust gas is at a temperature between 225°C and 425°C.

22. The method of claim 21, wherein the oxidation catalyst comprises a Pt catalyst deposited upon a through-flow honeycomb support.

23. The method of claim 22, wherein the exhaust gas stream has at least 90% less NOₓ as it exits the SCR catalyst than the exhaust gas stream contained before it entered the oxidation catalyst when the exhaust gas stream is at a temperature between 225°C and 425°C.

* * * * *