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Plasma assisted gas processing with zirconia

The present invention relates to the purification of gases, and in particular to the reduction of the emission
5 of carbonaceous and nitrogenous combustion products from the exhausts of internal combustion engines.

One of the major problems associated with the development and use of internal combustion engines is the
10 noxious exhaust emissions from such engines. Two of the most deleterious materials, particularly in the case of diesel engines, are particulate matter (primarily carbon) and oxides of nitrogen (NO_x). Increasingly severe
15 emission control regulations are forcing internal combustion engine and vehicle manufacturers to find more efficient ways of removing these materials in particular from internal combustion engine exhaust emissions.
Unfortunately, in practice, it is found that techniques
20 which improve the situation in relation to one of the above components of internal combustion engine exhaust emissions tend to worsen the situation in relation to the other. Even so, a variety of systems for trapping
particulate emissions from internal combustion engine exhausts have been investigated, particularly in relation
25 to making such particulate emission traps capable of being regenerated when they have become saturated with particulate material.

Examples of such diesel exhaust particulate filters
30 are to be found in European patent application EP 0 010 384; US patents 4,505,107; 4,485,622; 4,427,418; and 4,276,066; EP 0 244 061; EP 0 112 634 and EP 0 132 166.

In all the above cases, the particulate matter is
35 removed from diesel exhaust gases by a simple physical

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trapping of particulate matter in the interstices of a porous, usually ceramic, filter body, which is then regenerated by heating the filter body to a temperature at which the trapped diesel exhaust particulates are
5 burnt off. In most cases the filter body is monolithic, although EP 0 010 384 does mention the use of ceramic beads, wire meshes or metal screens as well. US patent 4,427,418 discloses the use of ceramic coated wire or ceramic fibres.

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GB patent 2,274,3412 discloses a method and apparatus for removing particulate and other pollutants from internal combustion engine exhaust gases, in which the exhaust gases are passed through a bed of charged
15 pellets of material, preferably ferroelectric, having high dielectric constant (that is of the order of at least 1,000). In addition to removing particulates by oxidation, especially electric discharge assisted oxidation, there is disclosed the reduction of NO_x gases
20 to nitrogen, by the use of pellets adapted to catalyse the NO_x reduction as exemplified by the use of barium titanate as the ferroelectric material for the pellets.

Also, US patents 3 983 021, 5 147 516 and 5 284 556
25 disclose the catalytic reduction of nitrogen oxides. However, US 3 983 021 is solely concerned with the reduction of NO to N in a silent glow discharge, the temperature of which is kept below a value at which the oxidation of N or NO to higher oxides of nitrogen does
30 not occur. There is no mention of any simultaneous removal of hydrocarbons.

Although, so-called contact bodies are used in the process of US 3 983 021, and some of those disclosed may
35 have some catalytic properties, catalysis does not appear

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to be a necessary feature of the process of US 3 983 021. Other surface properties, such as adsorption on large surface area materials, are the basis of the process of US 3 983 021.

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US patent 5 147 516 does refer to the use of catalysts to remove NO_x, but the catalytic materials involved are defined very specifically as being sulphur tolerant and deriving their catalytic activity from their form rather than their surface properties.

Also, the operating conditions are very tightly defined. There is no specific mention of the type, if any, of electric discharge involved. All that is disclosed is that the NO_x removal depends upon electron-molecule interactions, facilitated by the structure of the 'corona-catalytic' materials not the inter-molecular interactions involved in the present invention. There is no mention of the simultaneous removal of hydrocarbons from the gas streams being treated by the invention of US 5 147 516.

US patent 5 284 556 does disclose the removal of hydrocarbons from internal combustion engine exhaust emissions. However, the process involved is purely one of dissociation in an electrical discharge of the so-called 'silent' type, that is to say, a discharge which occurs between two electrodes at least one of which is insulated. The device described is an open discharge chamber, not a packed bed device. Mention is made of the possible deposition of a NO_x-reducing catalyst on one of the electrodes.

In a broader context, the precipitation of charged particulate matter by electrostatic forces also is known.

However, in this case, precipitation usually takes place upon larger planar electrodes or metal screens.

It is an object of the present invention to provide
5 an improved method for the removal of particulates and nitrogenous oxides from the exhaust gases emitted by internal combustion engines.

According to the present invention there is provided
10 a reactor for the plasma assisted processing of a gaseous medium, comprising a reactor chamber including at least two electrodes between which there is disposed a gas permeable bed of active material and means for
15 constraining the gaseous medium to pass through the active material characterised in that the bed of active material includes zirconia.

According to the present invention in one aspect there is provided a reactor for reducing the emission of
20 pollutants from an internal combustion engine, comprising a reactor chamber adapted to form part of an internal combustion engine exhaust system, the reactor chamber including at least two gas permeable electrodes between which there is disposed a gas permeable bed of active
25 material and means for constraining exhaust gases to pass through the bed of active material, characterised in that the bed of active material consists at least primarily of zirconia.

30 The invention provides in another of its aspects, a reactor for reducing emission of pollutants from the exhaust of an internal combustion engine, comprising a reactor chamber adapted to form part of an internal combustion engine exhaust system, the reactor chamber
35 including at least two electrodes between which, in use, exhaust gases are constrained to pass, wherein the active



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material comprises zirconia in a form which does not significantly adsorb water from the vapour phase.

The zirconia may have a bimodal pore structure.

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The invention will now be described, by way of example, with reference to the accompanying drawing which is a longitudinal section of a schematic plasma assisted reactor embodying the invention for the treatment of
10 internal combustion engine exhaust gases.

Referring to the drawing, a reactor 1 for the treatment of internal combustion engine exhaust gases to reduce emissions of pollutants such as carbonaceous and
15 nitrogenous combustion products therefrom consists of a stainless steel reactor chamber 2 which has an inlet stub 3 and an outlet stub 4, by means of which it can be connected into the exhaust system of an internal combustion engine (not shown). The chamber 2 is arranged
20 in use to be connected to an earthing point 5. Within the chamber 2 are a cylindrical inner electrode 6 made of perforated stainless steel sheet and an earthed outer electrode 14 co-axial with the inner electrode 6 and also made of perforated stainless steel sheet. The electrodes
25 6 and 14 are held in position by two insulating supports 7 and 8. The space 11 between the electrodes 6 and 14 and the supports 7 and 8 is filled with a bed of pellets illustrated highly diagrammatically at 12 made of zirconia or a mixture of zirconia and titania, as
30 discussed further below. The upstream electrode support 7 has a number of regularly spaced axially-oriented holes 13 around its periphery so that exhaust gases entering the reactor 1 pass into the space 15 between the outer electrode 14 and the wall of the chamber 2 before passing
35 radially through the bed of pellets 12 and leaving the reactor 1 via the inner electrode 6, as shown in the

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drawing. An insulated feed-through 10 connects output from a source 9 of electrical potential to the inner electrode 6. The potential thus applied across the bed of pellets 12 is sufficient to excite a plasma within the
5 interstices between the pellets 12. A convenient potential for this purpose is about 10 kV to 30 kV, and may be a pulsed direct or continuously varying alternating potential, or may be an interrupted continuous direct potential. Typically we employ a
10 potential of 20 kV per 30 mm of bed depth.

Zirconia as an active material in the gas permeable bed is expected to have a catalytic effect in addition to promoting the establishing of a plasma in the exhaust
15 gases passing through the reactor 2, but in a number of forms has shown poor performance in the treatment of exhaust gases from internal combustion engines. We have now found improved performance is achieved by using a form of zirconia manufactured by Norton Chemical Process
20 Products Corporation and marketed under their product code XZ 16052. In pellet form this material has a nominal surface area of $95 \text{ m}^2 \text{ g}^{-1}$, a pore volume of $0.31 \text{ cm}^3 \text{ g}^{-1}$ and a density of 1.17 g cm^{-3} . This form of zirconia has the property that it does not adsorb water from the
25 vapour phase. It also has a bimodal pore structure with the respective pore diameters centred around 40 nm and 8 nm.

Further, we have found that when pellets of zirconia
30 in this form are mixed in the gas permeable bed with pellets of anatase titania there is a symbiotic improvement in performance in the treatment of internal combustion engine exhaust gases as compared with the performance of the zirconia or anatase titania on their

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own. It is convenient for this purpose to provide equal parts by volume of titania and zirconia in the mixture.

As an example of the use of the invention to reduce the emissions of nitrogenous and particulate carbonaceous combustion products from internal combustion engines, the exhaust gases from a diesel generator set were passed through a reactor similar to that described above, in which the bed of active material (12) comprised pellets of zirconia as described above. The concentrations of nitrogenous oxides (NO_x) at the inlet and outlets 3 and 4 respectively, of the reactor 2 were measured. The difference between the two values was taken as a measure of the ability of the reactor 2 to remove NO_x from the exhaust gases. Similarly, the inlet and outlet concentrations of carbon monoxide were measured for the same reactor and operating conditions. An increase in the difference between the two concentrations of carbon monoxide was taken as an indication of the removal of particulate carbonaceous combustion products in the exhaust by oxidation to carbon monoxide.

The experiment was repeated for different values of the potential difference applied across the bed of active material 12. The results are tabulated below:

Electric potential across reactor bed (Kv)	NO_x reduction (ppm)	CO production (ppm)
0.0	68	5
5.5	64	8
6.6	67	13
7.7	80	13
10.2	93	14
11.6	97	16
13.3	108	15

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Electric potential across reactor bed (Kv)	NO _x reduction (ppm)	CO production (ppm)
15.2	123	50
17.1	121	59
18.0	119	77
21.0	99	107

Claims

1. A reactor for the plasma assisted processing of a gaseous medium, comprising a reactor chamber (2)
5 including at least two electrodes (6, 14) between which there is disposed a gas permeable bed of active material (12) and means (6, 7, 13, 14) for constraining the gaseous medium to pass through the active material (12) characterised in that the bed of active material (12)
10 includes zirconia.
2. A reactor for reducing the emission of pollutants from an internal combustion engine, comprising a reactor chamber (2) adapted to form part of an internal
15 combustion engine exhaust system, the reactor chamber (2) including at least two gas permeable electrodes (6, 14) between which there is disposed a gas permeable bed of active material (12) and means (6, 7, 13, 14) for
20 constraining exhaust gases to pass through the bed of active material (12), characterised in that the bed of active material (12) consists at least primarily of zirconia.
3. A reactor according to claim 1 or claim 2
25 characterised in that the active material (12) comprises zirconia in a form which is porous with a bimodal pore structure.
4. A reactor according to any of claims 1 to 3
30 characterised in that the zirconia is in a form which does not significantly adsorb water from the vapour phase.
5. A reactor according to any preceding claim
35 characterised in that the bed of active material (12) includes titania.

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6. A reactor according to claim 5 characterised in that the bed of active material (12) is a mixture of equal parts by volume of zirconia and titania.
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7. A reactor according to claim 5 or claim 6 characterised in that the titania is in the anatase phase.
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8. A reactor according to claim 5 or claim 6 characterised in that the titania is textured rutile phase titania.
9. A reactor according to claim 5 or claim 6
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- characterised in that the titania is in the form of a mixture of anatase and textured rutile phase titania.
10. A reactor according to any preceding claim characterised in that the zirconia is that manufactured
- 20
- by the Norton Chemical Process Products Corporation and marketed under their product code XZ 16052.

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