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(54) [Title of invention] Catalytic filter, method of manufacturing same, and an exhaust gas cleaning system

(57) [Abstract]

[Task] To provide a catalytic filter wherein the amount of noble metal catalyst can be reduced without change in the soot regeneration rate despite regeneration being repeated to some extent and wherein pressure loss is small.

[Solution] A catalytic filter characterised as a ceramic filter wherein the two ends of a honeycomb structure possessing a plurality of through-holes separated by cell walls are alternately closed with plugs, and wherein catalyst is supported, a predefined amount of the aforesaid catalyst being supported at one end and relatively little of the catalyst being supported going towards the other end.

[diagram: see Drawings, Figure 5]

[Claims]

[Claim 1] A catalytic filter, characterised as a ceramic filter wherein the two ends of a honeycomb structure possessing a plurality of through-holes separated by cell walls are alternately closed with plugs and wherein catalyst is supported, a predefined amount of the aforesaid catalyst being supported at one end and relatively little of the catalyst being supported going towards the other end.

[Claim 2] A catalytic filter, characterised as a ceramic filter wherein the two ends of a honeycomb structure possessing a plurality of through-holes separated by cell walls are alternately closed with plugs and wherein catalyst is supported; wherein a catalyst support site is provided in a zone extending from one end face to a point displaced towards the other end face by a predefined length and a non-catalyst supporting site is provided in a zone extending from the said point to the other end face.

[Claim 3] A catalytic filter, characterised as a ceramic filter wherein the two ends of a honeycomb structure possessing a plurality of through-holes separated by cell walls are alternately closed with plugs and wherein catalyst is supported; wherein a catalyst support site is provided in a zone extending from one end face to a point displaced towards the other end face by 1/2-4/5 of the overall length of the filter and a non-catalyst supporting site is provided in a zone extending from the said point to the other end face.

[Claim 4] The catalytic filter set down in any of Claims 1-3 characterised in that the aforesaid catalyst comprises at least one element chosen from the group comprising noble metal elements, elements of periodic table Group VI and elements of periodic table Group VIII.

[Claim 5] The catalytic filter set down in any of Claims 1-3 characterised in that the aforesaid catalyst comprises at least one element chosen from the group comprising alkali metal elements, alkaline earth metal elements, rare earth elements and transition metal elements.

[Claim 6] A catalytic filter, characterised as a ceramic filter wherein the two ends of a honeycomb structure possessing a plurality of through-holes separated by cell walls are alternately closed with plugs and wherein catalyst is supported; wherein a predefined amount of NO_x selective reduction catalyst component and/or NO_x occlusion catalyst component are/is supported towards one end and relatively little of the NO_x selective reduction catalyst component and/or NO_x occlusion catalyst component are/is supported going towards the other end.

[Claim 7] A catalytic filter, characterised as a ceramic filter wherein the two ends of a honeycomb structure possessing a plurality of through-holes separated by cell walls are alternately closed with plugs and wherein catalyst is supported; wherein a site supporting an NOx selective reduction catalyst component and/or NOx occlusion catalyst component is provided in a zone extending from one end face to a point displaced towards the other end face by a predefined length and a site not supporting NOx selective reduction catalyst component and/or NOx occlusion catalyst component is provided in a zone extending from the said point to the other end face.

[Claim 8] A catalytic filter, characterised as a ceramic filter wherein the two ends of a honeycomb structure possessing a plurality of through-holes separated by cell walls are alternately closed with plugs and wherein catalyst is supported; wherein a site supporting an NOx selective reduction catalyst component and/or NOx occlusion catalyst component is provided in a zone extending from one end face to a point displaced towards the other end face by 1/2-4/5 of the overall length of the filter and a site not supporting NOx selective reduction catalyst component and/or NOx occlusion catalyst component is provided in a zone extending from the said point to the other end face.

[Claim 9] The catalytic filter set down in any of Claims 6-8 characterised in that the aforesaid NOx occlusion catalyst component is constituted by a component comprising at least one element chosen from the group comprising alkali metals, alkaline earth metals, rare earths and transition metals in addition to noble metal elements.

[Claim 10] The catalytic filter set down in any of Claims 1-9 characterised in that a support material is supported on the cell wall surface of the aforesaid filter.

[Claim 11] The catalytic filter set down in any of Claims 1-9 characterised in that a predefined amount of support material is supported on the cell wall surface towards one end of the aforesaid filter and relatively little of the support material is supported going towards the other end.

[Claim 12] The catalytic filter set down in any of Claims 1-9 characterised in that a site supporting a support material is provided on the cell wall surface of the aforesaid filter in a zone extending from one end face to a point displaced towards the other end face by a predefined length and a site not supporting support material is provided in a zone extending from the said point to the other end face.

[Claim 13] The catalytic filter set down in any of Claims 1-9 characterised in that a site supporting a support material is provided on the cell wall surface of the aforesaid filter in a zone extending from one end face to a point displaced towards the other end face by 1/2-4/5 of the overall length of the filter and a site not supporting support material is provided in a zone extending from the said point to the other end face.

[Claim 14] The catalytic filter set down in any of Claims 10-13 characterised in that the aforesaid support material comprises at least one material chosen from the group comprising alumina, zirconia, titania and silica.

[Claim 15] The catalytic filter set down in any of Claims 10-14 characterised in that the aforesaid support material is constituted by acicular alumina.

[Claim 16] The catalytic filter set down in any of Claims 1-15 characterised in that the aforesaid filter is constituted by a ceramic porous body containing silicon.

[Claim 17] The catalytic filter set down in any of Claims 1-15 characterised in that the aforesaid filter is constituted by a ceramic porous body containing at least one ceramic chosen from the group comprising silicon carbide, silicon nitride, cordierite, mullite, sialon, and silica.

[Claim 18] The catalytic filter set down in any of Claims 1-17 characterised in that a predefined amount of catalyst promoter is supported on the cell wall surface of the aforesaid filter towards one end, and relatively little of the catalyst promoter is supported going towards the other end.

[Claim 19] The catalytic filter set down in any of Claims 1-17 characterised in that a catalyst promoter support site is provided on the cell wall surface of the aforesaid filter in a zone extending from one end face to a point displaced towards the other end face by a predefined length and a non-catalyst promoter supporting site is provided in a zone extending from the said point to the other end face.

[Claim 20] The catalytic filter set down in any of Claims 1-17 characterised in that a catalyst promoter support site is provided on the cell wall surface of the aforesaid filter in a zone extending from one end face to a point displaced towards the other end face by 1/2-4/5 of the overall length of the filter and a non-catalyst promoter supporting site is provided in a zone extending from the said point to the other end face.

[Claim 21] The catalytic filter set down in any of Claims 18-20 characterised in that the aforesaid catalyst promoter is constituted by one comprising rare earth oxide.

[Claim 22] The catalytic filter set down in any of Claims 18-20 characterised in that the aforesaid catalyst promoter comprises at least one element chosen from the group comprising alkali metals, alkaline earth metals, rare earth elements and transition metal elements.

[Claim 23] The catalytic filter set down in any of Claims 18-20 characterised in that the aforesaid catalyst comprises at least one entity or compound chosen from the group comprising cerium (Ce), lanthanum (La), barium (Ba), calcium (Ca) and potassium (K).

[Claim 24] The catalytic filter set down in any of Claims 1-23 characterised in that the zones wherein the support material, catalyst promoter and catalyst are supported on the cell wall surface of the aforesaid filter are of the same length from one end face towards the other end face.

[Claim 25] A method of manufacturing a catalytic filter, characterised in that a zone extending from one end face of the filter to a point displaced towards the other end face by a predefined length is impregnated with a solution of metal compounds containing noble metal and then dried.

[Claim 26] A method of manufacturing a catalytic filter, characterised in that an alumina support material is applied to a filter by a process comprising a solution impregnation step wherein a zone extending from one end face of the filter to a point displaced towards the other end face by a predefined length is impregnated in a solution of metal compounds containing aluminium, a drying step wherein the impregnated filter is dried, a precalcination step wherein an amorphous alumina film is formed by heating and calcining the dried filter at a temperature of not less than 300-500°C, a hydrothermal treatment step wherein the precalcined filter is treated by immersion in hot water and then dried, and a final calcination step wherein the hydrothermally treated filter is calcined at 500-1200°C.

[Claim 27] A method of manufacturing a catalytic filter, characterised in that a rare earth oxide film is applied to a filter by a process comprising a solution impregnation step wherein a zone extending from one end face of the filter to a point displaced towards the other end face by a predefined length is impregnated in a solution of metal compounds containing rare earth elements, a drying step wherein the impregnated filter is dried, and a calcination step wherein the dried filter is heated and calcined in a nitrogen atmosphere at a temperature of 500-800°C, forming a rare earth oxide film.

[Claim 28] An exhaust gas cleaning system characterised in that the filter of any of Claims 1-24 is installed in a diesel engine exhaust passage such that the end where a relatively large amount of catalyst is supported faces the exhaust gas inlet side and the end where relatively little or no catalyst is supported faces the discharge side.

[Claim 29] An exhaust gas cleaning system characterised in that the filter of any of Claims 1-24 is installed in a diesel engine exhaust passage such that the end where a relatively large amount of catalyst is supported faces the exhaust gas inlet side and the end where relatively little or no catalyst is supported faces the discharge side, a heater is installed on the exhaust gas inlet side of the aforesaid filter, and the filter is regenerated using the heater.

[Claim 30] An exhaust gas cleaning system characterised in that the filter of any of Claims 1-24 is installed in the exhaust passage of a diesel engine with post-ignition, with the end where a relatively large amount of catalyst is supported facing the exhaust gas inlet side and the end where relatively little or no catalyst is supported facing the discharge side.

[Claim 31] A catalytic filter characterised in that a specified amount of catalyst is supported at one end and relatively little of the catalyst is supported going towards the other end.

[Detailed Description of Invention]

[0001]

[Inventive field of art] The invention relates to a catalytic filter, a method of manufacturing a catalytic filter, and an exhaust gas cleaning system.

[0002]

[Prior art] The number of motor vehicles has increased dramatically since the turn of the century, and this increase has been matched by a continual, steep increase in the amount of exhaust gas discharged from the internal combustion engines of vehicles. The various substances contained in the exhaust gas from diesel engines in particular cause pollution and because of this they are now seriously impacting on the global environment. Research findings have recently been reported indicating that the suspended particulate matter (hereunder abbreviated to PM) in exhaust gas, such as soot and SOF (soluble oil fraction), are sometimes responsible for allergic disorders and reduced sperm counts. Thus, the formulation of measures to remove PM from exhaust gas is considered an urgent task facing mankind.

[0003] Many diverse kinds of exhaust gas cleaner apparatus have been proposed in this context. Figure 18 is a schematic sketch of an ordinary exhaust gas cleaner. As shown in

Figure 18, the ordinary exhaust gas cleaner 101 has a construction whereby the exhaust channel 104 connected with the exhaust manifold 103 of a diesel engine is provided along its path with a casing 105, within which is mounted a filter 10 containing fine pores. Besides a metal or alloy, the material wherefrom the filter 10 is formed can be a ceramic. A honeycomb filter of cordierite is a known example typifying a filter 10 comprising ceramic. The use of silicon carbide as filter-forming material has recently been regarded ideal from the standpoint of high heat resistance, mechanical strength and trapping efficiency, chemical stability, and small pressure loss.

[0004] The aforesaid honeycomb filter has numerous cells extending in its axial direction. Hence, when exhaust gas passes through the filter 10, PM is trapped by the filter walls (cell walls). As the amount of PM trapped in the filter increases, the resistance within the filter is increased, and the pressure loss increases. Regeneration, a procedure whereby the temperature in the filter is increased to a predefined temperature (ignition temperature) to ignite and burn off the PM, has therefore been adopted.

[0005] Currently, an exhaust gas cleaner effects ignition either with exhaust gas heat only (self ignition mode) or with heat from a heating means such as a burner or heater in addition to the exhaust gas heat (heated ignition mode), and a method frequently used is to lower the ignition temperature by supporting a catalyst uniformly on the cell walls of the filter. Japan Patent Kokai No. 2001-207836 further discloses art whereby an NO_x absorption catalyst component is for the most part supported on the exhaust gas inlet side of the honeycomb filter.

[0006]

[Problem addressed by the invention] However, it has been found that, when regeneration of the whole diesel particulate filter (DPF) whereon PM has been trapped is repeated at fixed intervals, filter performance deteriorates. Figure 19 is a graph of the relation between the number of regeneration cycles and regeneration rate. "Regeneration rate" is here the ratio of the weight of accumulated soot removed from the filter (the amount of regeneration) to the weight of soot accumulated in the filter, expressed as a percentage. It will be seen from the graph in Figure 19 that initially the PM is burned off by regeneration at a high regeneration rate, but as the process is repeated again and again, the regeneration rate decreases and the reactivity of the catalyst progressively declines.

[0007]

[Means of solving the problem] To solve the problem of deterioration in filter performance, the inventors conducted wide-ranging trial and error tests. Firstly, supposing that catalyst

loading was linked to deterioration in performance, increase in the amount of catalyst was considered. However, it was impossible to halt deterioration in filter performance this way since pressure loss increased when the catalyst loading was increased. Contrary to expectations, when the temperature was measured at different locations with thermocouples inserted in the filter under regeneration, the temperature was found to be higher on the exit side than the exhaust gas inlet side. This was considered to be a problem of filter and heater location, and regeneration was therefore carried out with the heater fitted on the exhaust gas inlet side that tended to fall in temperature. Figure 20 is a graph of the change in temperature in the filter during regeneration. It was found that, while the exhaust gas inlet side of the filter could be controlled to around 600°C, at which the catalyst reacts well, the discharge side rose above 800°C, as shown by the graph in Figure 20. When attention was turned to the catalyst, it was further established that the noble metal used as catalyst undergoes sintering above 800°C (the metal transforming to large particles), whereupon reactivity deteriorates and the catalyst becomes unusable.

[0008] On the basis of these observations, the inventors turned their attention to the catalyst loading on the exhaust gas inlet side and established that if the catalyst support location was changed from overall uniform support to support at varying concentration or partial support, the soot regeneration rate remained unchanged after regeneration had to a degree been repeated. The inventors were also able to prevent wasteful consumption of the noble metals, etc, used as catalyst, which are a valuable resource, thus reducing cost, and succeeded in creating a catalytic filter that has little pressure loss.

[0009] The basis of this is that reduction in the amount of noble metal, etc, on the exhaust gas discharge side reduces the amount of catalyst of noble metal, etc, degrading.

[0010] (1) The catalytic filter of the invention is characterised as a ceramic filter wherein the two ends of a honeycomb structure possessing a plurality of through-holes separated by cell walls are alternately closed with plugs and wherein catalyst is supported, a predefined amount of the aforesaid catalyst being supported at one end and relatively little of the catalyst being supported going towards the other end.

[0011] (2) The catalytic filter of the invention is characterised as a ceramic filter wherein the two ends of a honeycomb structure possessing a plurality of through-holes separated by cell walls are alternately closed with plugs and wherein catalyst is supported; wherein a catalyst support site is provided in a zone extending from one end face to a point displaced towards the other end face by a predefined length and a non-catalyst supporting site is provided in a zone extending from the said point to the other end face.

[0012] (3) The catalytic filter of the invention is characterised as a ceramic filter wherein the two ends of a honeycomb structure possessing a plurality of through-holes separated by cell walls are alternately closed with plugs and wherein catalyst is supported; wherein a catalyst support site is provided in a zone extending from one end face to a point displaced towards the other end face by 1/2-4/5 of the overall length of the filter and a non-catalyst supporting site is provided in a zone extending from the said point to the other end face.

[0013] (4) The catalytic filter in any of (1)-(3) above is characterised in that the aforesaid catalyst comprises at least one element chosen from the group comprising noble metal elements, elements of periodic table Group VI and elements of periodic table Group VIII.

[0014] (5) The catalytic filter in any of (1)-(3) above is characterised in that the aforesaid catalyst comprises at least one element chosen from the group comprising alkali metal elements, alkaline earth metal elements, rare earth elements and transition metal elements.

[0015] (6) The catalytic filter of the invention is characterised as a ceramic filter wherein the two ends of a honeycomb structure possessing a plurality of through-holes separated by cell walls are alternately closed with plugs and wherein catalyst is supported; wherein a predefined amount of NOx selective reduction catalyst component and/or NOx occlusion catalyst component are/is supported towards one end and relatively little of the NOx selective reduction catalyst component and/or NOx occlusion catalyst component are/is supported going towards the other end.

[0016] (7) The catalytic filter of the invention is characterised as a ceramic filter wherein the two ends of a honeycomb structure possessing a plurality of through-holes separated by cell walls are alternately closed with plugs and wherein catalyst is supported; wherein a site supporting an NOx selective reduction catalyst component and/or NOx occlusion catalyst component is provided in a zone extending from one end face to a point displaced towards the other end face by a predefined length and a site not supporting NOx selective reduction catalyst component and/or NOx occlusion catalyst component is provided in a zone extending from the said point to the other end face.

[0017] (8) The catalytic filter of the invention is characterised as a ceramic filter wherein the two ends of a honeycomb structure possessing a plurality of through-holes separated by cell walls are alternately closed with plugs and wherein catalyst is supported; wherein a site supporting an NOx selective reduction catalyst component and/or NOx occlusion catalyst component is provided in a zone extending from one end face to a point displaced towards the

other end face by 1/2-4/5 of the overall length of the filter and a site not supporting NOx selective reduction catalyst component and/or NOx occlusion catalyst component is provided in a zone extending from the said point to the other end face.

[0018] (9) The catalytic filter in any of (6)-(8) above is characterised in that the aforesaid NOx occlusion catalyst component is constituted by a component comprising at least one element chosen from the group comprising alkali metals, alkaline earth metals, rare earths and transition metals in addition to noble metal elements.

[0019] (10) The catalytic filter in any of (1)-(9) above is characterised in that a support material is supported on the cell wall surface of the aforesaid filter.

[0020] (11) The catalytic filter in any of (1)-(9) above is characterised in that a predefined amount of support material is supported on the cell wall surface of the aforesaid filter towards one end and relatively little of the support material is supported going towards the other end.

[0021] (12) The catalytic filter in any of (1)-(9) above is characterised in that a site supporting support material is provided on the cell wall surface of the aforesaid filter in a zone extending from one end face to a point displaced towards the other end face by a predefined length and a site not supporting support material is provided in a zone extending from the said point to the other end face.

[0022] (13) The catalytic filter in any of (1)-(9) above is characterised in that a site supporting a support material is provided on the cell wall surface of the aforesaid filter in a zone extending from one end face to a point displaced towards the other end face by 1/2-4/5 of the overall length of the filter and a site not supporting support material is provided in a zone extending from the said point to the other end face.

[0023] (14) The catalytic filter in any of (10)-(13) above is characterised in that the aforesaid support material comprises at least one material chosen from the group comprising alumina, zirconia, titania and silica.

[0024] (15) The catalytic filter in any of (10)-(14) above is characterised in that the aforesaid support material is constituted by acicular alumina.

[0025] (16) The catalytic filter in any of (1)-(15) above is characterised in that the aforesaid filter is constituted by a ceramic porous body containing silicon.

[0026] (17) The catalytic filter in any of (1)-(15) above is characterised in that the aforesaid filter is constituted by a ceramic porous body comprising at least one ceramic chosen from the group comprising silicon carbide, silicon nitride, cordierite, mullite, sialon, and silica.

[0027] (18) The catalytic filter in any of (1)-(15) above is characterised in that a predefined amount of catalyst promoter is supported on the cell wall surface of the aforesaid filter towards one end, and relatively little of the catalyst promoter is supported going towards the other end.

[0028] (19) The catalytic filter in any of (1)-(17) above is characterised in that a catalyst promoter support site is provided on the cell wall surface of the aforesaid filter in a zone extending from one end face to a point displaced towards the other end face by a predefined length and a non-catalyst promoter supporting site is provided in a zone extending from the said point to the other end face.

[0029] (20) The catalytic filter in any of (1)-(17) above is characterised in that a catalyst promoter support site is provided on the cell wall surface of the aforesaid filter in a zone extending from one end face to a point displaced towards the other end face by 1/2-4/5 of the overall length of the filter and a non-catalyst promoter supporting site is provided in a zone extending from the said point to the other end face.

[0030] (21) The catalytic filter in any of (18)-(20) above is characterised in that the aforesaid catalyst promoter is constituted by one comprising rare earth oxide.

[0031] (22) The catalytic filter in any of (18)-(20) above is characterised in that the aforesaid catalyst promoter comprises at least one element chosen from the group comprising alkali metals, alkaline earth metals, rare earth elements and transition metal elements.

[0032] (23) The catalytic filter in any of (18)-(20) above is characterised in that the aforesaid catalyst comprises at least one entity or compound chosen from the group comprising cerium (Ce), lanthanum (La), barium (Ba), calcium (Ca) and potassium (K).

[0033] (24) The catalytic filter in any of (1)-(23) above is characterised in that the zones wherein the support material, catalyst promoter and catalyst are supported on the cell wall surface of the aforesaid filter are of the same length from one end face towards the other end face.

[0034] (25) The method of manufacturing the catalytic filter of the invention is characterised

in that a zone extending from one end face of the filter to a point displaced towards the other end face by a predefined length is impregnated with a solution of metal compounds containing noble metal and then dried.

[0035] (26) The method of manufacturing the catalytic filter of the invention is characterised in that an alumina support material is applied to a filter by a process containing a solution impregnation step wherein a zone extending from one end face of the filter to a point displaced towards the other end face by a predefined length is impregnated in a solution of metal compounds containing aluminium, a drying step wherein the impregnated filter is dried, a precalcination step wherein an amorphous alumina film is formed by heating and calcining the dried filter at a temperature of not less than 300-500°C, a hydrothermal treatment step wherein the precalcined filter is treated by immersion in hot water and then dried, and a final calcination step wherein the hydrothermally treated filter is calcined at 500-1200°C.

[0036] (27) The method of manufacturing the catalytic filter of the invention is characterised in that a rare earth oxide is applied to a filter by a process comprising a solution impregnation step wherein a zone extending from one end face of the filter to a point displaced towards the other end face by a predefined length is impregnated in a solution of metal compounds containing rare earth elements, a drying step wherein the impregnated filter is dried, and a calcination step wherein the dried filter is heated and calcined in a nitrogen atmosphere at a temperature of 500-800°C, forming a rare earth oxide film.

[0037] (28) The inventive gas cleaning system is characterised in that the filter in any of (1)-(24) above is installed in a diesel engine exhaust passage such that the end where a relatively large amount of catalyst is supported faces the exhaust gas inlet side and the end where relatively little or no catalyst is supported faces the discharge side.

[0038] (29) The inventive exhaust gas cleaning system is characterised in that the filter in any of (1)-(24) above is installed in a diesel engine exhaust passage such that the end where a relatively large amount of catalyst is supported faces the exhaust gas inlet side and the end where relatively little or no catalyst is supported faces the discharge side, a heater is installed on the exhaust gas inlet side of the aforesaid filter, and the filter is regenerated using the heater.

[0039] (30) The inventive exhaust gas cleaning system is characterised in that the filter of any of Claims 1-24 is installed in the exhaust passage of a diesel engine with post-ignition, with the end where a relatively large amount of catalyst is supported facing the exhaust gas inlet side and the end where relatively little or no catalyst is supported facing the discharge side.

[0040] (31) The catalytic filter of the invention is characterised in that a specified amount of catalyst is supported towards one end and relatively little of the catalyst is supported going towards the other end.

[0041] According to the invention in (1), by supporting little catalyst at the end reaching high temperature during regeneration, as at the exhaust gas discharge end of the filter, it is possible to reduce wastage of catalyst due to sintering. In addition, foul exhaust gas with the highest concentration of PM can be efficiently cleaned at the exhaust gas inlet end.

[0042] According to the invention in (2), by supporting little catalyst at the end reaching high temperature during regeneration, as at the exhaust gas discharge end of the filter, it is possible to reduce wastage of catalyst due to sintering. In addition, foul exhaust gas with the highest concentration of PM can be efficiently cleaned at the exhaust gas inlet end. Furthermore, the pressure loss can be made smaller than when catalyst is uniformly supported on the cell wall surface as in the prior art.

[0043] According to the invention in (3), by supporting little catalyst at the end reaching high temperature during regeneration, as at the exhaust gas discharge end of the filter, it is possible to reduce wastage of catalyst due to sintering. In addition, foul exhaust gas with the highest concentration of PM can be efficiently cleaned at the exhaust gas inlet end. Furthermore, the pressure loss can be made smaller than when catalyst is uniformly supported on the cell wall surface as in the prior art. Note here that when the catalyst support site is shorter than half the overall filter length, the regeneration rate declines, and the pressure loss increases when the filter is re-used since the PM is incompletely burned off. Again, when the catalyst support site is longer than 4/5 of the overall filter length, pressure loss increases and wastage of catalyst due to sintering increases.

[0044] According to the invention in (4), oxygen is activated by using noble metal elements, elements of periodic table Group VIa and elements of periodic table Group VIII as the catalyst, enabling oxidative clean-up of PM, HC, CO, etc.

[0045] According to the invention in (5), it is possible to effect reductive cleaning to harmless gas by taking up the gases NO_x and SO_x in the form of nitrate and sulphate salts with alkali metal elements, alkaline earth metal elements, rare earth elements, and transition metal elements, thereby creating a reducing atmosphere; and by absorbing and releasing active oxygen while trapping PM, it is possible to accomplish the aforesaid reactions without the release of reducing agent into the exhaust gas.

[0046] According to the invention in (6)-(9) by having little catalyst at the end reaching high temperature during regeneration, as at the exhaust gas discharge end of the filter, it is possible to reduce wastage of catalyst due to sintering; at the same time, the pressure loss can be made smaller than when catalyst is uniformly supported on the cell wall surface as in the prior art. In addition, foul exhaust gas with the highest concentration of PM can be efficiently cleaned up at the exhaust gas inlet end. Note here that when the catalyst support site is shorter than half the overall filter length, the regeneration rate declines and the pressure loss increases when the filter is re-used since the PM is incompletely burned off. Again, when the catalyst support site is longer than 4/5, pressure loss increases and catalyst is wasted.

[0047] Again, the active oxygen gases NO_x and SO_x can be taken up in the form of nitrate and sulphate salts by the alkali metal elements, alkaline earth metal elements, rare earth elements, and transition metal elements. When the surface then temporarily assumes an oxygen deficient state (reducing atmosphere) due to the PM trapped by the filter, active NO and SO₂ oxygen is released from the sulphate and nitrate salts and the active oxygen oxidises the PM. The PM can hence be oxidised even at locations where filter PM is difficult to oxidise. The NO and SO₂ are oxidised by Pt, etc, and taken up again in the form of nitrate and sulphate salts. The [NO] may, of course, also be reduced by reaction with unburned HC and CO and be released as N₂.

[0048] According to the invention in (10), since a support material of large specific surface area is supported on the cell wall surface in the aforesaid filter, the degree of dispersion of the catalyst can be increased. The catalyst reaction sites can thereby be increased. Again, since sintering of the catalyst metal can be prevented by the support material, the heat resistance of the catalyst improves.

[0049] According to the invention in (11) and (12), by coating support material on the cell wall surface at the end of the filter that supports the catalyst, it is possible to increase the specific surface area and raise the degree of dispersion of the catalyst. The catalyst reaction sites can therefore be increased. Again, since sintering of the catalyst metal can be prevented by the support material, the heat resistance of the catalyst improves. In addition, this enables pressure loss to be reduced.

[0050] According to the invention in (13), by coating support material on the cell wall surface at the end of the filter that supports the catalyst, it is possible to increase the specific surface area and raise the degree of dispersion of the catalyst. The catalyst reaction sites can therefore be increased. Again, since sintering of the catalyst metal can be prevented by the support

material, the heat resistance of the catalyst improves. In addition, this enables pressure loss to be reduced. When the length of the catalyst support site is less than half the overall filter length, the regeneration rate declines, and the pressure loss increases when the filter is re-used since the PM is incompletely burned off. Again, when the length is more than 4/5 of the overall filter length, pressure loss increases and wastage of catalyst due to sintering increases; it is therefore more efficient to match the site supporting the support material to the catalyst support site.

[0051] According to the invention in (14), the support material comprises at least one material chosen from the group comprising alumina, zirconia, titania and silica; these ceramic oxides have a high specific surface area and are suitable for supporting catalyst. When titania in particular is chosen, it is possible to promote isolation of the sulphur components that interfere with catalyst activity from the ceramic support. Using the said oxides as a support material should be particularly effective when a catalyst-supporting filter is used to clean the exhaust gas from a diesel engine, since the fuel contains many sulphur components.

[0052] According to the invention in (15), acicular alumina is used as the support material thereby enabling individual coating on the particles that form the filter. It is therefore possible to reduce the pressure loss further than is possible with alumina that has been supported in such a way as to infill the pores on the cell wall, as in wash coating. The invention requires that the catalyst is allowed to react efficiently in part of the filter. The use of acicular alumina as support material is able to increase the degree of dispersion of the catalyst, promoter, NOx selective reduction catalyst and NOx occlusion catalyst, improving reactivity.

[0053] According to the invention in (16), a filter of superior heat resistance and thermal conductivity can be provided by using a filter containing silicon (Si).

[0054] According to the invention in (17), a filter of superior mechanical strength, heat resistance and thermal conductivity can be provided by using a porous body of any of silicon carbide, silicon nitride, cordierite, mullite, sialon or silica.

[0055] According to the invention in (18) and (19), it is possible to widen the reacting oxygen concentration range with a promoter, and to enhance the activity of the oxygen and effect oxidative clean up of PM, HC, CO, etc. By reducing the amount of promoter at the end reaching high temperature during regeneration when cleaning exhaust gas, it also possible to reduce wastage of catalyst due to sintering.

[0056] According to the invention in (20), it is possible to widen the reacting oxygen concentration range with a promoter, enhance the activity of the oxygen, and achieve oxidative clean up of PM, HC, CO, etc. Note here that when the length of the site supporting promoter is less than half the overall filter length, the regeneration rate declines and when the length is greater than 4/5 of the overall filter length, pressure loss increases and promoter is wasted; it is therefore more efficient to match the promoter to the catalyst support site.

[0057] According to the invention in (21)-(23), a more outstanding promoter effect can be obtained by using a promoter comprising rare earth oxides, alkali metals, alkaline earth metals, rare earth elements, and transition metal elements.

[0058] According to the invention in (24), the filter catalyst, promoter and catalyst support zones have the same length. A low pressure loss is thereby obtained, the respective zones exerting a synergistic effect for exhaust gas cleaning. Additionally, wastage of noble metal, etc, is eliminated.

[0059] According to the invention in (25), since the position at which the solution is applied can be identified, the catalyst can be easily supported from an end face of the filter in a zone extending from the end face for a predefined length towards the other end face of the filter.

[0060] According to the invention in (26), acicular alumina support material can be easily supported from an end face of the filter in a zone extending from the end face for a predefined length towards the other end face of the filter. The support material is coated in order to exploit the specific surface area of the catalyst; if coated to match the position where the catalyst is to be coated, therefore, support material will be coated in the correct amount to eliminate wastage, and a filter of low pressure loss and high specific surface area can be obtained.

[0061] According to the invention in (27), a rare earth oxide film can be easily supported on the filter from an end face in a zone extending from the end face of the filter for a predefined length towards the other end face. The rare earth oxide film widens the catalyst's reacting oxygen concentration range and enhances the activity of the oxygen; if coated to match the position where the catalyst is to be coated, therefore, the correct amount of rare earth oxide film to eliminate wastage will be coated and a filter of low pressure loss can be obtained.

[0062] According to the invention in (28), it is possible to oxidise trapped PM by raising the filter to high temperature installed in a diesel engine exhaust passage such that the end supporting a relatively large amount of catalyst faces the exhaust gas inlet side and the end

supporting relatively little or no catalyst faces the discharge side. It is also possible to clean the foul exhaust gas of highest PM concentration most efficiently from the inlet end.

[0063] According to the invention in (29), it is possible to oxidise trapped PM even at low exhaust gas temperature by installing the filter in a diesel engine exhaust passage such that the end supporting a relatively large amount of catalyst faces the exhaust gas inlet side and the end supporting relatively little or no catalyst faces the discharge side, and raising the filter to high temperature using a heater.

[0064] According to the invention in (30), the exhaust gas temperature and the filter temperature can be increased, enabling oxidative clean-up of PM without the use of a heater, burner, etc, by employing an engine system of post-injection type. "Post-injection" denotes injection of a small amount of fuel after the cylinder expansion stroke has commenced because of the main fuel injection and before the cylinder goes into the compression stroke; the exhaust gas temperature can be increased to not less than 450°C in diesel engines using this principle, which means the exhaust gas discharged from a post-injection diesel engine has a high temperature at entry to the filter, and the active temperature of the catalyst and the temperature of incipient combustion of graphite (ca. 600°C) are reliably attained in a shorter time.

[0065] According to the invention in (31), wastage of catalyst due to sintering can be reduced by having little catalyst at the end that attains high temperature during regeneration. It is also possible to clean the foul exhaust gas of highest PM concentration most efficiently from the inlet end.

[0066]

[Practical embodiment of the invention] A practical embodiment of the invention is described in detail hereunder with reference to the Drawings. As shown in Figures 1-3, the catalytic filter 10 in this embodiment possesses a ceramic support 15 comprising a porous, sintered silicon-containing ceramic, wherein cell walls 12 have been formed. The surfaces of each of the SiC particles 4 constituting the cell wall 12 have been individually coated to a predefined thickness with a catalyst coating layer 2. Although a ceramic, metal, or alloy filter can be used as the catalytic filter 10 in the embodiment, a ceramic is preferably used from the standpoint of weight, etc; particularly preferred is a filter comprising a silicon-containing ceramic, for example a porous, sintered silicon-containing ceramic, ideally silicon carbide.

[0067] It is preferred to use a columnar filter segmented via sealant layers for the catalytic filter 10. It is also desirable that the sealant has bonding power. Because the filter is segmented, heat may be rapidly transported to the rear.

[0068] The catalyst coating layer 2 is a layer wherein catalyst, promoter, NOx selective reduction catalyst, NOx occlusion catalyst, etc, have been supported on a support material. In this embodiment the aforesaid support material is a film 3 comprising alumina (Al_2O_3) (hereunder called alumina film). Provided it contains, other than alumina, at least one oxide chosen from zirconia (zirconium dioxide: ZrO_2), titania (titanium dioxide: TiO_2) and silica (silicon oxide: SiO_2), the material may be varied as desired.

[0069] Specifically, a single oxide material may be ZrO_2 , TiO_2 or SiO_2 . A dual oxide material may be $\text{Al}_2\text{O}_3/\text{ZrO}_2$, $\text{Al}_2\text{O}_3/\text{TiO}_2$, $\text{Al}_2\text{O}_3/\text{SiO}_2$, $\text{ZrO}_2/\text{TiO}_2$ or $\text{ZrO}_2/\text{SiO}_2$. A triple oxide material may be $\text{Al}_2\text{O}_3/\text{ZrO}_2/\text{TiO}_2$, $\text{Al}_2\text{O}_3/\text{ZrO}_2/\text{SiO}_2$, $\text{Al}_2\text{O}_3/\text{TiO}_2/\text{SiO}_2$ or $\text{ZrO}_2/\text{TiO}_2/\text{SiO}_2$. A quadruple oxide material may be $\text{Al}_2\text{O}_3/\text{ZrO}_2/\text{TiO}_2/\text{SiO}_2$.

[0070] A support wherein an organic binder, lubricant, plasticiser and water have been incorporated in an oxide[*sic*] ceramic like silicon carbide powder and silicon nitride powder, or a ceramic powder in the oxide ceramic category like sialon, mullite, cordierite, etc, mixed, extrusion formed and then sintered can be used as the nitrogen[*sic*]-containing ceramic support 15. A filter of wall flow honeycomb type as illustrated in Figures 1(a) and (b) and Figure 2 is thus formed.

[0071] An example where sintered SiC is used as a carbon-containing support 15 will be described here. The reason for adopting sintered SiC is that, compared with other ceramics, it has the advantages of outstanding mechanical strength, heat-resistance and thermal conductivity, and chemical stability. Consequently the filter has good heat response, very rapidly conducting the temperature of the filter, which varies with the exhaust gas, from the inlet end to the discharge end.

[0072] Japan Patent Kokai No. 2001-207836 teaches that a material of low thermal conductivity such as alumina, silica-alumina, zeolite, cordierite and laminar oxide can be used in the filter it describes; however, the filter becomes difficult to cool if a material of low thermal conductivity is used. Hence, at certain sites in the filter, the temperature becomes too high, catalyst sintering occurs, wasting catalyst, while at other sites, because the temperature is too low, the PM is incompletely burned off, resulting in poor regeneration.

[0073] The ceramic support 15 is constituted by sintered SiC of approximately square cross-sectional geometry wherein cells 11 have been regularly formed as a plurality of through-holes in the axial direction. The cells 11 are mutually separated by cell walls 12, the openings of each cell 11 being closed with a plug 14 at one end face with the other end face of the same cell 11 is left open, and are arranged so that the openings and plugs as a whole form a chequered pattern at each end face. A plurality of cells 11 of rectangular cross-section are formed in the ceramic support 15 comprising the sintered SiC. In other words, the ceramic support 15 has a honeycomb structure.

[0074] The density of the cells 11 is 200-350 per square inch. Thus, of the many cells 11, approximately half are open at the upstream end and the remainder are open at the downstream end, with the thickness of the cell walls 12 separating each of the cells 11 set at about 0.4 mm.

[0075] When such a ceramic support 15 is to be manufactured, a starting material is used wherein, for example, approximately 30 parts by weight of silicon carbide powder of mean pore diameter around 0.5 μm , approximately 6 parts by weight of methylcellulose binder to 100 parts by weight of ceramic powder, and approximately 25 parts by weight of dispersing solution comprising organic solvent and water to 100 parts by weight of ceramic powder are combined with 70 parts by weight of silicon carbide powder of mean pore diameter around 10 μm . The combined starting material is next mixed and then formed into a honeycomb shape by extrusion forming, whereupon some of the cells 11 are closed in a chequerboard pattern. The moulding is next dried and degreased, and then calcined for 4 hours at 2200°C in an inert atmosphere, thereby providing the desired ceramic support 15.

[0076] The most characteristic aspect of the constitution here embodied, as shown in Figure 5, is that in supporting the catalyst coating layer 2 on the surface of the cell walls 12 that substantially make up the ceramic support 15, one end of the filter 10 is provided with a catalyst support site supporting most catalyst while the other end is provided with a non-catalyst supporting site that supports little catalyst. The pressure loss can hence be reduced compared with supporting the catalyst coating layer 2 on the entire surface of the cell walls 12, and costs are reduced.

[0077] Although in this embodiment the catalyst coating layer 2 can be applied in areas that are not closed off as shown in Figure 5(a), it is also possible to apply the catalyst coating layer 2 in areas that are closed off as in Figure 5(b) by replacing the slurry of support material, promoter and catalyst supporting solution with a strongly penetrating slurry. Clean-up reactions of the gas components in the exhaust gas can thereby be effected. Since such

reactions are accompanied by evolution of heat, the temperature rises in the filter as a whole and regenerating efficiency can be increased.

[0078] It is also possible to impart gradation to the catalyst coating layer 2 as shown in Figure 5(c) by repeatedly impregnating the filter with the slurry of support material, promoter and catalyst supporting solution while shifting the impregnation zone. It is additionally possible to impart gradation to the catalyst coating layer 2 as shown in Figure 5(c) by impregnating with solutions of different concentration while shifting the impregnation zone. Again, as shown in Figure 5(d), it is possible to impart gradation to the catalyst coating layer 2 as far as the opposite end face of the ceramic support 15. This enables cleaning from the inlet end in keeping with the pollutant concentration of the exhaust gas, and efficient delivery of the heat from cleaning to the discharge end; also, the pressure loss is lower. The pressure loss characteristics when the catalyst coating layer 2 is only partially applied will now be described.

[0079] In general the pressure loss characteristics when exhaust gas passes through the cell walls 12 may be viewed as follows. Thus, the pressure loss when exhaust gas passes through the ceramic support 15 can be illustrated as in Figure 4, where the each of the resistances ΔP_1 , ΔP_2 and ΔP_3 depends on the filter cell structure and the value of $\Delta P_i = (\Delta P_1 + \Delta P_2 + \Delta P_3)$ denotes the initial pressure loss, which is constant irrespective of variations in accumulation, etc, of diesel particulates with time. ΔP_4 is the resistance when the exhaust passes through the accumulated diesel particulates and takes a value of at least 2-3 times the initial pressure loss.

[0080] Now when the whole surface is coated, the resistance to passage through the catalyst coating layer 2 increases in addition to the resistance ΔP_3 to passage through the interior of the cell wall 12. Furthermore, the aperture is smaller so that ΔP_1 also increases. Compared with an uncoated filter 10, therefore, the pressure loss will be markedly larger, and when particulates have accumulated in the filter 10 this tendency will be more prominent still.

[0081] However, when a catalyst support site supporting most catalyst is provided at one end of the filter 10 while a catalyst non-support site supporting little catalyst is provided at the other end, as in the present embodiment, it is possible to reduce both the resistance to passage through the catalyst coating layer 2 and the resistance ΔP_3 to passage through the interior of the cell wall 12. A lower pressure loss will therefore be possible than when the whole surface of the cell wall is coated. Unless the PM is completely burned off, however, a resistance ΔP_4 will develop, making it difficult to reduce pressure loss.

[0082] The resistance to washing when the filter has been partially coated with a catalyst coating layer will now be explained. The chief constituent of the particulates accumulated on the surface of the cell wall 12 is carbon, which can be oxidatively removed by means such as combustion. Even after combustion, however, some material remains as ash. Examples are material from oxidation or sulphation of compounds of Ca, Mg, Zn, etc, that have been added to the engine oil to function as neutralising agents or lubricants. Others are catalysts deposited along with the particulates, such as the CeO_2 and CuO pre-incorporated in the fuel for carbon combustion purposes. The said ash progressively accumulates with prolonged driving of the vehicle, increasing the pressure loss in the filter 10, which must therefore be washed with pressurised water, etc; wherein the ash can be completely removed on washing at a pressure of not less than 30 kg/cm^2 . When most catalyst is supported at one end of the filter 10 while little catalyst is supported at the other end, as in the present embodiment, the resistance in the catalyst-free areas decreases; the cleaning capacity with pressurised water, etc, therefore increases, and the ash can be reliably removed.

[0083] The acicular alumina used in the present embodiment will be explained. This refers to coating the surface of the cell walls 12 substantially constituting the ceramic support 15, particularly the surface of the SiC particles 4 constituting the said cell walls 12, with an alumina film 3. More accurately, it appertains to the SiC particles 4 constituting the said cell walls 12, and refers to coating the surface of each SiC particle 4 individually with an alumina film 3 by assorted means.

[0084] Figures 6(a) and (b) show a catalytic filter manufactured by the prior art wherein the catalyst coating layer 2 is formed as a uniform coating on the surface of the cell wall 12 by the wash coat process; and Figures 3(a) and (b) are diagrams of the ceramic support 15 used in the present embodiment, showing the situation where an alumina film 3 has been individually coated on the surface of each SiC particle 4 making up the cell wall.

[0085] Thus, in the catalytic filter 10 in the embodiment, the surface of the cell wall 12 is not simply coated uniformly with the catalytic coating layer 2 as heretofore. When the cell wall 12 is coated uniformly as heretofore, for example, the gaps between the SiC particles 4 are closed off, which means that permeability is obstructed owing to blockage. In contrast, the ceramic support 15 used in the embodiment is so constructed that the surface of each SiC particle 4 making up the cell wall 12 is coated individually with an alumina film 3.

[0086] Accordingly, in the case of the embodiment, the pores in the cell wall 12 itself, i.e. the gaps formed between each of the SiC particles 4, can never be completely closed off, and since the pores are maintained intact as pores, the pressure loss is quite small compared with

a conventional catalyst coating layer 2. Moreover, the embodiment also has superior heat resistance, and since the alumina film 3 individually coats the SiC particles 4 themselves, detachment of the alumina film 3 from the cell wall 12 due to washing, for example, does not arise; as a result, washing resistance is outstanding. Furthermore, because the area over which the exhaust gas makes contact with the catalyst is larger, oxidation of the CO and HC in the exhaust gas can be accelerated.

[0087] The pressure loss characteristics of the alumina film 3 will therefore be described. As noted above, the initial pressure loss is $\Delta P_i = (\Delta P_1 + \Delta P_2 + \Delta P_3)$. ΔP_4 is the resistance to passage through the accumulated diesel particulates and takes a value at least 2-3 times greater than the initial pressure loss.

[0088] The specific surface area of a ceramic support 15 with a 14/200 cell structure is $8.931 \text{ cm}^2/\text{cm}^3$, and since the density of the ceramic support is 0.675 g/cm^3 , the specific surface area of the cell walls 12 works out to $0.0013 \text{ m}^2/\text{g}$. On the other hand, as measured by mercury porosimeter, the specific surface area of the fine pores in the cell wall 12 is $0.12 \text{ m}^2/\text{g}$, an approximately 50-100 fold greater surface area. This means that in forming an alumina film 3 of the same weight on the surface of the cell wall 12, the thickness of alumina film 3 needed to obtain the same effect when the surface of each SiC particle 4 making up the cell wall 12 is individually coated can be reduced to 1/50-1/100 compared with when the surface of the cell walls 12 are simply given a uniform coating.

[0089] When a uniform alumina film 3 is formed by wash coating, a thickness of $50 \text{ }\mu\text{m}$ is required for coating with the 3 wt% or so of alumina necessary for catalyst activity; in the present embodiment, however, around $0.5 \text{ }\mu\text{m}$ suffices when alumina is coated on the surface of the SiC particles 4 making up the cell wall 12.

[0090] Consequently, in addition to the resistance ΔP_3 to passage through the interior of the cell wall 12, the resistance to passage through the catalyst coating layer 2 can be reduced; moreover, the aperture decreases[*sic*] so that ΔP_1 can also be made smaller. The pressure loss therefore decreases markedly compared with a filter 10 wherein a uniform alumina film 3 has been formed by wash coating, this trend becoming even more noticeable when particulates accumulate on the filter 10.

[0091] The wash resistance of the alumina film 3 will now be explained. As noted above, ash accumulates on the surface of the cell walls 12, necessitating washing with pressurised water, etc. Note here that alumina coating of the surface of the cell walls 12 by wash coating gives a thick coating layer due to physical adsorption, and much of this is detached during washing.

In the alumina film 3 of the present embodiment, however, the alumina is thinly and individually coated on the surface of each of the SiC particles making up the ceramic support 15, and as Si supplied from the SiC making up the ceramic support 15 also combines chemically therewith, a state is assumed wherein the individual SiC particles tightly cohere. They are accordingly highly cohesive with great resistance to washing, and as a coating, therefore, they have strong endurance.

[0092] The heat resistance of the alumina film 3 will now be explained. In general, alumina has a high specific surface area, making it suitable as a catalyst-supporting film. In particular, given that it is now wished to develop a catalytic filter 10 of high heat resistance that functions stably at higher temperatures, higher heat resistance is required of the alumina film 3. As well having alumina particles of fibrillar geometry, therefore, it was decided to incorporate a rare earth oxide such as ceria (cerium oxide). Having alumina particles of fibrillar geometry means there are fewer points of contact between neighbouring alumina fibrils, and inhibits grain growth via reduction in the rate of combustion, increasing the specific surface area and enhancing heat resistance.

[0093] Heat resistance is also improved by the addition of ceria, etc. This is because new compounds are formed on the surface of the crystal grains constituting the alumina film 3, hindering the growth of alumina particles. Heat resistance is also enhanced because Si supplied during heat treatment from the SiC, and from the SiO₂ present at the extreme surface layer, has the effect of blocking the mass transfer pathway. Research by the inventors has shown that heat resistance further improves when an oxide film is intentionally formed by treating SiC at high temperature.

[0094] The regeneration characteristics afforded by the ordinary catalysts that may be used in the present embodiment will now be considered. Although in itself the DPF serving as exhaust gas cleaning filter simply has the function of trapping PM at the cell walls 12, oxidative degradation of the hydrocarbon (HC), carbon monoxide (CO), etc, in the exhaust gas can be achieved by supporting a catalyst component therein. Active catalyst components comprising noble metals including Pt, Pd and Rh are known catalysts of this kind. The catalysts bring about oxidation by activating the oxygen in the exhaust gas.

[0095] The further addition of rare earth oxides such as ceria (CeO₂) and lanthana (La₂O₃) not only improves the heat resistance of the alumina but performs the role of regulating the oxygen concentration at the catalyst surface. As a result, a brisk supply of oxygen into the exhaust gas is created, the efficiency in burning off diesel particulates adhering to the filter 10 improves, and hence the regeneration rate of the catalyst support is markedly improved.

[0096] In general, the HC or CO present in the exhaust gas is removed by oxidation and NO_x is removed by reduction. Since combustion in a diesel engine is normally accomplished with excess air present, the exhaust gas contains a large amount of excess air. Thus, if the air-fuel ratio of the exhaust gas is taken to be the ratio of the air to the fuel that are fed into the intake passage and fuel chamber, the said ratio lies in the lean region. However, since the PM discharged from the diesel engine enters a partially oxygen deficient state on contact with the catalyst surface, the ratio temporarily passes into the rich region. Thus, the operating environment at the catalyst surface will fluctuate wildly.

[0097] The ceria added to the catalyst has a relatively small Ce³⁺/Ce⁴⁺ redox potential and the reaction $2\text{CeO}_2 \rightleftharpoons \text{Ce}_2\text{O}_3 + \frac{1}{2}\text{O}_2$ proceeds reversibly. Thus, when the exhaust gas enters the rich region (oxygen deficient region) the above reaction proceeds to the right and oxygen is delivered into the environment; conversely when the gas enters the rich region (oxygen excess region) the reaction proceeds to the left and excess oxygen is occluded from the environment. By regulating the oxygen concentration in the environment, the ceria thus has the function of widening the range of air-fuel ratio wherein hydrocarbon, carbon monoxide or NO_x can be efficiently removed.

[0098] The ceria oxygen at the cell walls 2 of the filter 10 can oxidise the PM more efficiently than the oxygen in the exhaust gas since the ceria is in direct contact with the trapped PM. Moreover, because it supports noble metal catalyst, the ceria here increases the OSC (oxygen storage capability). That is to say, the aforesaid OSC increases because the catalyst (noble metal) activates both the oxygen in the exhaust gas and the oxygen at the ceria surface in proximity to the noble metal.

[0099] The graphs in Figure 7 show the results from examination of regeneration characteristics in relation to the effect of adding rare earth oxides such as ceria to the alumina film 3. Reference Example 1 is for a catalytic filter 10 with a catalyst of Pt (3.5 g/L), promoter of CeO₂ (40 wt%), and support material of acicular Al₂O₃ (1 wt%). Reference Example 2 is for a catalytic filter 10 using Pt (3.5 g/L)/acicular Al₂O₃ (1 wt%). Reference Example 3 is for a catalyst filter 10 using only Pt (3.5 g/L). The experiment consisted in housing the diesel particulate filter with soot deposited thereon (DPF, overall length 150 mm) in an electric oven and then heating to 650°C, connecting a diesel engine set at an engine speed of 1100 rpm and engine load of 3.9 Nm, taking the exhaust gas therefrom (350°C) to the said filter and examining the changes in filter temperature (measured at a point 145 mm from the inlet).

[0100] As shown in Figure 7, in Reference Example 3 (Pt alone), O₂ was found to be rate-determining and the temperature peaked at 50 sec-680°C; in Reference Example 2 (with alumina (coating) and Pt but not ceria (promoter)), O₂ was again rate-determining and the temperature peaked 60 sec-750°C. However, in Reference Example 1 (with alumina (coating), Pt and ceria (promoter)), O₂ was rate-determining and the filter rapidly attained a high peak temperature at 50 sec-900°C, from which it is clear that there is a high efficiency for oxidative removal of soot, indicating a high regeneration rate.

[0101] The graphs in Figure 9 compare the actual regeneration rates. Clearly, the effect is outstanding in Reference Example 1 (the catalyst containing ceria). The regeneration rate is here the ratio of the weight of soot accumulated in the DPF that has been removed (“regenerated”) to the weight of soot accumulated, expressed as a percentage. It follows that the best arrangement has alumina, catalyst and promoter on the ceramic support 15 as illustrated by Reference Example 1.

[0102] Note in regard to the aforesaid rare earth oxide that, rather than the simple oxide (CeO₂) in the aforementioned example, it is preferred to use a complex oxide of the rare earth element and zirconium, for example. The rationale for this is that the oxygen concentration control characteristic improves when zirconium oxide is contained in the rare earth oxide, owing to inhibition of grain growth in the rare earth oxide.

[0103] The aforesaid rare earth oxide in the form of a complex oxide with zirconium is preferably given a particle size of the order of 1-30 nm; more preferable still is a size of 2-20 nm. This is because a complex oxide of particle size less than 1 nm is difficult to produce. On the other hand, if the particle size exceeds 30 nm, the particles become susceptible to sintering; the particle surface area therefore decreases, the area of contact with the exhaust gas then diminishes and the problem of declining activity persists. Another potential problem is that pressure loss during passage of exhaust gas will increase.

[0104] It is desirable to support elements chosen from the noble metals, periodic table Groups VIa elements and periodic table Group VIII elements as the aforesaid catalyst. Specifically, the elements may be listed as platinum (Pt), palladium (Pd), rhodium (Rh), nickel (Ni), cobalt (Co), molybdenum (Mo), tungsten (W), cerium (Ce), copper (Cu), vanadium (V), iron (Fe), gold (Au), silver (Ag), etc., wherefrom at least one element or compound thereof may be chosen.

[0105] For example, a binary alloy or ternary alloy derived by combination of the aforesaid elements is used as the said compound. The alloys are advantageously used with the

aforementioned rare earth oxide such as the ceria or lanthana serving as promoter. A catalytic filter 10 thus constituted has excellent durability since it experiences little degradation by poisoning (lead poisoning, phosphorous poisoning, sulphur poisoning) and little thermal degradation. Other than alloy combinations of the aforesaid elements, the compound may be derived by combination with other elements (an oxide, nitride, or carbide).

[0106] Examples of binary compounds in this context are Pt/Pd, Pt/Rh, Pt/Ni, Pt/Co, Pt/Mo, Pt/W, Pt/Ce, Pt/Cu, Pt/V, Pt/Fe, Pt/Au, Pt/Ag, Pd/Rh, Pd/Ni, Pd/Co, Pd/W, Pd/Ce, Pd/Cu, Pd/V, Pd/Fe, Pd/Au, Pd/Ag, Rh/Ni, Rh/Co, Rh/Mo, Rh/W, Rh/Ce, Rh/Cu, Rh/V, Rh/Fe, Rh/Au, Rh/Ag, Ni/Co, Ni/Mo, Ni/W, Ni/Ce, Ni/Cu, Ni/V, Ni/Fe, Ni/Au, Ni/Ag, Co/Mo, Co/W, Co/Ce, Co/Cu, Co/V, Co/Fe, Co/Au, Co/Ag, Mo/W, Mo/Ce, Mo/Cu, Mo/V, Mo/Fe, Mo/Au, Mo/Ag, W/Ce, W/Cu, W/V, W/Fe, W/Au, W/Ag, Ce/Cu, Ce/V, Ce/Fe, Ce/Au, Ce/Ag, Cu/V, Cu/Fe, Cu/Au, Cu/Ag, V/Fe, V/Au, V/Ag, Fe/Au, Fe/Ag and Au/Ag.

[0107] Examples of ternary compounds are Pt/Pd/Rh, Pt/Pd/Ni, Pt/Pd/Co, Pt/Pd/Mo, Pt/Pd/W, Pt/Pd/Ce, Pt/Pd/Cu, Pt/Pd/V, Pt/Pd/Fe, Pt/Pd/Au, Pt/Pd/Ag, Pt/Rh/Ni, Pt/Rh/Co, Pt/Rh/Mo, Pt/Rh/W, Pt/Rh/Ce, Pt/Rh/Cu, Pt/Rh/V, Pt/Rh/Fe, Pt/Rh/Au, Pt/Rh/Ag, Pt/Ni/Co, Pt/Ni/Mo, Pt/Ni/W, Pt/Ni/Ce, Pt/Ni/Cu, Pt/Ni/V, Pt/Ni/Fe, Pt/Ni/Au, Pt/Ni/Ag, Pt/Co/Mo, Pt/Co/W, Pt/Co/Ce, Pt/Co/Cu, Pt/Co/V, Pt/Co/Fe, Pt/Co/Au, Pt/Co/Ag, Pt/Mo/W, Pt/Mo/Ce, Pt/Mo/Cu, Pt/Mo/V, Pt/Mo/Fe, Pt/Mo/Au, Pt/Mo/Ag, Pt/W/Ce, Pt/W/Cu, Pt/W/V, Pt/W/Fe, Pt/W/Au, Pt/W/Ag, Pt/Ce/Cu, Pt/Ce/V, Pt/Ce/Fe, Pt/Ce/Au, Pt/Ce/Ag, Pt/Cu/V, Pt/Cu/Fe, Pt/Cu/Au, Pt/Cu/Ag, Pt/V/Fe, Pt/V/Au, Pt/V/Ag, Pt/Fe/Au, Pt/Fe/Ag and Pt/Au/Ag.

[0108] If an NO_x selective reduction catalyst component or occlusion catalyst component capable of reducing NO_x in an oxidising environment like diesel exhaust gas (hereinafter abbreviated to NO_x catalyst) is additionally supported, it is further possible to reduce NO_x. Although "NO_x catalyst" has hitherto meant a zeolite partially substituted with an alkali metal element, and having a metal element (Pt, Au, Cu, Ag) added thereto, whereby NO_x is reduced to N₂ on discharge of reducing agent into the oxidising environment, it has been found that the recently adopted NO_x occlusion catalysts not only occlude and reduce NO_x but, by discharging active oxygen, serve also to oxidise PM; they are advantageous as diesel engine clean-up catalysts and will therefore be described in detail below.

[0109] The term NO_x occlusion catalyst refers to a catalyst wherein, in addition to a noble metal like platinum (Pt), elements chosen from among alkali metal elements (periodic table Group Ia), alkaline earth metal elements (elements of periodic table Group IIa), rare earth elements (periodic table Group IIIb) and transition metal elements have been supported as an active oxygen release agent. An active oxygen release agent promotes oxidation of

particulates by releasing active oxygen; ideally it takes up oxygen when excess oxygen is present in the surroundings, retains the oxygen, and releases the retained oxygen in the form of active oxygen when the surrounding oxygen concentration falls.

[0110] Specifically, the aforesaid elements that are active oxygen release agents may be listed as lithium (Li), sodium (Na), potassium (K), cerium (Ce), beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba), scandium (Cs), yttrium (Y) and lanthanum (La), wherefrom at least one element or compound thereof may be chosen.

[0111] However, to act effectively as an active oxygen release agent, it is desirable to use an alkali metal or alkaline earth metal with a greater tendency to ionisation than calcium (Ca). The description will in this case use platinum (Pt) and lithium (Li) as an example but a similar mechanism obtains if other noble metals, alkali metal elements (periodic table Group Ia), alkaline earth metal elements (elements of periodic table Group IIa), rare earth elements (periodic table Group IIIb) and transition metal elements are selected.

[0112] Since combustion usually takes place under air excess conditions in a diesel engine, the exhaust gas contains much excess air. Thus, if the ratio of air to fuel fed into the intake passage and combustion chamber is defined as the air-fuel ratio of the exhaust gas, the said ratio will be lean. Since NO is evolved in the combustion chamber, the exhaust gas contains NO. Furthermore, sulphur (S) contained in the fuel (gas oil) will form SO₂ by reaction with oxygen in the combustion chamber. Hence, the exhaust gas contains SO₂. It follows that in a diesel engine exhaust gas containing excess oxygen, NO and SO₂ enter the filter on the exhaust upstream side.

[0113] Figures 8(a)-(c) are enlarged views representing in schematic fashion the events at the exhaust gas contact surface of the filter. The symbol 20 in Figures 8(a) and (b) indicates a particle of platinum (Pt), and 21 indicates the active oxygen release agent containing lithium (Li). Thus, as the inflowing exhaust gas has a large oxygen excess, excess oxygen O₂ adheres to the surface of the platinum (Pt) 20 as O²⁻ and O₂⁻ as shown in Figure 8(a). The NO in the inflowing exhaust gas reacts with the O²⁻ and O₂⁻ to form NO₂ (2NO+O₂ → 2NO₂). Part of the NO₂ thus produced is further oxidised on the platinum (Pt), while also being absorbed in the active oxygen release agent and combining with lithium oxide (Li₂O). As a result, it is dispersed as nitrate ion NO₃⁻ in the active oxygen release agent, producing lithium nitrate (LiNO₃).

[0114] Thus, in this working example, the harmful NO gas contained in the exhaust gas absorbs in the active oxygen release agent and the amount emitted into the ambient air can be

vastly reduced. Again, as hereinbefore noted, the exhaust gas also contains SO_2 and this too is absorbed in the active oxygen release agent by a similar mechanism to NO . Thus, as shown in Figure 8(b), excess oxygen O_2 adheres to the surface of the platinum (Pt) 20 as O^{2-} and O_2^- while the SO_2 in the inflowing exhaust gas reacts with the O^{2-} and O_2^- to form SO_3 ($2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$). Part of the SO_3 formed in this way is further oxidised on the platinum (Pt) and is absorbed in the active oxygen release agent, combining with lithium oxide (Li_2O). As a result, it is dispersed as sulphate ion SO_4^{2-} in the active oxygen release agent, producing lithium sulphate (Li_2SO_4). Lithium nitrate (LiNO_3) and lithium sulphate (Li_2SO_4) are thus produced in the active oxygen release agent.

[0115] The PM 22 in the exhaust gas adheres to the surface of the active oxygen release agent supported on the filter as shown in Figure 8(c). The oxygen concentration at the surface of contact between the PM and active oxygen release agent then falls. When the oxygen concentration falls, a difference in oxygen concentration arises in the interior of the active oxygen release agent whereupon the oxygen within the active oxygen release agent tends to migrate towards the surface of contact between the PM and active oxygen release agent. As a result, the lithium nitrate (LiNO_3) formed within the active oxygen release agent is decomposed to lithium (Li), oxygen (O) and NO ; the oxygen (O) proceeds to the surface of contact between the PM 22 and the active oxygen release agent 21 and is liberated from the active oxygen release agent 21. The NO released is oxidised on the platinum (Pt) and reabsorbed in the active oxygen release agent 21. Obviously it can also react with unburned HC and CO, which react more readily than PM, to be discharged as N_2 .

[0116] Meanwhile, the lithium sulphate (Li_2SO_4) formed within the active oxygen release agent 21 is similarly decomposed to lithium (Li), oxygen (O) and SO_2 , the oxygen (O) proceeds to the surface of contact between the PM 22 and active oxygen release agent 21, and SO_2 is liberated from the active oxygen release agent 21. The SO_2 liberated is oxidised on the platinum (Pt) and reabsorbed in the active oxygen release agent. However, since lithium sulphate (Li_2SO_4) is stable, the active oxygen is difficult to release compared with lithium nitrate (LiNO_3). To decompose the sulphate, therefore, a support material containing titania is chosen; it is then possible to promote elimination from the ceramic support of the sulphur components hindering catalyst activity.

[0117] Moreover, the oxygen (O) that makes its way to the surface of contact between the PM 22 and active oxygen release agent 21 is oxygen decomposed from compounds such as lithium nitrate (LiNO_3) and lithium sulphate (Li_2SO_4). Oxygen (O) decomposed from compounds is highly energetic and has very high activity. Accordingly, the oxygen making its way to the surface of contact between the PM 22 and active oxygen release agent 21

constitutes active oxygen (O). Active oxygen (O) that oxidises the particulates 22 is also released when NO and SO₂ are absorbed into the active oxygen release agent 21.

[0118] Now since the platinum 20 (Pt) and active oxygen release agent 21 are activated more the higher the filter temperature, the amount of active oxygen (O) released from the active oxygen release agent 21 per unit time increases the higher the filter temperature; oxidative removal would also be expected to be easier the higher the temperature of the PM itself. Hence, the quantity of microparticles capable of oxidative removal that can oxidatively remove the PM 22 on the filter increases the higher the temperature of the PM 22.

[0119] Although it is in essence desirable to effect 100% regeneration of the filter with active oxygen, PM will always remain unburned when the temperature is low in respect of the PM and the amount of active oxygen is low. Since a vicious circle develops when PM proceeds to accumulate on the unburned PM, the need ultimately arises to raise the temperature, thereby raising the temperature of the PM itself and increasing its activity.

[0120] The invention is characterised in that locating more catalyst in the upstream part than in the downstream part encourages release of active oxygen in the upstream part of the filter, where there is inevitably a strong tendency for the temperature to be lower, and thereby promotes oxidation of PM regardless of the low temperature. Again, since the exhaust gas from a diesel engine is basically an oxygen excess environment as hereinbefore noted, PM trapped by the filter makes contact with the active oxygen release agent present at the filter surface. Oxidation reactions are therefore initiated even during operation under rich conditions by the active oxygen released from the active oxygen release agent.

[0121] PM oxidation reactions are normally accompanied by evolution of heat, which means that in addition to gaseous conduction by the exhaust gas, and allied with conduction in the solid that forms the filter in the case of a filter with high thermal conduction as herein petitioned, the heat instantly propagates, raising the temperature at the filter discharge end.

[0122] Consequently, with an NO_x occlusion-reduction catalyst of this kind, rise in temperature occurs at the exhaust gas discharge end regardless of the position of the heater. Even if the amount of catalyst supported at the discharge end is reduced, therefore, the regeneration system functions because the amount of catalyst supported at the inlet end has been relatively increased.

[0123] The procedure for coating the alumina film 3, promoter, and catalyst on the surface of the SiC particles 4 making up the aforesaid ceramic support 15 will now be described. Specifically, the processes (A), (B) and (C) set out hereunder are practised in that order.

[0124] (A) Alumina coating process

Solution impregnation step

This step comprises treatment for coating with an alumina film by impregnating the respective surfaces of the ceramic support 15 constituting the cell walls 12 by the sol-gel process using a solution of a metal compound containing aluminium, for example an aqueous solution of aluminium nitrate.

[0125] As to the aforesaid aqueous solution, an inorganic metal compound or organic metal compound may serve as the starting compound for the solution of aluminium-containing compound. $\text{Al}(\text{NO}_3)_3$, AlCl_3 , AlOCl , AlPO_4 , $\text{Al}_2(\text{SO}_4)_3$, Al_2O_3 , $\text{Al}(\text{OH})_3$, Al , etc. may be used as the inorganic metal compound; in particular, $\text{Al}(\text{NO}_3)_3$ and AlCl_3 are ideal since they readily dissolve in solvents such as alcohol and water and are easily handled.

[0126] Examples of organic metal compound are metal alcoholates, metal acetylacetonates, and metal carboxylates. $\text{Al}(\text{OCH}_3)_3$, $\text{Al}(\text{OC}_2\text{H}_5)_3$ [*sic*], and $\text{Al}(\text{iso-OC}_3\text{H}_7)_3$ serve as specific examples. As solvent for the aforesaid mixed solution, a mixture of at least more than one of water, alcohols, diols, polyhydric alcohols, ethylene glycol, ethylene oxide, triethanolamine, xylene, etc. is used taking into account the solubility of the aforesaid metal compounds. Hydrochloric acid, sulphuric acid, nitric acid, acetic acid or hydrofluoric acid can also be added as a catalyst when making the solution.

[0127] $\text{Al}(\text{NO}_3)_3$ can be cited as an example of the metal compounds preferred in the present embodiment; these dissolve in solvents at a relatively low temperature and stock solutions are easily prepared. 1,3-Butanediol may be cited as an example of the preferred solvents, firstly because it has a suitable viscosity and in the gelled state a gel film of suitable thickness can be applied to the SiC particles 4, and secondly because the solvent forms a metal alkoxide in solution and so readily forms the precursor of a metal oxide polymer derived by oxygen-metal-oxygen bonding, i.e. a metal oxide gel.

[0128] The preferred amount of $\text{Al}(\text{NO}_3)_3$ is 10-50 wt%. This is because an amount of alumina of sufficient surface area to maintain prolonged catalyst activity cannot be supported at less than 10 wt%, while at more than 50 wt% a large amount of heat is evolved during dissolution, leaving the solution susceptible to gelation. A temperature of 50-130°C is desirable when an impregnating solution of the aforesaid metal compound is being prepared.

This is because the solute has low solubility at less than 50°C, while above 130°C the reaction proceeds rapidly to gelation and the product is unusable as a coating solution. A stirring time of 1-9 hours is desirable. This is because the viscosity of the solution is stable within the aforesaid range.

[0129] It is important in the present embodiment to effect partial impregnation and fixing of the solution of metal compound prepared as just described. For this reason, a predefined time is allowed for impregnation in the vessel to the point desired for loading the ceramic support 15 (filter 10) (for example, in a zone extending for 2/3 of the overall length of the filter from one end face of the filter 10 to the other). Areas where the solution has and has not deposited are thereby defined, providing a support site and non-support site. The process then proceeds to the drying step.

[0130] Drying step

This step comprises treatment whereby NO₂ and other volatile components are removed by evaporation, the solution is gelled and immobilised at the ceramic particle surface, and at the same time excess solution is removed; it entails heating at 120-170°C for around 2 hours. If the heating temperature is below 120°C the volatile components are difficult to evaporate, while if the temperature is higher than 170°C the thickness of the gelled layer is uneven.

[0131] Precalcination step

This step comprises precalcination treatment to remove residual components and form an amorphous alumina film 3; wherein heating at a temperature of 300-500°C is desirable. Thus, if the precalcination temperature is below 300°C it is difficult to remove residual organic matter, while above 500°C the Al₂O₃ crystallises and short fibrous projections of boehmite can no longer be formed by subsequent hydrothermal treatment.

[0132] Hydrothermal treatment step

This step comprises treatment whereby the precalcined filter 10 is immersed in hot water in order to fashion the aforementioned structure of the alumina film 3 unique to the present embodiment. When subjected to such hydrothermal treatment, the particles of the amorphous alumina film surface undergo immediate peptization and are released into the solution in sol form, while the boehmite particles formed by hydration condense into short fibrous protrusions, creating a state stable towards peptization.

[0133] Thus, the alumina deposited by the hydrothermal treatment on the surface of the individual ceramic particles densely covers the surface in short fibrous form (acicular particles), providing a rough surface of so-called flocked structure. An alumina film of high

specific surface area is therefore formed. The temperature of the aforesaid hydrothermal treatment is preferably 50-100°C. Hydration of the amorphous alumina film 3 does not proceed if the temperature is below 50°C, and short fibrous projections of boehmite do not form. If the temperature is higher than 100°C, on the other hand, water evaporates, making it difficult to maintain the treatment step for long. The treatment time should be not less than 1 hour, since hydration of amorphous alumina is inadequate if the time is shorter than 1 hour.

[0134] Final calcination step

In this step the boehmite formed by hydration is treated to dehydrate it to alumina crystals. The preferred temperature in final calcination is 500-1000°C, with treatment for 5-20 hours. Crystallisation does not proceed when the temperature is lower than 500°C, while if the temperature is higher than 1000°C crystallisation proceeds too far, and the surface area tends to decrease.

[0135] The following process may also be noted as an alternative method of support. Thus, as a method of preparing the solution, a powder of the support material is finely comminuted with a grinder or the like and the solution is prepared by agitating and mixing the powder of support material with solvent. Specifically, a powder of an oxide such as alumina, titania and zirconia is produced by the sol-gel process, etc. For use as the catalyst coating layer, material having the highest possible specific surface area is best used, and it is desirable to select material of specific surface area preferably not less than 250 m²/g. Because of the high specific surface area, it is desirable to choose γ -alumina.

[0136] An inorganic binder such as hydrated alumina, alumina sol or silica sol is added to the powder, around 5-20 wt% of a solvent such as pure water, water, alcohol, diol, polyhydric alcohol, ethylene glycol, ethylene oxide, triethanolamine, or xylene, is added, and the mixture is comminuted and agitated. In practice, the oxide used as support material is comminuted until no larger than about 500 nm. By finely comminuting the material, it is possible to form the alumina film 3 uniformly on the particles, unlike the catalyst coating layer 13 afforded by a wash-coat of the prior art on the surface layer of the cell walls 12.

[0137] The aforesaid powder-loaded solution of metal oxide is partially impregnated as described earlier. The product is dried by heating at 110-200°C for around 2 hours whereupon final calcination is carried out. The preferred final calcination temperature is 500-1000°C, with treatment for 1-20 hours. Crystallisation does not proceed when the temperature is lower than 500°C, while if the temperature is higher than 1000°C crystallisation proceeds too far and the surface area tends to decrease. The loading can be calculated by measuring the weight before and after these steps.

[0138] Prior to alumina impregnation, a treatment of heating and oxidation for 5-100 hours at 800-1600°C may be applied to provide the amount of Si necessary to encourage chemical bonding with alumina at the respective surfaces of the SiC particles 4. Treatment in this way enables sufficient SiO₂ to form at the surface to supply Si, and does not impair the pressure loss characteristic since the porosity and pore size of the ceramic support 15 are left virtually intact.

[0139] (B) Process for supporting promoter and NO_x catalyst

Solution impregnation step

This step comprises treatment to apply a rare earth oxide film, or film containing an alkali metal, alkaline earth metal, rare earth element and transition metal element, to the surface of the ceramic support 15 constituting the cell walls 12 by respectively impregnating with solutions of metal compounds containing a rare earth element, for example aqueous solutions of cerium nitrate and lithium acetate, by the sol-gel process. Of the aforesaid aqueous solutions, Ce(NO₃)₃, CeCl₃, Ce₂(SO₄)₃, CeO₂, Ce(OH)₃, Ce₂(CO₃)₃, etc, are used for the solution of a cerium-containing compound.

[0140] As solvent for the aforesaid mixed solutions, a mixture of at least more than one of water, alcohols, diols, polyhydric alcohols, ethylene glycol, ethylene oxide, triethanolamine, xylene, etc, is used taking into account the solubility of the aforesaid metal compounds. Hydrochloric acid, sulphuric acid, nitric acid, acetic acid or hydrofluoric acid can also be added as a catalyst when making the solution. Furthermore, besides the rare earth oxide, one of or a compound of Li, K, Ca, Sr, Ba, La, Pr, Nd, Si and Zr may be added to the starting material to enhance the heat resistance of the alumina film 3.

[0141] Ce(NO₃)₃ can be cited as an example of the preferred metal compounds in the present embodiment; these dissolve in solvents at a relatively low temperature and stock solutions are easily prepared. Ethylene glycol is recommended as an example of the preferred solvents. This is because it has a suitable viscosity and a gel film of suitable thickness can be applied to the SiC particles 4. The amount of Ce(NO₃)₃ preferred is 1-30 wt%. Soot oxidation cannot be promoted at less than 1 wt%, and when the amount is greater than 30 wt% grain growth of CeO₂ occurs after sintering.

[0142] The proportion in which Al(NO₃)₃ and Ce(NO₃)₃ are combined is preferably set at 10:2. This is because the degree of dispersion of CeO₂ particles after calcination can be improved by making the proportion Al(NO₃)₃ rich. A temperature of 50-130°C is desirable when an impregnating solution of the aforesaid metal compounds is being prepared. The

solute has low solubility below 50°C, while above 130°C the reaction proceeds rapidly to gelation, making the product unusable as a coating solution. A stirring time of 1-9 hours is desirable. This is because the viscosity of the solution is stable within the aforesaid range.

[0143] Besides the foregoing example in respect of the aforesaid cerium-containing metal compound $\text{Ce}(\text{NO}_3)_3$, it is preferable to use $\text{ZrO}(\text{NO}_3)_2$ or ZrO_2 , for example, as the zirconium source to produce a complex oxide or solid solution with zirconium, and obtain the aforesaid complex oxide by dissolving the compounds in water or ethylene glycol to form a mixed solution, impregnating with the mixed solution, and then drying and calcining.

[0144] It is important in the present embodiment to partially impregnate and fix the solution of metal compounds prepared as just described. For this reason, a predefined time is set for impregnation to the point desired for loading the ceramic support 15 (filter 10) in the vessel (for example, the zone extending from one end face of the filter 10 towards the other end face for 2/3 of the overall length of the filter). Areas where the solution has and has not deposited are thereby defined, providing a support site and non-support site. Thereafter, the process proceeds to the drying step.

[0145] Drying step

This step comprises treatment whereby NO_2 and other volatile components are removed by evaporation and the solution is dispersed and immobilised at the ceramic particle surface while excess solution is removed, and entails heating at 120-170°C for around 2 hours. If the heating temperature is below 120°C the volatile components are difficult to evaporate, while if the temperature is higher than 170°C dispersion is uneven.

[0146] Calcination step

This step comprises calcination treatment to remove residual components and form CeO_2 on the alumina film 3; heating for 1-2 hours at a temperature of 500-800°C in a nitrogen atmosphere is desirable. It is difficult to remove residual organic matter if the precalcination temperature is below 500°C, while above 800°C grain growth occurs.

[0147] (C) Supporting the catalyst (active component)

A rare earth oxide-containing alumina film 3, for example, is coated on the surface of the SiC ceramic support 15 (filter 10), and an active component of Pt, etc, is supported on the irregular surface of the alumina film 3. The amount of active component supported is here determined so that the surface begins to be wetted slightly on impregnating with the aqueous solution containing Pt, etc, by an amount equal to the water absorption of the support.

[0148] As an example of the water absorption retained in the SiC ceramic support 15, suppose the observed water absorption of the dry support is 22.46 wt%. If the support has a mass of 110 g and volume of 0.163L, the support will absorb 24.7 g/L of water. A dinitrodiammine platinum nitrate solution ($[\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2]\text{HNO}_3$, Pt concentration 4.53 wt%) will here be used as an example of the Pt starting material. To support a predefined amount of Pt 1.7 g/L on the whole filter 10, $1.7 \text{ (g/L)} \times 0.163 \text{ (L)} = 0.272 \text{ g}$ should be supported on the support; the dinitrodiammine platinum nitrate solution (Pt concentration 4.53%) is therefore diluted with distilled water. Thus, calculation of the weight ratio X (%) of dinitrodiammine platinum nitrate solution (Pt concentration 4.53%)/distilled water as $X = 0.272 \text{ (amount of Pt, g)}/24.7 \text{ (water content, g)}/4.53 \text{ (Pt concentration, wt\%)}$ gives a result of 24.8 wt%.

[0149] Impregnation step

A predetermined amount of the aqueous dinitrodiammine platinum nitrate solution prepared as above, adjusted for the amount it is wished to support on the desired filter 10, is poured into a pallet. When absorption is to be effected extending from one end face towards the other up to 2/3 of the overall length of the filter, for example, the prescribed time is allowed to effect water absorption to the 2/3 point, with the concentration set at the aforesaid condition (24.8 wt%) and the amount of aqueous solution set at $24.8 \times 2/3 = 16.47 \text{ g/L}$. Areas where the solution has and has not deposited are thereby defined; and Pt is uniformly dispersed and immobilised on the alumina supporting film surface that covers the SiC support 15.

[0150] Drying and calcination step

The support 15 impregnated with aqueous solution is dried by treatment at 110°C for about 2 hours to remove the water, and then calcined under conditions of approximately 500°C for about 1 hour in a nitrogen atmosphere with the aim of metallising the Pt. In supporting the active components of platinum, etc, the present embodiment achieves support through water absorption, but it is equally permissible to use impregnation wherein the support is immobilised at a predefined position in the solution and impregnated for a predefined time to effect support up to the target position, or to use evaporation to dryness, equilibrium adsorption, the incipient wetness method or a spraying process. In the foregoing steps the support material, promoter, NOx occlusion catalyst and catalyst are supported on the ceramic support 15. Although no particular restriction attaches to the respective heights they are supported to (the length in the direction of exhaust gas flow through the filter 10), it is desirable that all the others are matched to the height to which the catalyst is laid down. This is because when the support material, promoter, NOx occlusion catalyst, and catalyst are all matched one with another, a synergistic effect operates to increase the regenerative effect, and

because by omitting them wherever unnecessary, the pressure loss is reduced and waste of starting materials is eliminated, reducing cost.

[0151] Accordingly, the following effects can be achieved by means of the present embodiment. The catalytic filter 10 of the embodiment is used as a diesel particulate filter (DPF) with an alternately closed honeycomb. Although the DPF itself only has the function of trapping particulates at the cell walls 12, the hydrocarbon and carbon monoxide in the exhaust gas can be oxidised by supporting catalyst on the DPF.

[0152] Again, if NO_x selective reduction catalyst components and occlusion catalyst components capable of reducing NO_x in an oxidising environment like diesel exhaust gas are supported thereon, reduction of NO_x is also possible. Moreover, as it accumulates, the aforesaid PM trapped in the DPF elicits an increase in pressure loss in the aforesaid DPF, and normally therefore it must be removed by combustion, etc, to regenerate the DPF. The temperature at which the soot (carbon) comprising the chief constituent of the PM usually contained in diesel exhaust gas begins to burn is approximately 550-630°C. If a catalyst active component is then supported on the DPF, the soot combustion reaction pathway changes and the energy barrier can be lowered, with the result that the combustion temperature can be greatly reduced to 300-400°C and the energy required for regeneration can be reduced, so that in conjunction with the aforementioned action of ceria, a DPF system of high regeneration efficiency can be constructed.

[0153] It was found, however, that the noble metal catalyst frequently used as catalyst active component rapidly sinters above around 800°C, depressing the regeneration rate. Although in principle it is beneficial to regenerate at a high temperature for effective catalysis, it was clear that a particular requirement to maintain the efficacy of the initial production phase and allow repeated regeneration is to control the temperature to not more than 800°C. As already noted, the temperature at which soot (carbon) begins to burn is approximately 550-630°C. Taking this into account, it is most effective to control the temperature of the filter 10 to 600-750°C.

[0154] From regeneration tests carried out with the catalytic filter 10 of the present embodiment, characterised in that a predefined amount of catalyst is supported at one end and relatively little catalyst is supported going towards the other end, it was established that regeneration was possible with the temperature of the filter controlled to 600-750°C, and that the soot regeneration rate was unaffected after regeneration had to some extent been repeated. An additional benefit obtained was that, besides preventing wasteful use of the valuable resource of noble metal, etc, used as catalyst and lowering cost, a catalytic filter of reduced pressure loss was created.

[0155]

[Working examples] The invention is described in further detail hereunder with working examples and comparative examples. In the first working example, alumina, platinum and ceria were coated on the filter, which was then regenerated with a heater. The operating conditions and characteristics are shown in the table in Figure 10. All the filters 10 used a honeycomb filter of SiC; the cell structure was 14/200, porosity 42% and mean pore size 10 μm , and when the catalyst, etc, were supported thereon, adjustments were made so that the amounts of alumina (8 g/L), ceria (2 g/L) and Pt (1.7 g/L) per unit volume were the same.

[0156] This working example had alumina film 3 (8 g/L) on the surface of the SiC particles 4 of the ceramic support 15. Working Example 1-1 had a zone extending for 2/3 (67%) of the overall length of the filter from one end face of the filter 10 towards the other end face as catalyst support site, whereon alumina, ceria and Pt were coated. Working Example 1-2 similarly had a zone extending for half (50%) of the length as catalyst support site, whereon alumina, ceria and Pt were coated. Working Example 1-3 similarly had a zone extending for 4/5 (80%) of the length as catalyst support site, whereon alumina, ceria and Pt were coated.

[0157] Comparative Example 1-1 had the zone extending from one end face of the ceramic support 15 to the other end face (100%) as the catalyst support site, coated with alumina, ceria and Pt. Test Example 1-1 had a zone extending from one end face of the ceramic support towards the other end face for 1/3 (33%) of the overall length of the filter as the catalyst support site, whereon alumina, ceria and Pt were coated. Comparative Example 1-2 had the whole extent of the filter 10 as a non-catalyst supporting site, i.e. none of alumina, ceria and platinum were coated thereon.

[0158] To provide a method of regeneration, an exhaust gas cleaner 101 is mounted in-line in the exhaust passage 104 leading from a diesel engine 102 serving as the internal combustion engine as indicated in Figure 11. Each exhaust gas cleaner 101 is equipped with a casing 105 whose interior houses a honeycomb filter 10 for exhaust gas cleaning. The filter 10 comprises the aforementioned catalytic filter 10 and is mounted such that the end where relatively more catalyst is supported points in the exhaust gas inlet direction while the end supporting relatively little or no catalyst points in the discharge direction. A layer of heat insulation 107 is arranged between the outer peripheral surface of the filter 10 and the inner peripheral surface of the casing 105. The layer of heat insulation 107 is a mat formed with a content of ceramic fibre and has a thickness of 1 mm to 50 mm.

[0159] Within the casing 105 there is provided an electrical heater 108 that heats the filter 10. Each electrical heater 108 is an electrical resistance heater of spiral geometry positioned close to the gas inlet end face of the filter 10, and is powered from a battery (not illustrated) aboard the vehicle. The geometry of the electrical heater 108 is not restricted to helical. The exhaust gas discharged from the diesel engine 102 passes along the exhaust passage 104 and through the filter 10. The exhaust gas is here cleaned as a result of the particulates contained in the exhaust gas being trapped by the filter 10.

[0160] In this case electrocouples for measuring the honeycomb temperature were fitted at three points 10 mm, 75 mm, and 140 mm from the end face of the filter on the exhaust gas inlet side. A pressure sensor, not shown, was also fitted in-line in the exhaust channel 104 extending from the diesel engine 102 in front of the exhaust gas cleaner 101. The diesel engine 102 was then operated at a load of 50 N.m with the engine speed set at 3000 rpm, and 8 g/L of PM was trapped in the filter 10.

[0161] The results from measurement of back pressure with the pressure sensor are shown in the graph of Figure 12. Comparing the working examples and comparative examples from Figure 12, it will be seen that because the catalyst coating layer 2 is partially absent, the filters in Working Examples 1-1, 1-2 and 1-3 and Test Example 1-1 have low pressure loss characteristics closer to Comparative Example 1-2 than Comparative Example 1-1.

[0162] Heating of the filter 10 with the electric heater 108 was then commenced and the ensuing temperature change in the filter 10 was measured with thermocouples. The temperature change in Working Example 1-1 is shown as representative in the graph in Figure 13; all the examples are contained in the table in Figure 14. It was clear from the results that in Working Examples 1-1, 1-2 and 1-3 and Comparative Example 1-1 the temperature at the front of the filter 10 rose quickly to 600°C, the temperature at which graphite begins to burn, with a rise to almost 700°C at the rear, regeneration of the filter 10 proceeding satisfactorily even in the absence of catalyst. In Test Example 1-1 and Comparative Example 1-2, however, regeneration was inadequate without rise in temperature. Determination of the regeneration rate from actual measurements of weight gave the table of results shown in Figure 15, from which it will be seen that catalyst must be supported over not less than half the overall length of the filter from one end face.

[0163] The results for regeneration rate when the aforesaid regeneration was repeated 10 successive times gave the table in Figure 16 and graph of Figure 17, from which it was clear that regeneration is satisfactory in repeated use for about 10 cycles if catalyst is supported over not less than half the overall length of the filter from one end face.

[0164] The pressure loss of the filters in the working examples, comparative examples and test example was also measured at first use and the tenth use; the results are shown in Figure 21. Clearly, as indicated in Figure 21, the pressure loss in the first cycle and pressure loss in the tenth cycle are very different in the filters of the comparative examples and test example, whereas no notable difference is evident among the filters of the working examples. It was hence found that the pressure loss does not increase appreciably even if the filter is used repeatedly.

[0165] In the second working example, after alumina, platinum and ceria had been coated on the filter, the filter was regenerated by switching diesel engine operation to post-injection rather than by using a heater. The actual conditions and characteristics are shown in the table of Figure 22. The filters 10 used a honeycomb filter of SiC; the cell structure was 12/300, porosity 50% and mean pore size 10 μm , and when the catalyst, etc, were supported thereon, adjustments were made so that the amounts of alumina (60 g/L), ceria (5 g/L) and Pt (2 g/L) per unit volume were the same.

[0166] This working example has an alumina film 3 (60 g/L) on the surface of the SiC particles 4 of the ceramic support 15. Working Example 2-1 has a zone extending for 2/3 (67%) of the overall length of the filter from one end face of the filter 10 towards the other end face as the catalyst support site, Working Example 2-2 similarly has a zone extending for half (50%) the length as the catalyst support site, and Working Example 1-3 similarly has a zone extending for 4/5 (80%) of the length as the catalyst support site, with alumina, ceria and Pt coated thereon in each instance.

[0167] Comparative Example 2-1 has from one end face to the other end face (100%) of the ceramic support 15 as catalyst support site while Test Example 2-1 has a region extending 1/3 (33%) of the overall filter length towards the other end face as catalyst support site, with alumina, ceria and Pt coated thereon. Comparative Example 2-2 has the whole extent of the filter 10 as the non-catalyst supporting site, that is to say it has none of alumina, ceria or platinum coated thereon.

[0168] The table in Figure 23 shows the temperature changes in the filters 10 as measured with thermocouples when using the exhaust gas cleaner shown in Figure 11 as in the first working example. The results showed that in Example 2-1, 2-2, 2-3 and Comparative Example 2-1 the temperature at the front of the filter 10 rose quickly to 600°C, the temperature at which graphite begins to burn, with a similar rise to almost 650°C at the rear; regeneration of the filter 10 thus proceeding satisfactorily even in the absence of catalyst.

However, in Test Example 2-1 and Comparative Example 2-2 the temperature failed to rise and regeneration was inadequate. Determination of the regeneration rate from actual weight measurements gave the table shown in Figure 24. It will be seen from the table that catalyst must be supported up to not less than half the overall filter length from one end. Note that, to increase the regeneration rate in this instance, a somewhat longer regeneration time was set.

[0169] The aforesaid regeneration was then performed 15 times in succession and the regeneration rate was determined, giving the results in the table in Figure 25 and graph in Figure 26. It was again found that for 15 cycles of repeated use it was sufficient to support catalyst up to not less than half the overall filter length from one end.

[0170] Also measured was the pressure loss in the filters of the working examples, comparative examples and test example in the first cycle and 20th cycle of use. The results are tabulated in Figure 27. As shown in Figure 27, the pressure loss in the 20th cycle is clearly very different from the pressure loss in the first cycle in the filters of the comparative examples and test example, whereas no marked difference is evident in the filters of the working examples. It was hence found that the pressure loss in the filters of the working examples changed little despite repeated use.

[0171] The filter in the third working example was coated with alumina, platinum and lithium oxide and then ignited solely by exhaust gas heat, without recourse to a heater. In this case regeneration was conducted with intervening changes in the air-fuel ratio. The operating conditions and characteristics are given in the table of Figure 28. Honeycomb filters of SiC were used; the cell structure was 14/200, porosity 65% and mean pore size 20 μm , and when catalyst, etc, were supported thereon, adjustments were made so that the amounts of alumina (200 g/L), lithium oxide (2 mol/L) and Pt (2.0 g/L) per unit volume were the same. Porosity during manufacture of the 65% porosity honeycomb filter was regulated by adding a porosifier comprising acrylic particles.

[0172] This Working Example has an alumina film 3 (200 g/L) on the surface of the SiC particles 4 of the ceramic support 15. Working Example 3-1 has a region extending from one end of the filter 10 towards the other end for 2/3 (67%) of the overall filter length as catalyst support site; Working Example 3-2 similarly has a region extending for 1/2 (50%) of the length as catalyst support site; Working Example 3-3 similarly has a zone extending for 4/5 (80%) of the length as catalyst support site, with alumina, lithium oxide and Pt coated thereon in each case.

[0173] Comparative Example 3-1 has the region from one end of the ceramic support 15 to

the other end (100%) as catalyst support site, while Test Example 3-1 has a region extending towards the other end for 1/3 (33%) of overall filter length as the catalyst support site, with alumina, lithium oxide and Pt coated thereon. Comparative Example 3-2 has the whole extent of the filter 10 as the non-catalyst supporting site, that is to say it has none of alumina, lithium oxide or platinum coated thereon.

[0174] The table in Figure 29 shows the temperature changes in the filters 10 as measured with thermocouples when using the exhaust gas cleaner shown in Figure 11 as in the first working example. The results showed that in Working Example 3-1, 3-2, 3-3 and Comparative Example 3-1 the temperature at the front of the filter 10 rose quickly to 500°C, the temperature at which graphite begins to burn, with a similar rise to almost 600°C at the rear; regeneration of the filter 10 thus proceeded satisfactorily even in the absence of catalyst. However, in Test Example 3-1 and Comparative Example 3-2 the temperature failed to rise and regeneration was inadequate.

[0175] Also measured was the pressure loss in the filters of the working examples, comparative examples and test example at commencement of use and again 500 hours after use commenced; the results are shown in Figure 30. As shown in Figure 30, the pressure loss at commencement of use is clearly very different from the pressure loss after 500 hours in the filters of the comparative examples and test example, whereas no marked difference is evident in the filters of the working examples. It was hence found that the pressure loss in the filters of the working examples changed little despite repeated use.

[0176] The filter in the fourth working example was coated with alumina, titania, platinum and lithium oxide and then ignited and regenerated solely by exhaust gas heat, without recourse to a heater. The operating conditions and characteristics are given in the table of Figure 31. Honeycomb filters of SiC were used; the cell structure was 14/200, porosity 65% and mean pore size 20 μm , and when catalyst, etc, were supported thereon, adjustments were made so that the amounts of alumina (150 g/L), titania (50 g/L), Pt (2.0 g/L) and lithium oxide (2 mol/L) per unit volume were the same.

[0177] This working example has an alumina film (150 g/L) and titania film (50 g/L) on the SiC particles of the ceramic support. Working Example 4-1 has the region extending from one end of the filter 10 towards the other end for 2/3 (67%) of the overall filter length as catalyst support site; Working Example 4-2 similarly has a region extending for 1/2 (50%) of the length as catalyst support site; Working Example 4-3 similarly has a zone extending for 4/5 (80%) of the length as the catalyst support site, with alumina, titania, Pt and lithium oxide coated thereon in each case.

[0178] Comparative Example 4-1 has the region from one end of the ceramic support 15 to the other end (100%) as catalyst support site, while Test Example 4-1 has the region extending towards the other end for 1/3 (33%) of overall filter length as the catalyst support site, with alumina, titania, Pt and lithium oxide coated thereon

[0179] The pressure loss in the filters of the working examples, comparative examples and test example was measured as in the first working example at commencement of use and again 500 hours after use commenced; the results are shown in Figure 32. As shown in Figure 32, the pressure loss at commencement of use is clearly very different from the pressure loss after 500 hours in the filters of the comparative examples and test example, whereas no marked difference is evident in the filters of the working examples. It was hence found that the pressure loss in the filters of the working examples changed little despite repeated use.

[0180] The embodiment of the invention may be varied as follows.

- The filter 10 may be stood upright in the orientation it is desired to impart a concentration difference and slowly dried to impart concentration difference by gravity.

[0181] - Although the alumina, ceria, platinum, etc, were supported separately in the embodiment, they may all be supported from the same solution. To prevent sintering, however, they are best calcined in a nitrogen atmosphere.

[0182] - Although the embodiment used a ceramic filter of honeycomb structure as the filter support 15, the filter is not limited thereto; a filter of ceramic foam or mesh structure may be used, and a filter fabricated from metal, alloy, etc, may be used.

[Benefit of invention] As hereinbefore described in detail, the invention set down in (1)-(24) and (31) enables the amount of noble metal catalyst deteriorating to be reduced by decreasing the amount of catalyst towards one end, while also providing a catalytic filter of low pressure loss. According to the invention set down in (25)-(27) a catalytic filter whereon relatively more support material, catalyst, and promoter are supported towards one end is simple to manufacture. According to the invention set down in (28)-(30), an exhaust gas cleaning system can be provided that can be regenerated after soot has been trapped on the filter.

[Brief Description of Drawings]

[Figure 1] Figure (a) is a sketch of the catalytic filter in an embodiment and (b) is a sectional view thereof.

[Figure 2] An enlarged perspective view of part of the catalytic filter.

[Figure 3] Figure (a) is a schematic view of the alumina film in the embodiment, and (b) shows part of an SiC particle enlarged.

[Figure 4] A diagram explaining pressure loss characteristics.

[Figure 5] Figure (a) is a sectional view through the catalytic filter of the embodiment; (b)-(d) show catalytic filters in different embodiments.

[Figure 6] Figure (a) is a schematic view of a wash coat alumina layer; (b) is a schematic enlargement of part of (a).

[Figure 7] Figures (a)-(c) are graphs comparing the soot oxidation characteristic that affects the regeneration characteristic of a DPF.

[Figure 8] A schematic diagram explaining the NO_x occlusion effect.

[Figure 9] A graph comparing the regeneration rates of DPFs.

[Figure 10] A table showing the porosity, etc, in the examples, comparative examples and test examples in the first working example.

[Figure 11] A sketch of the exhaust gas cleaning system.

[Figure 12] A graph comparing the pressure loss during soot trapping in the examples, comparative examples and test examples in the first working example.

[Figure 13] A temperature graph of PDF regeneration in the examples, comparative examples and test examples in the first working example.

[Figure 14] A table showing filter temperature during regeneration in the first working example.

[Figure 15] A table of the results for the first regeneration rate in the first working example.

[Figure 16] A table showing the changes in regeneration rate due to repeated regeneration of the DPF in the first working example.

[Figure 17] A graph of the change in regeneration rate due to repeated regeneration of the DPF in the first working example.

[Figure 18] A sketch of an ordinary exhaust gas cleaner.

[Figure 19] A graph of the change in regeneration rate due to repeated regeneration of a DPF.

[Figure 20] A graph of the temperature change during regeneration of a DPF.

[Figure 21] A graph of the relation between the number of regeneration cycles and pressure loss in the DPF in the first working example.

[Figure 22] A table showing the porosity, etc, in the examples, comparative examples and test example in the second working example.

[Figure 23] A table showing the filter temperature in regeneration after one hour of trapping and the pressure loss [*sic*] in the second working example.

[Figure 24] A table showing the results for regeneration rate at commencement of use in the second working example.

[Figure 25] A table showing the change in regeneration rate due to repeated regeneration of the DPF in the second working example.

[Figure 26] A graph of the change in regeneration rate due to repeated regeneration of the DPF in the second working example.

[Figure 27] A graph of the relation between number of regeneration cycles of the DPF and the pressure loss in the second working example.

[Figure 28] A table showing the porosity, etc, of the examples, comparative examples and test example in a third working example.

[Figure 29] A table showing the filter temperature during regeneration in the third working example.

[Figure 30] A graph of the relation between the time of regeneration of the DPF and pressure loss in the third working example.

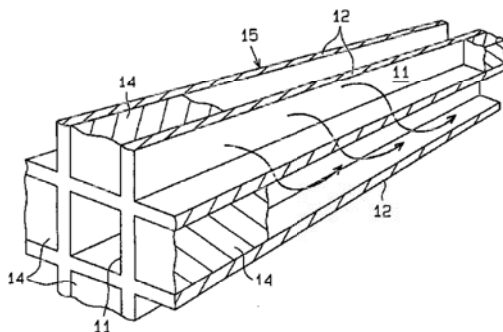
[Figure 31] A table showing the porosity, etc, of the examples, comparative examples and test example in a fourth working example.

[Figure 32] A graph of the relation between the time of regeneration of the DPF and pressure loss in the fourth working example.

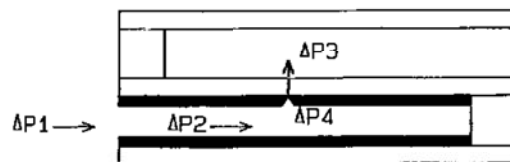
[Key to symbols]

- 2 Catalyst coating layer
- 3 Support material (alumina film)
- 4 SiC particles
- 10 Catalytic filter
- 11 Through-hole
- 12 Cell wall
- 14 Plug
- 101 Diesel engine
- 102 Exhaust passage

[Figure 2]



[Figure 4]



$$\Delta P = \Delta P_1 + \Delta P_2 + \Delta P_3 + \Delta P_4$$

ΔP_1 : Resistance due to narrowing of the channel opening

ΔP_2 : Resistance to passage through duct

ΔP_3 : Resistance to passage through wall

ΔP_4 : Resistance to passage through accumulated PM

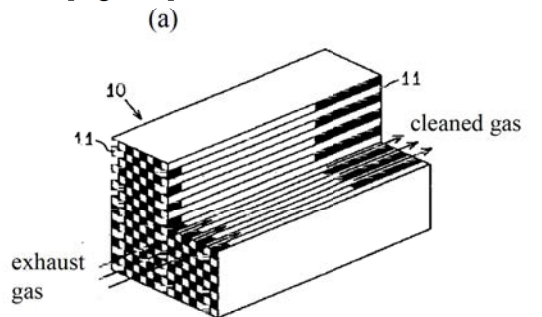
[Figure 15]

	Working Example 1-1	Working Example 1-2	Working Example 1-3	Comparative Example 1-1	Test Example 1-1	Comparative Example 1-2
First cycle	80	70	85	90	40	0

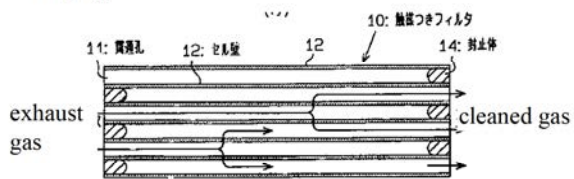
[Figure 24]

	Working Example 2-1	Working Example 2-2	Working Example 2-3	Comparative Example 2-1	Test Example 2-1	Comparative Example 2-2
At start	80	70	85	90	40	0

[Figure 1]

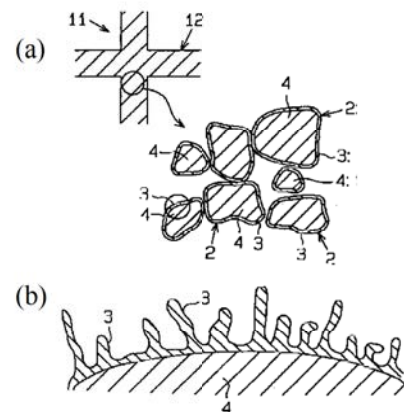


(b)
 11: through-hole, 12: cell wall, 10: catalytic filter
 14: plug

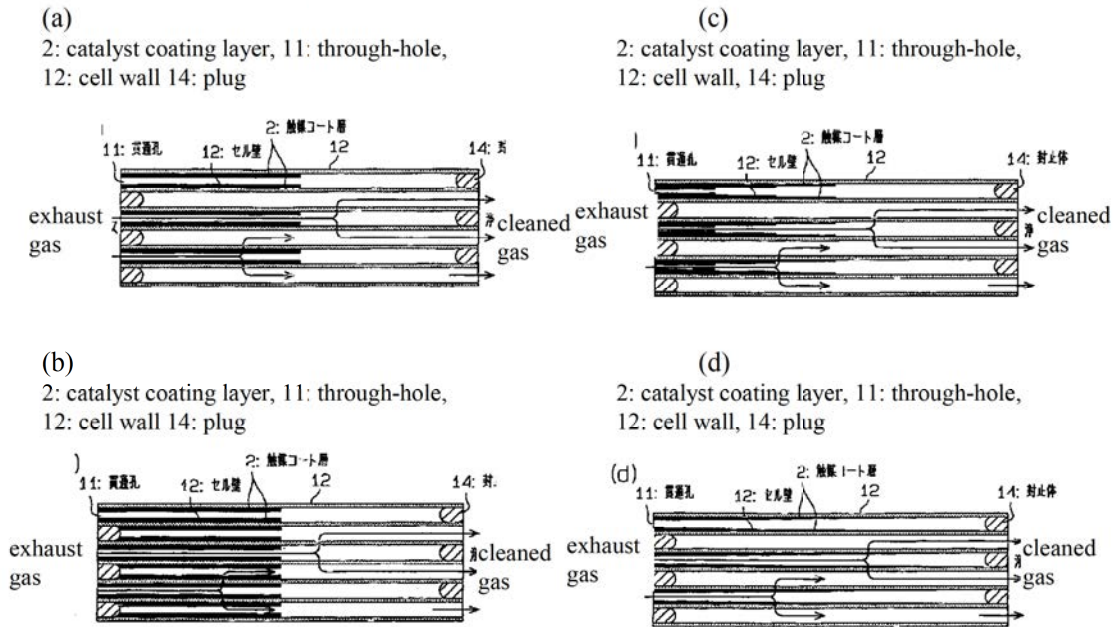


[Figure 3]

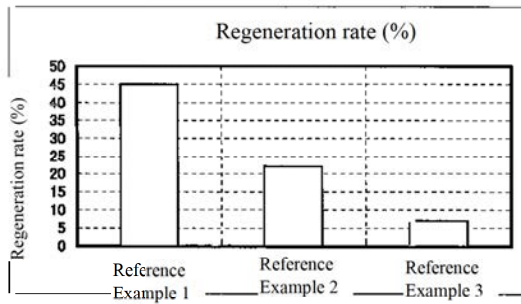
2: catalyst coating layer, 3: alumina film,
 4: SiC particles



[Figure 5]



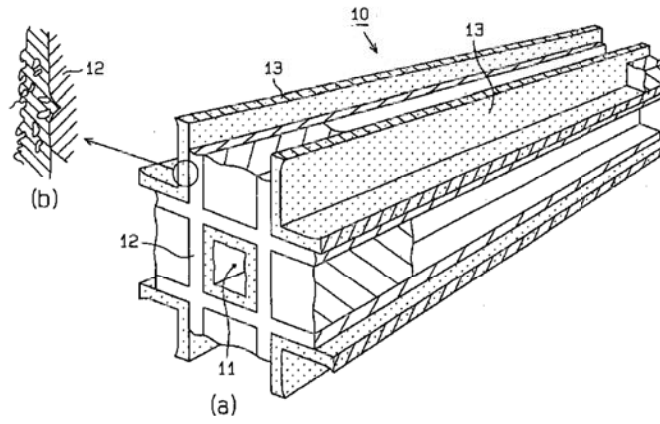
[Figure 9]



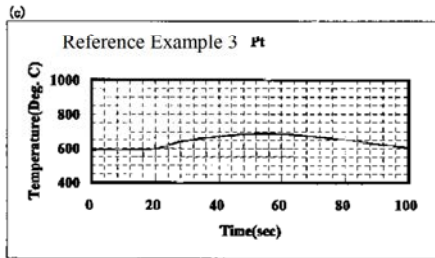
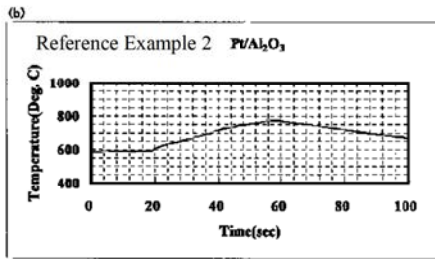
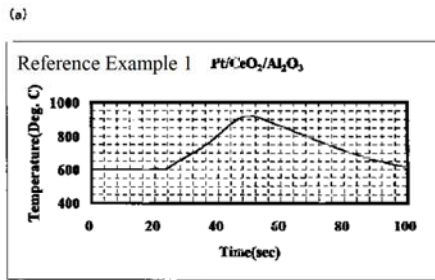
[Figure 16]

	Working Example 1-1	Working Example 1-2	Working Example 1-3	Comparative Example 1-1	Test Example 1-1	Comparative Example 1-2
First cycle	80	70	85	90	40	0
Fifth cycle	60	55	63	65	35	0
Tenth cycle	55	50	55	55	30	0

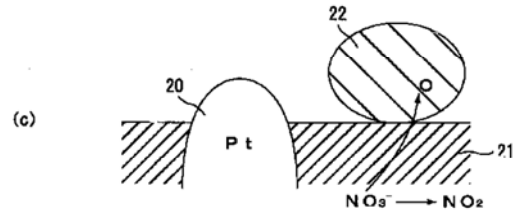
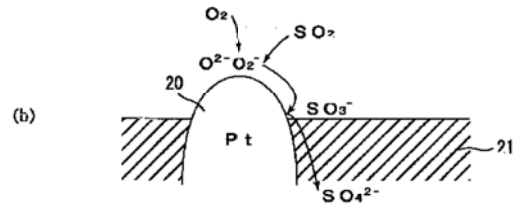
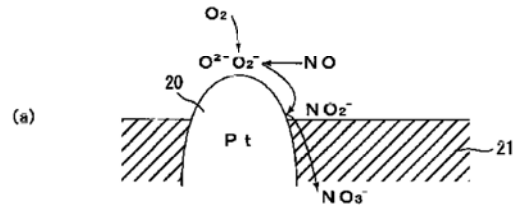
[Figure 6]



[Figure 7]



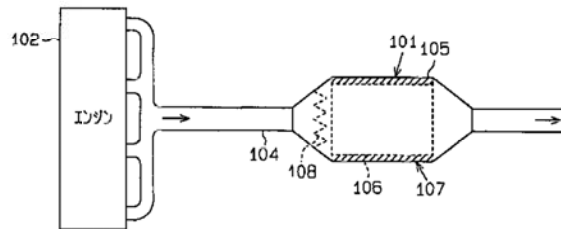
[Figure 8]



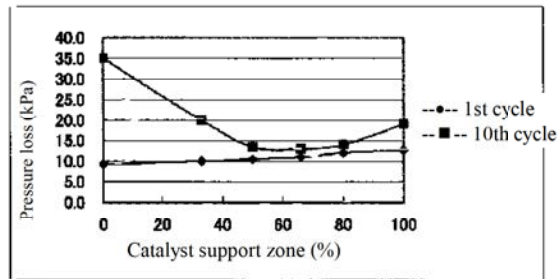
[Figure 10]

	Working Example 1-1	Working Example 1-2	Working Example 1-3	Comparative Example 1-1	Test Example 1-1	Comparative Example 1-2
Honeycomb support	SiC-DPF	SiC-DPF	SiC-DPF	SiC-DPF	SiC-DPF	SiC-DPF
Cell structure	14/200	14/200	14/200	14/200	14/200	14/200
Porosity	42%	42%	42%	42%	42%	42%
Pore size	10 μm	10 μm	10 μm	10 μm	10 μm	10 μm
Amount of alumina	8 g/L	8 g/L	8 g/L	8 g/L	8 g/L	-
Amount of ceria	2 g/L	2 g/L	2 g/L	2 g/L	2 g/L	-
Amount of platinum	1.7 g/L	1.7 g/L	1.7 g/L	1.7 g/L	1.7 g/L	-
Zone of support from end	2/3 (67%)	1/2 (50%)	4/5 (80%)	1 (100%)	1/3 (33%)	0

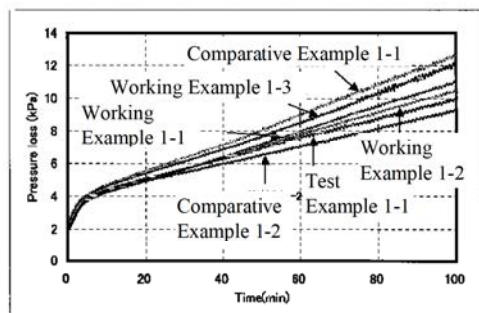
[Figure 11]



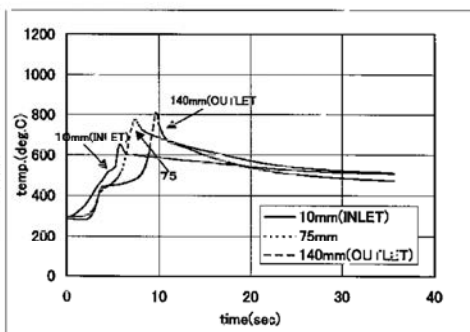
[Figure 21]



[Figure 12]



[Figure 13]



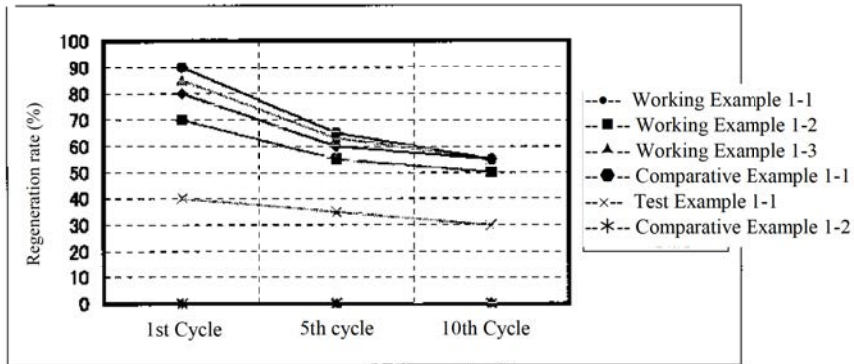
[Figure 14]

	Working Example 1-1	Working Example 1-2	Working Example 1-3	Comparative Example 1-1	Test Example 1-1	Comparative Example 1-2
Maximum regeneration temperature (10 mm)	620	620	620	620	620	620
Maximum regeneration temperature (75 mm)	780	660	780	780	635	625
Maximum regeneration temperature (140 mm)	800	700	825	850	650	630
Catalyst support site	67%	50%	80%	100%	33%	0%

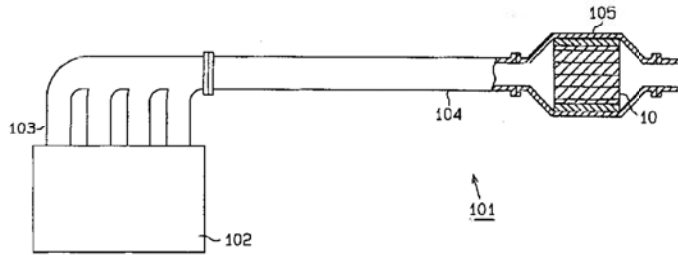
[Figure 22]

	Working Example 2-1	Working Example 2-2	Working Example 2-3	Comparative Example 2-1	Test Example 2-1	Comparative Example 2-2
Honeycomb support	SiC-DPF	SiC-DPF	SiC-DPF	SiC-DPF	SiC-DPF	SiC-DPF
Cell structure	12/300	12/300	12/300	12/300	12/300	12/300
Porosity	50%	50%	50%	50%	50%	50%
Pore size	10 μm	10 μm	10 μm	10 μm	10 μm	10 μm
Amount of alumina	60 g/L	60 g/L	60 g/L	60 g/L	60 g/L	-
Amount of ceria	2 g/L	2 g/L	2 g/L	2 g/L	2 g/L	-
Amount of platinum	1.7 g/L	1.7 g/L	1.7 g/L	1.7 g/L	1.7 g/L	-
Zone of support from end	2/3 (67%)	1/2 (50%)	4/5 (80%)	1 (100%)	1/3 (33%)	0

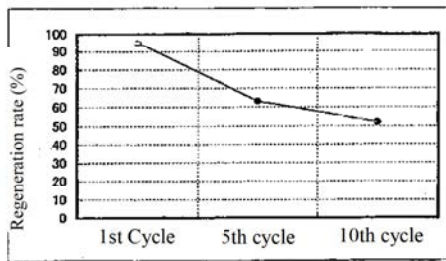
[Figure 17]



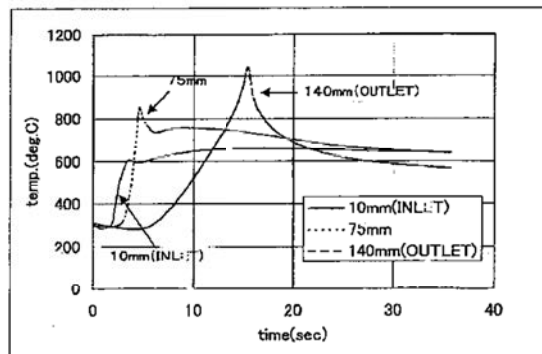
[Figure 18]



[Figure 19]



[Figure 20]



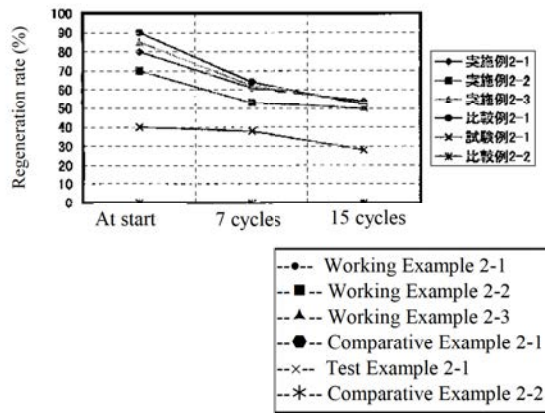
[Figure 23]

	Working Example 2-1	Working Example 2-2	Working Example 2-3	Comparative Example 2-1	Test Example 2-1	Comparative Example 2-2
Maximum regeneration temperature (10 mm)	600	600	600	600	600	600
Maximum regeneration temperature (75 mm)	645	630	650	680	630	610
Maximum regeneration temperature (140 mm)	670	650	680	700	640	620
Catalyst support site	67%	50%	80%	100%	33%	0%

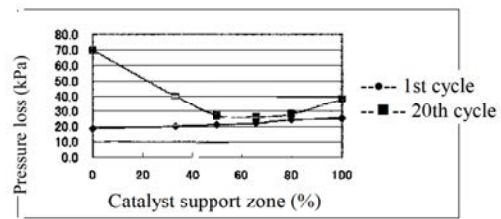
[Figure 25]

	Working Example 2-1	Working Example 2-2	Working Example 2-3	Comparative Example 2-1	Test Example 2-1	Comparative Example 2-2
First cycle	80	70	85	90	40	0
7th cycle	61	53	62	64	38	0
15th cycle	54	50	53	52	28	0

[Figure 26]



[Figure 27]



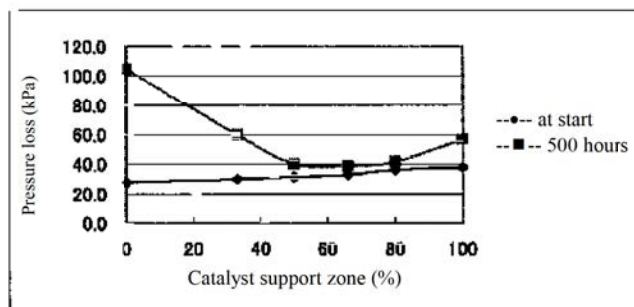
[Figure 29]

	Working Example 3-1	Working Example 3-2	Working Example 3-3	Comparative Example 3-1	Test Example 3-1	Comparative Example 3-2
Maximum regeneration temperature (10 mm)	500	500	500	500	500	500
Maximum regeneration temperature (75 mm)	590	560	600	520	540	530
Maximum regeneration temperature (140 mm)	630	600	640	650	570	550
Catalyst support site	67%	50%	80%	100%	33%	0%

[Figure 28]

	Working Example 3-1	Working Example 3-2	Working Example 3-3	Comparative Example 3-1	Test Example 3-1	Comparative Example 3-2
Honeycomb support	SiC-DPF	SiC-DPF	SiC-DPF	SiC-DPF	SiC-DPF	SiC-DPF
Cell structure	14/200	14/200	14/200	14/200	14/200	14/200
Porosity	65%	65%	65%	65%	65%	65%
Pore size	20 μm	20 μm	20 μm	20 μm	20 μm	20 μm
Amount of alumina	200 g/L	200 g/L	200 g/L	200 g/L	200 g/L	-
Amount of lithium oxide	2 mol/L	2 mol/L	2 mol/L	2 mol/L	2 mol/L	-
Amount of platinum	2 g/l.	2 g/l.	2 g/l.	2 g/l.	2 g/l.	-
Zone of support from end	2/3 (67%)	1/2 (50%)	4/5 (80%)	1 (100%)	1/3 (33%)	0

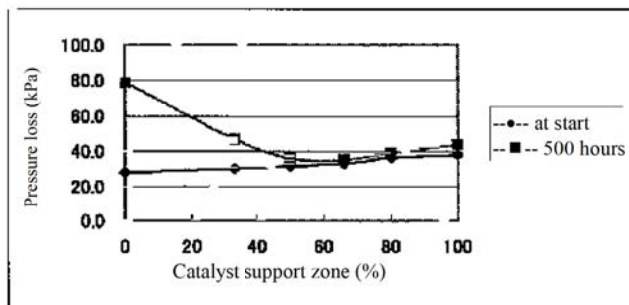
[Figure 30]



[Figure 31]

	Working Example 4-1	Working Example 4-2	Working Example 4-3	Comparative Example 4-1	Test Example 4-1	Comparative Example 4-2
Honeycomb support	SiC-DPF	SiC-DPF	SiC-DPF	SiC-DPF	SiC-DPF	SiC-DPF
Cell structure	14/200	14/200	14/200	14/200	14/200	14/200
Porosity	65%	65%	65%	65%	65%	65%
Pore size	20 μm	20 μm	20 μm	20 μm	20 μm	20 μm
Amount of alumina	150 g/L	150 g/L	150 g/L	150 g/L	150 g/L	-
Amount of titania	50 g/L	50 g/L	50 g/L	50 g/L	50 g/L	-
Amount of lithium oxide	2 mol/L	2 mol/L	2 mol/L	2 mol/L	2 mol/L	-
Amount of platinum	2 g/L	2 g/L	2 g/L	2 g/L	2 g/L	-
Zone of support from end	2/3 (67%)	1/2 (50%)	4/5 (80%)	1 (100%)	1/3 (33%)	0

[Figure 32]



Continued from front page

(51) Int. Class.	Identifier	FI	(for reference)
F O 1 N 3/02	3 0 1	F O 1 N 3/02	3 2 1 A
	3 2 1		3 4 1 Z
	3 4 1	3/08	A
3/08		3/10	A
3/10		3/24	E
3/24			R
		3/28	3 0 1 C
3/28	3 0 1		3 0 1 Q
		B O 1 D 53/36	1 0 4 A
			1 0 4 B

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F-terms (for reference)	3G090 AA03 BA01 BA04 EA04
	3G091 AA02 AA18 AB06 AB09 AB13
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	GB05W GB06W GB07W GB10X
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