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(54) **EXHAUST PURIFICATION DEVICE FOR INTERNAL COMBUSTION ENGINE**

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Description

Technical Field

[0001] The present invention relates to an exhaust purification system of an internal combustion engine.

Background Art

[0002] Known in the art is an internal combustion engine, as disclosed in e.g. EP2239432A or EP1154130A, which arranges, in an engine exhaust passage, an NO_x storage catalyst which stores NO_x which is contained in exhaust gas when the air-fuel ratio of the inflowing exhaust gas is lean and which releases the stored NO_x when the air-fuel ratio of the inflowing exhaust gas becomes rich, which arranges, in the engine exhaust passage upstream of the NO_x storage catalyst, an oxidation catalyst which has an adsorption function, and which feeds hydrocarbons into the engine exhaust passage upstream of the oxidation catalyst to make the air-fuel ratio of the exhaust gas flowing into the NO_x storage catalyst rich when releasing NO_x from the NO_x storage catalyst (for example, see Patent Literature 1).

[0003] In this internal combustion engine, the hydrocarbons which are fed when releasing NO_x from the NO_x storage catalyst are made gaseous hydrocarbons at the oxidation catalyst, and the gaseous hydrocarbons are fed to the NO_x storage catalyst. As a result, the NO_x which is released from the NO_x storage catalyst is reduced well.

Citation List

Patent Literature

[0004] Patent Literature 1: Japanese Patent No. JP 3969450 B

Summary of Invention

Technical Problem

[0005] However, there is the problem that when the NO_x storage catalyst becomes a high temperature, the NO_x purification rate falls.

[0006] An object of the present invention is to provide an exhaust purification system of an internal combustion engine which can obtain a high NO_x purification rate even if the temperature of the exhaust purification catalyst becomes a high temperature.

Solution to Problem

[0007] According to the present invention, there is provided an exhaust purification system of an internal combustion engine wherein an exhaust purification catalyst for reacting NO_x contained in exhaust gas and reformed hydrocarbons to produce a reducing intermediate con-

taining nitrogen and hydrocarbons is arranged in an engine exhaust passage, a precious metal catalyst is carried on an exhaust gas flow surface of the exhaust purification catalyst and a basic exhaust gas flow surface part is formed around the precious metal catalysts, the exhaust purification catalyst has a property of producing the reducing intermediate and reducing NO_x contained in exhaust gas by a reducing action of the produced reducing intermediate if a concentration of hydrocarbons flowing into the exhaust purification catalyst is made to vibrate within a predetermined range of amplitude and within a predetermined range of period and has a property of being increased in storage amount of NO_x which is contained in exhaust gas if a vibration period of the hydrocarbon concentration is made longer than the predetermined range, at the time of engine operation, to produce NO_x contained in the exhaust gas in the exhaust purification catalyst, the concentration of hydrocarbons flowing into the exhaust purification catalyst is made to vibrate within the predetermined range of amplitude and within the predetermined range of period, wherein said vibration period of the hydrocarbon concentration is between 0.3 second to 5 seconds, and, when a stored SO_x should be released from the exhaust purification catalyst, an air-fuel ratio of the exhaust gas which flows into the exhaust purification catalyst is lowered to a targeted rich air-fuel ratio to make the reducing intermediate built up on the exhaust purification catalyst desorb in the form of ammonia and the desorbed ammonia is used to make the exhaust purification catalyst release the stored SO_x.

Advantageous Effects of Invention

[0008] Even if the temperature of the exhaust purification catalyst becomes a high temperature, a high NO_x purification rate can be obtained.

Brief Description of Drawings

[0009]

FIG. 1 is an overall view of a compression ignition type internal combustion engine.

FIG. 2 is a view schematically showing a surface part of a catalyst carrier.

FIG. 3 is a view for explaining an oxidation reaction in an exhaust purification catalyst.

FIG. 4 is a view showing a change of an air-fuel ratio of exhaust gas flowing into an exhaust purification catalyst.

FIG. 5 is a view showing an NO_x purification rate.

FIG. 6A, 6B, and 6C are views for explaining an oxidation reduction reaction in an exhaust purification catalyst.

FIG. 7A and 7B are views for explaining an oxidation reduction reaction in an exhaust purification catalyst.

FIG. 8 is a view showing a change of an air-fuel ratio of exhaust gas flowing into an exhaust purification

catalyst.

FIG. 9 is a view of an NO_x purification rate.

FIG. 10 is a time chart showing a change of an air-fuel ratio of exhaust gas flowing into an exhaust purification catalyst.

FIG. 11 is a time chart showing a change of an air-fuel ratio of exhaust gas flowing into an exhaust purification catalyst.

FIG. 12 is a view showing relationship between an oxidizing strength of an exhaust purification catalyst and a demanded minimum air-fuel ratio X.

FIG. 13 is a view showing a relationship between an oxygen concentration in exhaust gas and an amplitude ΔH of a hydrocarbon concentration giving the same NO_x purification rate.

FIG. 14 is a view showing a relationship between an amplitude ΔH of a hydrocarbon concentration and an NO_x purification rate.

FIG. 15 is a view showing a relationship of a vibration period ΔT of a hydrocarbon concentration and an NO_x purification rate.

FIG. 16 is a view showing a map of the hydrocarbon feed amount W.

FIG. 17 is a view showing a change in the air-fuel ratio of the exhaust gas flowing to the exhaust purification catalyst etc.

FIG. 18 is a view showing a map of an exhausted NO_x amount NOXA.

FIG. 19 is a view showing a fuel injection timing.

FIG. 20 is a view showing a map of a hydrocarbon feed amount WR.

FIGS. 21A and 21B are views for explaining an SO_x storage and release action.

FIGS. 22A, 22B, and 22C are views for explaining SO_x release control.

FIGS. 23A and 23B are views showing the change in the air-fuel ratio of exhaust gas flowing into an exhaust purification catalyst at the time of SO_x release control.

FIG. 24 is a time chart showing SO_x release control.

FIG. 25 is a flow chart for exhaust purification control.

Description of Embodiments

[0010] FIG. 1 is an overall view of a compression ignition type internal combustion engine.

[0011] Referring to FIG. 1, 1 indicates an engine body, 2 a combustion chamber of each cylinder, 3 an electronically controlled fuel injector for injecting fuel into each combustion chamber 2, 4 an intake manifold, and 5 an exhaust manifold. The intake manifold 4 is connected through an intake duct 6 to an outlet of a compressor 7a of an exhaust turbocharger 7, while an inlet of the compressor 7a is connected through an intake air amount detector 8 to an air cleaner 9. Inside the intake duct 6, a throttle valve 10 driven by a step motor is arranged. Furthermore, around the intake duct 6, a cooling device 11 is arranged for cooling the intake air which flows through

the inside of the intake duct 6. In the embodiment shown in FIG. 1, the engine cooling water is guided to the inside of the cooling device 11 where the engine cooling water is used to cool the intake air.

[0012] On the other hand, the exhaust manifold 5 is connected to an inlet of an exhaust turbine 7b of the exhaust turbocharger 7. The outlet of the exhaust turbine 7b is connected through an exhaust pipe 12 to an inlet of the exhaust purification catalyst 13, while the outlet of the exhaust purification catalyst 13 is connected to a particulate filter 14 for trapping particulate which is contained in the exhaust gas. Inside the exhaust pipe 12 upstream of the exhaust purification catalyst 13, a hydrocarbon feed valve 15 is arranged for feeding hydrocarbons comprised of diesel oil or other fuel used as fuel for a compression ignition type internal combustion engine. In the embodiment shown in FIG. 1, diesel oil is used as the hydrocarbons which are fed from the hydrocarbon feed valve 15. Note that, the present invention can also be applied to a spark ignition type internal combustion engine in which fuel is burned under a lean air-fuel ratio. In this case, from the hydrocarbon feed valve 15, hydrocarbons comprised of gasoline or other fuel used as fuel of a spark ignition type internal combustion engine are fed.

[0013] On the other hand, the exhaust manifold 5 and the intake manifold 4 are connected with each other through an exhaust gas recirculation (hereinafter referred to as an "EGR") passage 16. Inside the EGR passage 16, an electronically controlled EGR control valve 17 is arranged. Further, around the EGR passage 16, a cooling device 18 is arranged for cooling EGR gas flowing through the inside of the EGR passage 16. In the embodiment shown in FIG. 1, the engine cooling water is guided to the inside of the cooling device 18 where the engine cooling water is used to cool the EGR gas. On the other hand, each fuel injector 3 is connected through a fuel feed tube 19 to a common rail 20. This common rail 20 is connected through an electronically controlled variable discharge fuel pump 21 to a fuel tank 22. The fuel which is stored inside of the fuel tank 22 is fed by the fuel pump 21 to the inside of the common rail 20. The fuel which is fed to the inside of the common rail 20 is fed through each fuel feed tube 19 to the fuel injector 3.

[0014] An electronic control unit 30 is comprised of a digital computer provided with a ROM (read only memory) 32, a RAM (random access memory) 33, a CPU (microprocessor) 34, an input port 35, and an output port 36, which are connected with each other by a bidirectional bus 31. Downstream of the exhaust purification catalyst 13, a temperature sensor 23 is attached for detecting the exhaust gas temperature. At the particulate filter 14, a differential pressure sensor 24 is attached for detecting a differential pressure before and after the particulate filter 14. Output signals of this temperature sensor 23, differential pressure sensor 24, and intake air amount detector 8 are input through respectively corresponding AD converters 37 to the input port 35. Further, an accelerator pedal 40 has a load sensor 41 connected to it

which generates an output voltage proportional to the amount of depression L of the accelerator pedal 40. The output voltage of the load sensor 41 is input through a corresponding AD converted 37 to the input port 35. Furthermore, at the input port 35, a crank angle sensor 42 is connected which generates an output pulse every time a crankshaft rotates by, for example, 15°. On the other hand, the output port 36 is connected through corresponding drive circuits 38 to each fuel injector 3, a step motor for driving the throttle valve 10, hydrocarbon feed valve 15, EGR control valve 17, and fuel pump 21.

[0015] FIG. 2 schematically shows a surface part of a catalyst carrier which is carried on a substrate of the exhaust purification catalyst 13. At this exhaust purification catalyst 13, as shown in FIG. 2, for example, there is provided a catalyst carrier 50 made of alumina on which precious metal catalysts 51 and 52 are carried. Furthermore, on this catalyst carrier 50, a basic layer 53 is formed which includes at least one element selected from potassium K, sodium Na, cesium Cs, or another such alkali metal, barium Ba, calcium Ca, or another such alkali earth metal, a lanthanoid or another such rare earth and silver Ag, copper Cu, iron Fe, iridium Ir, or another metal able to donate electrons to NO_x. The exhaust gas flows along the top of the catalyst carrier 50, so the precious metal catalysts 51 and 52 can be said to be carried on the exhaust gas flow surface of the exhaust purification catalyst 13. Further, the surface of the basic layer 53 exhibits basicity, so the surface of the basic layer 53 is called the basic exhaust gas flow surface part 54.

[0016] On the other hand, in FIG. 2, the precious metal catalyst 51 is comprised of platinum Pt, while the precious metal catalyst 52 is comprised of rhodium Rh. That is, the precious metal catalysts 51 and 52 which are carried on the catalyst carrier 50 are comprised of platinum Pt and rhodium Rh. Note that, on the catalyst carrier 50 of the exhaust purification catalyst 13, in addition to platinum Pt and rhodium Rh, palladium Pd may be further carried or, instead of rhodium Rh, palladium Pd may be carried. That is, the precious metal catalysts 51 and 52 which are carried on the catalyst carrier 50 are comprised of platinum Pt and at least one of rhodium Rh and palladium Pd.

[0017] If hydrocarbons are injected from the hydrocarbon feed valve 15 into the exhaust gas, the hydrocarbons are reformed at the upstream side end of the exhaust purification catalyst 13. In the present invention, at this time, the reformed hydrocarbons are used to remove the NO_x at the exhaust purification catalyst 13. FIG. 3 schematically shows the reforming action performed at the upstream end of the exhaust purification catalyst 13 at this time. As shown in FIG. 3, the hydrocarbons HC which are injected from the hydrocarbon feed valve 15 become radical hydrocarbons HC with a small carbon number by the catalyst 51.

[0018] Note that, even if injecting fuel, that is, hydrocarbons, from the fuel injector 3 into the combustion chamber 2 during the latter half of the expansion stroke

or during the exhaust stroke, the hydrocarbons are reformed inside of the combustion chamber 2 or at the exhaust purification catalyst 13, and the NO_x which is contained in the exhaust gas is removed by the reformed hydrocarbons at the exhaust purification catalyst 13. Therefore, in the present invention, instead of feeding hydrocarbons from the hydrocarbon feed valve 15 to the inside of the engine exhaust passage, it is also possible to feed hydrocarbons into the combustion chamber 2 during the latter half of the expansion stroke or during the exhaust stroke. In this way, in the present invention, it is also possible to feed hydrocarbons to the inside of the combustion chamber 2, but below the present invention is explained taking as an example the case of injecting hydrocarbons from the hydrocarbon feed valve 15 to the inside of the engine exhaust passage.

[0019] FIG. 4 shows the timing of feeding hydrocarbons from the hydrocarbon feed valve 15 and the changes in the air-fuel ratio (A/F) in of the exhaust gas flowing into the exhaust purification catalyst 13. Note that, the changes in the air-fuel ratio (A/F) in depend on the change in concentration of the hydrocarbons in the exhaust gas which flows into the exhaust purification catalyst 13, so it can be said that the change in the air-fuel ratio (A/F) in shown in FIG. 4 expresses the change in concentration of the hydrocarbons. However, if the hydrocarbon concentration becomes higher, the air-fuel ratio (A/F) in becomes smaller, so, in FIG. 4, the more to the rich side the air-fuel ratio (A/F) in becomes, the higher the hydrocarbon concentration.

[0020] FIG. 5 shows the NO_x purification rate by the exhaust purification catalyst 13 with respect to the catalyst temperatures TC of the exhaust purification catalyst 13 when periodically making the concentration of hydrocarbons flowing into the exhaust purification catalyst 13 change so as to, as shown in FIG. 4, make the air-fuel ratio (A/F) in of the exhaust gas flowing to the exhaust purification catalyst 13 change. The inventors engaged in research relating to NO_x purification for a long time. In the process of research, they learned that if making the concentration of hydrocarbons flowing into the exhaust purification catalyst 13 vibrate by within a predetermined range of amplitude and within a predetermined range of period, as shown in FIG. 5, an extremely high NO_x purification rate is obtained even in a 400°C or higher high temperature region.

[0021] Furthermore, at this time, a large amount of reducing intermediate containing nitrogen and hydrocarbons is produced on the surface of the basic layer 53 of the upstream-side end of the exhaust purification catalyst 13, that is, on the basic exhaust gas flow surface part 54 of the upstream-side end of the exhaust purification catalyst 13. It is learned that this reducing intermediate plays a central role in obtaining a high NO_x purification rate. Next, this will be explained with reference to FIGS. 6A, 6B, and 6C. Note that, FIGS. 6A and 6B schematically show the surface part of the catalyst carrier 50 of the upstream-side end of the exhaust purification catalyst

13, while FIG. 6C schematically shows the surface part of the catalyst carrier 50 at the downstream side from this upstream-side end. These FIGS. 6A, 6B, and 6C show the reaction which is presumed to occur when the concentration of hydrocarbons flowing into the exhaust purification catalyst 13 is made to vibrate by within a predetermined range of amplitude and within a predetermined range of period.

[0022] FIG. 6A shows when the concentration of hydrocarbons flowing into the exhaust purification catalyst 13 is low, while FIG. 6B shows when hydrocarbons are fed from the hydrocarbon feed valve 15 and the concentration of hydrocarbons flowing into the exhaust purification catalyst 13 becomes higher.

[0023] Now, as will be understood from FIG. 4, the air-fuel ratio of the exhaust gas which flows into the exhaust purification catalyst 13 is maintained lean except for an instant, so the exhaust gas which flows into the exhaust purification catalyst 13 normally becomes a state of oxygen excess. Therefore, the NO which is contained in the exhaust gas, as shown in FIG. 6A, is oxidized on the platinum 51 and becomes NO₂. Next, this NO₂ is further oxidized and becomes NO₃. Further, part of the NO₂ becomes NO₂⁻. In this case, the amount of production of NO₃ is far greater than the amount of production of NO₂⁻. Therefore, a large amount of NO₃ and a small amount of NO₂⁻ are produced on the platinum 51. This NO₃ and NO₂⁻ are strong in activity. Below, these NO₃ and NO₂⁻ will be called the active NO₂⁺.

[0024] On the other hand, if hydrocarbons are fed from the hydrocarbon feed valve 15, as shown in FIG. 3, the hydrocarbons are reformed in the upstream-side end of the exhaust purification catalyst 13 and become radicalized. As a result, as shown in FIG. 6B, the hydrocarbon concentration around the active NO₂⁺ becomes higher. In this regard, after the active NO₂⁺ is produced, if the state of a high oxygen concentration around the active NO₂⁺ continues for a predetermined time or more, the active NO₂⁺ is oxidized and is absorbed in the basic layer 53 in the form of nitrate ions NO₃⁻. However, if the hydrocarbon concentration around the active NO₂⁺ is made higher before this predetermined time passes, as shown in FIG. 6B, the active NO₂⁺ reacts on the platinum 51 with the radical hydrocarbons HC, whereby a reducing intermediate R-NH₂ is produced. This reducing intermediate R-NH₂ is adhered or adsorbed on the surface of the basic layer 53 while moving to the downstream side.

[0025] Note that, at this time, the first produced reducing intermediate is considered to be a nitro compound R-NO₂. If this nitro compound R-NO₂ is produced, the result becomes a nitrile compound R-CN, but this nitrile compound R-CN can only survive for an instant in this state, so immediately becomes an isocyanate compound R-NCO. This isocyanate compound R-NCO, when hydrolyzed, becomes an amine compound R-NH₂. However, in this case, what is hydrolyzed is considered to be part of the isocyanate compound R-NCO. Therefore, as shown in FIG. 6B, the majority of the reducing interme-

diate which is held or adsorbed on the surface of the basic layer 53 is believed to be the isocyanate compound R-NCO and amine compound R-NH₂.

[0026] On the other hand, part of the active NO₂⁺ which is produced in the upstream-side end of the exhaust purification catalyst 13 is sent to the downstream side where it sticks to or is adsorbed at the surface of the basic layer 53. Therefore, a larger amount of NO₂⁺ is held in the downstream side of the exhaust purification catalyst 13 as compared with the upstream-side end. On the other hand, as explained above, inside the exhaust purification catalyst 13, the reducing intermediate moves from the upstream-side end toward the downstream side. These reducing intermediate R-NCO or R-NH₂, as shown in FIG. 6C, reacts with the active NO₂⁺ which is held inside the downstream side exhaust purification catalyst 13 to become N₂, CO₂, and H₂O whereby the NO₂⁺ is removed.

[0027] In this way, in the exhaust purification catalyst 13, the concentration of hydrocarbons which flow into the exhaust purification catalyst 13 is temporarily made high to generate the reducing intermediate so that the active NO₂⁺ reacts with the reducing intermediate and the NO₂⁺ is purified. That is, to use the exhaust purification catalyst 13 to remove the NO₂⁺, it is necessary to periodically change the concentration of hydrocarbons flowing into the exhaust purification catalyst 13.

[0028] Of course, in this case, it is necessary to raise the concentration of hydrocarbons to a concentration sufficiently high for producing the reducing intermediate. That is, it is necessary to make the concentration of hydrocarbons flowing into the exhaust purification catalyst 13 vibrate by within a predetermined range of amplitude. Note that, in this case, it is necessary to hold a sufficient amount of reducing intermediate R-NCO or R-NH₂ on the basic layer 53, that is, the basic exhaust gas flow surface part 24, until the produced reducing intermediate reacts with the active NO₂⁺. For this reason, the basic exhaust gas flow surface part 24 is provided.

[0029] On the other hand, if lengthening the feed period of the hydrocarbons, the time in which the oxygen concentration becomes higher becomes longer in the period after the hydrocarbons are fed until the hydrocarbons are next fed. Therefore, the active NO₂⁺ is absorbed in the basic layer 53 in the form of nitrates without producing a reducing intermediate. To avoid this, it is necessary to make the concentration of hydrocarbons flowing into the exhaust purification catalyst 13 vibrate by within a predetermined range of period.

[0030] Therefore, in an embodiment of the present invention, to make the NO₂⁺ contained in the exhaust gas and the reformed hydrocarbons react and produce the reducing intermediate R-NCO or R-NH₂ containing nitrogen and hydrocarbons, precious metal catalysts 51 and 52 are carried on the exhaust gas flow surface of the exhaust purification catalyst 13. To hold the produced reducing intermediate R-NCO or R-NH₂ inside the exhaust purification catalyst 13, a basic exhaust gas flow surface part 54 is formed around the precious metal cat-

alysts 51 and 52. NO_x is reduced by the reducing action of the reducing intermediate R-NCO or R-NH₂ held on the basic exhaust gas flow surface part 54, and the vibration period of the hydrocarbon concentration is made the vibration period required for continuation of the production of the reducing intermediate R-NCO or R-NH₂. Incidentally, in the example shown in FIG. 4, the injection interval is made 3 seconds.

[0031] If the vibration period of the hydrocarbon concentration, that is, the feed period of the hydrocarbons HC, is made longer than the above predetermined range of period, the reducing intermediate R-NCO or R-NH₂ disappears from the surface of the basic layer 53. At this time, the active NO_x^* which is produced on the platinum Pt 53, as shown in FIG. 7A, diffuses in the basic layer 53 in the form of nitrate ions NO_3^- and becomes nitrates. That is, at this time, the NO_x in the exhaust gas is absorbed in the form of nitrates inside of the basic layer 53.

[0032] On the other hand, FIG. 7B shows the case where the air-fuel ratio of the exhaust gas which flows into the exhaust purification catalyst 13 is made the stoichiometric air-fuel ratio or rich when the NO_x is absorbed in the form of nitrates inside of the basic layer 53. In this case, the oxygen concentration in the exhaust gas falls, so the reaction proceeds in the opposite direction ($\text{NO}_3^- \rightarrow \text{NO}_2$), and consequently the nitrates absorbed in the basic layer 53 become nitrate ions NO_3^- one by one and, as shown in FIG. 7B, are released from the basic layer 53 in the form of NO_2 . Next, the released NO_2 is reduced by the hydrocarbons HC and CO contained in the exhaust gas.

[0033] FIG. 8 shows the case of making the air-fuel ratio (A/F) in of the exhaust gas which flows into the exhaust purification catalyst 13 temporarily rich slightly before the NO_x absorption ability of the basic layer 53 becomes saturated. Note that, in the example shown in FIG. 8, the time interval of this rich control is 1 minute or more. In this case, the NO_x which was absorbed in the basic layer 53 when the air-fuel ratio (A/F) in of the exhaust gas was lean is released all at once from the basic layer 53 and reduced when the air-fuel ratio (A/F) in of the exhaust gas is made temporarily rich. Therefore, in this case, the basic layer 53 plays the role of an absorbent for temporarily absorbing NO_x .

[0034] Note that, at this time, sometimes the basic layer 53 temporarily adsorbs the NO_x . Therefore, if using term of storage as a term including both absorption and adsorption, at this time, the basic layer 53 performs the role of an NO_x storage agent for temporarily storing the NO_x . That is, in this case, if the ratio of the air and fuel (hydrocarbons) which are supplied into the engine intake passage, combustion chambers 2, and exhaust passage upstream of the exhaust purification catalyst 13 is referred to as the air-fuel ratio of the exhaust gas, the exhaust purification catalyst 13 functions as an NO_x storage catalyst which stores the NO_x when the air-fuel ratio of the exhaust gas is lean and releases the stored NO_x when the oxygen concentration in the exhaust gas falls.

[0035] FIG. 9 shows the NO_x purification rate when making the exhaust purification catalyst 13 function as an NO_x storage catalyst in this way. Note that, the abscissa of the FIG. 9 shows the catalyst temperature TC of the exhaust purification catalyst 13. When making the exhaust purification catalyst 13 function as an NO_x storage catalyst, as shown in FIG. 9, when the catalyst temperature TC is 300°C to 400°C, an extremely high NO_x purification rate is obtained, but when the catalyst temperature TC becomes a 400°C or higher high temperature, the NO_x purification rate falls.

[0036] In this way, when the catalyst temperature TC becomes 400°C or more, the NO_x purification rate falls because if the catalyst temperature TC becomes 400°C or more, the nitrates break down by heat and are released in the form of NO_2 from the exhaust purification catalyst 13. That is, so long as storing NO_x in the form of nitrates, when the catalyst temperature TC is high, it is difficult to obtain a high NO_x purification rate. However, in the new NO_x purification method shown from FIG. 4 to FIGS. 6A and 6B, as will be understood from FIGS. 6A and 6B, nitrates are not formed or even if formed are extremely fine in amount, consequently, as shown in FIG. 5, even when the catalyst temperature TC is high, a high NO_x purification rate is obtained.

[0037] Therefore, in the present invention, an exhaust purification catalyst 13 for reacting NO_x contained in exhaust gas and reformed hydrocarbons to produce a reducing intermediate containing nitrogen and hydrocarbons is arranged in the engine exhaust passage, precious metal catalysts 51 and 52 are carried on the exhaust gas flow surface of the exhaust purification catalyst 13, a basic exhaust gas flow surface part 54 is formed around the precious metal catalysts 51 and 52, the exhaust purification catalyst 13 has the property of producing the reducing intermediate and reducing the NO_x contained in exhaust gas by the reducing action of the produced reducing intermediate if the concentration of hydrocarbons flowing into the exhaust purification catalyst 13 is made to vibrate within a predetermined range of amplitude and within a predetermined range of period and has the property of being increased in storage amount of NO_x which is contained in exhaust gas if the vibration period of the hydrocarbon concentration is made longer than this predetermined range, and, at the time of engine operation, the concentration of hydrocarbons flowing into the exhaust purification catalyst 13 is made to vibrate within the predetermined range of amplitude and with the predetermined range of period to thereby reduce the NO_x which is contained in the exhaust gas in the exhaust purification catalyst 13.

[0038] That is, the NO_x purification method which is shown from FIG. 4 to FIGS. 6A and 6B can be said to be a new NO_x purification method designed to remove NO_x without forming almost any nitrates in the case of using an exhaust purification catalyst which carries a precious metal catalyst and forms a basic layer which can absorb NO_x . In actuality, when using this new NO_x purification

method, the nitrates which are detected from the basic layer 53 become much smaller in amount compared with the case where making the exhaust purification catalyst 13 function as an NO_x storage catalyst. Note that, this new NO_x purification method will be referred to below as the first NO_x purification method.

[0039] Next, referring to FIG. 10 to FIG. 15, this first NO_x purification method will be explained in a bit more detail.

[0040] FIG. 10 shows enlarged the change in the air-fuel ratio (A/F)_{in} shown in FIG. 4. Note that, as explained above, the change in the air-fuel ratio (A/F)_{in} of the exhaust gas flowing into this exhaust purification catalyst 13 simultaneously shows the change in concentration of the hydrocarbons which flow into the exhaust purification catalyst 13. Note that, in FIG. 10, ΔH shows the amplitude of the change in concentration of hydrocarbons HC which flow into the exhaust purification catalyst 13, while ΔT shows the vibration period of the concentration of the hydrocarbons which flow into the exhaust purification catalyst 13.

[0041] Furthermore, in FIG. 10, (A/F)_b shows the base air-fuel ratio which shows the air-fuel ratio of the combustion gas for generating the engine output. In other words, this base air-fuel ratio (A/F)_b shows the air-fuel ratio of the exhaust gas which flows into the exhaust purification catalyst 13 when stopping the feed of hydrocarbons. On the other hand, in FIG. 10, X shows the upper limit of the air-fuel ratio (A/F)_{in} used for producing the reducing intermediate without the produced active NO_x^* being stored in the form of nitrates inside the basic layer 53 much at all. To make the active NO_x^* and the reformed hydrocarbons react to produce a reducing intermediate, the air-fuel ratio (A/F)_{in} has to be made lower than this upper limit X of the air-fuel ratio.

[0042] In other words, in FIG. 10, X shows the lower limit of the concentration of hydrocarbons required for making the active NO_x^* and reformed hydrocarbon react to produce a reducing intermediate. To produce the reducing intermediate, the concentration of hydrocarbons has to be made higher than this lower limit X. In this case, whether the reducing intermediate is produced is determined by the ratio of the oxygen concentration and hydrocarbon concentration around the active NO_x^* , that is, the air-fuel ratio (A/F)_{in}. The upper limit X of the air-fuel ratio required for producing the reducing intermediate will below be called the demanded minimum air-fuel ratio.

[0043] In the example shown in FIG. 10, the demanded minimum air-fuel ratio X is rich, therefore, in this case, to form the reducing intermediate, the air-fuel ratio (A/F)_{in} is instantaneously made the demanded minimum air-fuel ratio X or less, that is, rich. As opposed to this, in the example shown in FIG. 11, the demanded minimum air-fuel ratio X is lean. In this case, the air-fuel ratio (A/F)_{in} is maintained lean while periodically reducing the air-fuel ratio (A/F)_{in} so as to form the reducing intermediate.

[0044] In this case, whether the demanded minimum air-fuel ratio X becomes rich or becomes lean depends

on the oxidizing strength of the exhaust purification catalyst 13. In this case, the exhaust purification catalyst 13, for example, becomes stronger in oxidizing strength if increasing the carried amount of the precious metal 51 and becomes stronger in oxidizing strength if strengthening the acidity. Therefore, the oxidizing strength of the exhaust purification catalyst 13 changes due to the carried amount of the precious metal 51 or the strength of the acidity.

[0045] Now, if using an exhaust purification catalyst 13 with a strong oxidizing strength, as shown in FIG. 11, if maintaining the air-fuel ratio (A/F)_{in} in lean while periodically lowering the air-fuel ratio (A/F)_{in}, the hydrocarbons end up becoming completely oxidized when the air-fuel ratio (A/F)_{in} is reduced. As a result, the reducing intermediate can no longer be produced. As opposed to this, when using an exhaust purification catalyst 13 with a strong oxidizing strength, as shown in FIG. 10, if making the air-fuel ratio (A/F)_{in} in periodically rich, when the air-fuel ratio (A/F)_{in} is made rich, the hydrocarbons will be partially oxidized, without being completely oxidized, that is, the hydrocarbons will be reformed, consequently the reducing intermediate will be produced. Therefore, when using an exhaust purification catalyst 13 with a strong oxidizing strength, the demanded minimum air-fuel ratio X has to be made rich.

[0046] On the other hand, when using an exhaust purification catalyst 13 with a weak oxidizing strength, as shown in FIG. 11, if maintaining the air-fuel ratio (A/F)_{in} in lean while periodically lowering the air-fuel ratio (A/F)_{in}, the hydrocarbons will be partially oxidized without being completely oxidized, that is, the hydrocarbons will be reformed and consequently the reducing intermediate will be produced. As opposed to this, when using an exhaust purification catalyst 13 with a weak oxidizing strength, as shown in FIG. 10, if making the air-fuel ratio (A/F)_{in} periodically rich, a large amount of hydrocarbons will be exhausted from the exhaust purification catalyst 13 without being oxidized and consequently the amount of hydrocarbons which is wastefully consumed will increase. Therefore, when using an exhaust purification catalyst 13 with a weak oxidizing strength, the demanded minimum air-fuel ratio X has to be made lean.

[0047] That is, it is learned that the demanded minimum air-fuel ratio X, as shown in FIG. 12, has to be reduced the stronger the oxidizing strength of the exhaust purification catalyst 13. In this way the demanded minimum air-fuel ratio X becomes lean or rich due to the oxidizing strength of the exhaust purification catalyst 13. Below, taking as example the case where the demanded minimum air-fuel ratio X is rich, the amplitude of the change in concentration of hydrocarbons flowing into the exhaust purification catalyst 13 and the vibration period of the concentration of hydrocarbons flowing into the exhaust purification catalyst 13 will be explained.

[0048] Now, if the base air-fuel ratio (A/F)_b becomes larger, that is, if the oxygen concentration in the exhaust gas before the hydrocarbons are fed becomes higher,

the feed amount of hydrocarbons required for making the air-fuel ratio (A/F) in the demanded minimum air-fuel ratio X or less increases. Therefore, the higher the oxygen concentration in the exhaust gas before the hydrocarbons are fed, the larger the amplitude of the hydrocarbon concentration has to be made.

[0049] FIG. 13 shows the relationship between the oxygen concentration in the exhaust gas before the hydrocarbons are fed and the amplitude ΔH of the hydrocarbon concentration when the same NO_x purification rate is obtained. From FIG. 13, it is learned that to obtain the same NO_x purification rate, the higher the oxygen concentration in the exhaust gas before the hydrocarbons are fed, the greater the amplitude ΔH of the hydrocarbon concentration has to be made. That is, to obtain the same NO_x purification rate, the higher the base air-fuel ratio (A/F)_b, the greater the amplitude ΔT of the hydrocarbon concentration has to be made. In other words, to remove the NO_x well, the lower the base air-fuel ratio (A/F)_b, the more the amplitude ΔT of the hydrocarbon concentration can be reduced.

[0050] In this regard, the base air-fuel ratio (A/F)_b becomes the lowest at the time of an acceleration operation. At this time, if the amplitude ΔH of the hydrocarbon concentration is about 200 ppm, it is possible to remove the NO_x well. The base air-fuel ratio (A/F)_b is normally larger than the time of acceleration operation. Therefore, as shown in FIG. 14, if the amplitude ΔH of the hydrocarbon concentration is 200 ppm or more, an excellent NO_x purification rate can be obtained.

[0051] On the other hand, it is learned that when the base air-fuel ratio (A/F)_b is the highest, if making the amplitude ΔH of the hydrocarbon concentration 10000 ppm or so, an excellent NO_x purification rate is obtained. Therefore, in the present invention, the predetermined range of the amplitude of the hydrocarbon concentration is made 200 ppm to 10000 ppm.

[0052] Further, if the vibration period ΔT of the hydrocarbon concentration becomes longer, the oxygen concentration around the active NO_x^* becomes higher in the time after the hydrocarbons are fed to when the hydrocarbons are next fed. In this case, if the vibration period ΔT of the hydrocarbon concentration becomes longer than about 5 seconds, the active NO_x^* starts to be absorbed in the form of nitrates inside the basic layer 53. Therefore, as shown in FIG. 15, if the vibration period ΔT of the hydrocarbon concentration becomes longer than about 5 seconds, the NO_x purification rate falls. Therefore, the vibration period ΔT of the hydrocarbon concentration has to be made 5 seconds or less.

[0053] On the other hand, if the vibration period ΔT of the hydrocarbon concentration becomes about 0.3 second or less, the fed hydrocarbons start to build up on the exhaust gas flow surface of the exhaust purification catalyst 13, therefore, as shown in FIG. 15, if the vibration period ΔT of the hydrocarbon concentration becomes about 0.3 second or less, the NO_x purification rate falls. Therefore, in the present invention, the vibration period

of the hydrocarbon concentration is made from 0.3 second to 5 seconds.

[0054] Now, in the present invention, by changing the hydrocarbon feed amount and injection timing from the hydrocarbon feed valve 15, the amplitude ΔH and vibration period ΔT of the hydrocarbons concentration are controlled so as to become the optimum values in accordance with the engine operating state. In this case, in this embodiment of the present invention, the hydrocarbon feed amount W able to give the optimum amplitude ΔH of the hydrocarbon concentration is stored as a function of the injection amount Q from the fuel injector 3 and engine speed N in the form of a map such as shown in FIG. 16 in advance in the ROM 32. Further, the optimum vibration amplitude ΔT of the hydrocarbon concentration, that is, the injection period ΔT of the hydrocarbons, is similarly stored as a function of the injection amount Q and engine speed N in the form of a map in advance in the ROM 32.

[0055] Next, referring to FIG. 17 to FIG. 20, an NO_x purification method in the case when making the exhaust purification catalyst 13 function as an NO_x storage catalyst will be explained in detail. The NO_x purification method in the case when making the exhaust purification catalyst 13 function as an NO_x storage catalyst in this way will be referred to below as the second NO_x purification method.

[0056] In this second NO_x purification method, as shown in FIG. 17, when the stored NO_x amount ΣNO_x of NO_x which is stored in the basic layer 53 exceeds a predetermined allowable amount MAX, the air-fuel ratio (A/F)_{in} of the exhaust gas flowing into the exhaust purification catalyst 13 is temporarily made rich. If the air-fuel ratio (A/F)_{in} of the exhaust gas is made rich, the NO_x which was stored in the basic layer 53 when the air-fuel ratio (A/F)_{in} of the exhaust gas was lean is released from the basic layer 53 all at once and reduced. Due to this, the NO_x is removed.

[0057] The stored NO_x amount ΣNO_x is, for example, calculated from the amount of NO_x which is exhausted from the engine. In this embodiment according to the present invention, the exhausted NO_x amount NO_xA of NO_x which is exhausted from the engine per unit time is stored as a function of the injection amount Q and engine speed N in the form of a map such as shown in FIG. 18 in advance in the ROM 32. The stored NO_x amount ΣNO_x is calculated from exhausted NO_x amount NO_xA . In this case, as explained before, the period in which the air-fuel ratio (A/F)_{in} of the exhaust gas is made rich is usually 1 minute or more.

[0058] In this second NO_x purification method, as shown in FIG. 19, the fuel injector 3 injects additional fuel WR into the combustion chamber 2 in addition to the combustion-use fuel Q so that the air-fuel ratio (A/F)_{in} of the exhaust gas flowing into the exhaust purification catalyst 13 is made rich. Note that, in FIG. 19, the abscissa indicates the crank angle. This additional fuel WR is injected at a timing at which it will burn, but will not

appear as engine output, that is, slightly before ATDC90° after compression top dead center. This fuel amount WR is stored as a function of the injection amount Q and engine speed N in the form of a map such as shown in FIG. 20 in advance in the ROM 32. Of course, in this case, it is also possible to make the amount of feed of hydrocarbons from the hydrocarbon feed valve 15 increase so as to make the air-fuel ratio (A/F) in of the exhaust gas rich.

[0059] In this regard, exhaust gas contains SO_x, that is, SO₂. If this SO₂ flows into the exhaust purification catalyst 13, this SO₂ is oxidized on the platinum Pt 51 and becomes SO₃ as show in FIG. 21A even when an NO_x purification action is performed by the first NO_x purification method and even when an NO_x purification action is performed by the second NO_x purification method. Next, this SO₃ is absorbed in the basic layer 53 and diffuses inside the basic layer 53 in the form of sulfate ions SO₄²⁻ to thereby produce the stable sulfate. However, sulfates are stable and hard to break down. If just simply making the air-fuel ratio of the exhaust gas rich, the sulfates will remain as they are without breaking down. Therefore, inside the basic layer 53, along with the elapse of time, a gradually increasing amount of SO_x will be stored. That is, the exhaust purification catalyst 13 will suffer from sulfur poisoning.

[0060] If the amount of SO_x which is stored in the basic layer 53 increases, the basicity of the basic layer 53 weakens and, as a result, the reaction whereby the NO₂ becomes NO₃, that is, the reaction for producing active NO_x^{*}, can no longer proceed. If the reaction for producing active NO_x^{*} can no longer proceed in this way, the action of producing the reducing intermediate at the upstream-side end of the exhaust purification catalyst 13 becomes weaker and, therefore the NO_x purification rate falls when the NO_x purification action is performed by the first NO_x purification method. Therefore, at this time, it is necessary to make the SO_x which is stored at the upstream-side end of the exhaust purification catalyst 13 be released from the upstream-side end.

[0061] On the other hand, even if the SO_x amount which is stored in the basic layer 53 increases, there will be little effect on the reaction of the reducing intermediate and active NO_x^{*} at the downstream side of the exhaust purification catalyst 13, that is, the NO_x purification method. However, if the stored amount of SO_x increases in the exhaust purification catalyst 13 as a whole, the amount of NO_x which the exhaust purification catalyst 13 can store falls and finally NO_x can no longer be stored. If the exhaust purification catalyst 13 can no longer store the NO_x, soon the second NO_x purification method will no longer be able to be used to remove the NO_x. Therefore, in this case, it is necessary to make the SO_x which is stored in the entirety of the exhaust purification catalyst 13 be released from the entirety of exhaust purification catalyst 13.

[0062] In this regard, in this case, if the reducing agent, that is, hydrocarbons, are fed in the state where the tem-

perature of the exhaust purification catalyst 13 is made to rise to the SO_x release temperature determined by the exhaust purification catalyst 13, and thereby the air-fuel ratio of the exhaust gas flowing into the exhaust purification catalyst 13 is made rich, SO_x can be released from the exhaust purification catalyst 13 by the reducing action of the reducing agent.

[0063] However, the reducing power of hydrocarbons HC themselves is not that strong. Therefore, when releasing SO_x from the exhaust purification catalyst 13, if using the reducing action of hydrocarbons HC to reduce the SO_x, a large amount of hydrocarbons HC becomes necessary. As opposed to this, ammonia NH₃ is far stronger in reducing ability compared with hydrocarbons HC. Therefore, if it were possible to produce ammonia NH₃ when releasing SO_x from the exhaust purification catalyst 13, it would become easy to reduce the SO_x.

[0064] The inventors engaged in repeated research regarding this point and as a result discovered that when a reducing intermediate builds up inside the exhaust purification catalyst 13, if the air-fuel ratio of the exhaust gas flowing into the exhaust purification catalyst 13 is made rich, the reducing intermediate will desorb from the exhaust purification catalyst 13 in the form of ammonia and that the SO_x which is stored in the exhaust purification catalyst 13 is reduced by this desorbed ammonia and released.

[0065] Therefore, in the present invention, when SO_x which has been stored at the exhaust purification catalyst 13 should be released, the air-fuel ratio of the exhaust gas which flows into the exhaust purification catalyst 13 is lowered to the targeted rich air-fuel ratio to make the reducing intermediate built up on the exhaust purification catalyst 13 desorb in the form of ammonia and the desorbed ammonia is used to make the stored SO_x be released from the exhaust purification catalyst.

[0066] That is, at this time, as shown in FIG. 21B, the partially oxidized hydrocarbons and the reducing intermediate react whereby the reducing intermediate is made to desorb in the form of ammonia NH₃. The stored sulfates are reduced by this desorbed ammonia NH₃ and is released from the basic layer 53 in the form of SO₂.

[0067] In this regard, in the present invention, as the SO_x release control for releasing SO_x from the exhaust purification catalyst 13, two SO_x release controls comprised of a first SO_x release control which uses the desorbed ammonia to release the stored SO_x from the upstream-side end of the exhaust purification catalyst 13 and a second SO_x release control which releases the stored SO_x from the entirety of the exhaust purification catalyst 13 are performed. FIG. 22A and FIG. 23A show this first SO_x release control, while FIG. 22B and FIG. 23B show this second SO_x release control.

[0068] First, referring to FIG. 22A and FIG. 22B, the first SO_x release control will be explained. As explained above, this first SO_x release control is performed when the SO_x storage amount of the upstream-side end 13a of the exhaust purification catalyst 13 for example ex-

ceeds a predetermined amount. That is, if it is judged at t_1 of FIG. 23A that SO_x should be released from the upstream-side end 13a, during the time t_x of FIG. 23A, the amount of feed of hydrocarbons from the hydrocarbon feed valve 15 per unit time is increased while performing the NO_x purification action by the first NO_x purification method, and thereby the temperature elevation control of the exhaust purification catalyst 13 is performed.

[0069] Next, if the temperature of the exhaust purification catalyst 13 reaches the SO_x release temperature, the air-fuel ratio (A/F) in of the exhaust gas flowing into the exhaust purification catalyst 13, as shown by RA, is made rich for a certain time, for example, 5 seconds, until the targeted rich air-fuel ratio. Note that, in the example shown in FIG. 23A, the air-fuel ratio (A/F) in of the exhaust gas is made rich for a certain time two times at a certain interval. In this case, the air-fuel ratio (A/F) in of the exhaust gas is made rich by injecting additional fuel into the combustion chamber 2 as shown by WR in FIG. 19 or by increasing the amount of feed of hydrocarbons from the hydrocarbon feed valve 15.

[0070] If the air-fuel ratio of the exhaust gas is made rich, the reducing intermediate which has built up at the upstream-side end 13a is made to be desorbed in the form of ammonia. This desorbed ammonia is used to make the stored SO_x be released from the upstream-side end 13a in the form of SO_2 . This released SO_2 , as shown in FIG. 22A, moves to the downstream side and is again stored inside the downstream-side catalyst part 13b at the downstream side from the upstream-side end 13a.

[0071] In this case, to prevent the SO_x which was released from the upstream-side end 13a from being stored at the downstream-side catalyst part 13b, it is necessary to make the atmosphere in the downstream-side catalyst part 13b as a whole rich over a long period of time. For that, it is necessary to make the air-fuel ratio (A/F) in of the exhaust gas flowing into the exhaust purification catalyst 13 considerably rich over a long period of time. However, if just making the SO_x be released from the upstream-side end 13a, that is, if it is all right that the released SO_2 be stored in the downstream-side catalyst part 13b, the air-fuel ratio (A/F) in of the exhaust gas does not have to be made that rich. Further, it is enough that the air-fuel ratio (A/F) in of the exhaust gas be made rich for a short time. Therefore, at the time of the first SO_x release control, as shown in FIG. 23A by RA, the targeted air-fuel ratio (A/F) in is not made that rich.

[0072] Note that, while saying in this way that the targeted air-fuel ratio (A/F) in is not made that rich, when the air-fuel ratio (A/F) in is made rich, the air-fuel ratio (A/F) in is lowered compared with before it was made rich. Therefore, in the present invention when SO_x which is stored in the exhaust purification catalyst 13 is to be released, the air-fuel ratio (A/F) in of the exhaust gas which flows into the exhaust purification catalyst 13 is lowered to the targeted rich air-fuel ratio. The amount of additional fuel or the amount of hydrocarbons required for making the air-fuel ratio (A/F) in this targeted rich air-

fuel ratio is stored in advance.

[0073] Note that, in FIG. 23A, during the rich time period shown by RA, it appears that the air-fuel ratio (A/F) in is continuously made rich in the drawing, but in actuality the air-fuel ratio (A/F) in vibrates by intervals far shorter than at the time of temperature elevation control t_x .

[0074] On the other hand, the second SO_x release control is performed when the SO_x and ΣSOX which is stored in the entirety of the exhaust purification catalyst 13 exceeds the allowable value SX. Note that, in the embodiment according to the present invention, the exhausted SO_x amount SOXA of the SO_x which is exhausted per unit time from an engine is stored as a function of the injection amount Q and the engine speed N in the form of a map such as in FIG. 22C in advance in the ROM 32. The exhausted SO_x amount SOXA is cumulatively added to calculate the stored SO_x amount ΣSOX .

[0075] That is, in FIG. 23B, if assuming that, at t_1 , the SO_x amount ΣSOX exceeds the allowable value SX, during the time TX of FIG. 23B, the amount of feed of hydrocarbons from the hydrocarbon feed valve 15 per unit time is increased while performing the NO_x purification action by the first NO_x purification method, and thereby the temperature elevation control of the exhaust purification catalyst 13 is performed.

[0076] Next, if the temperature of the exhaust purification catalyst 13 reaches the SO_x release temperature, the air-fuel ratio (A/F) in of the exhaust gas flowing into the exhaust purification catalyst 13, as shown by RA, is made rich for a certain time, for example, 5 seconds, until the targeted rich air-fuel ratio. Note that, in the case shown in FIG. 23B, the air-fuel ratio (A/F) in of the exhaust gas is repeatedly made rich for a certain time. In this case as well, the air-fuel ratio (A/F) in of the exhaust gas is made rich by injecting additional fuel into the combustion chamber 2 as shown by WR in FIG. 19 or by increasing the feed amount of hydrocarbons from the hydrocarbon feed valve 15.

[0077] If the air-fuel ratio of the exhaust gas is made rich, the reducing intermediate which builds up on the exhaust purification catalyst 13 is made to desorb in the form of ammonia. This desorbed ammonia enables the stored SO_x to be released from the entirety of the exhaust purification catalyst 13 in the form of SO_2 . This released SO_2 , as shown in FIG. 22B, is exhausted from the exhaust purification catalyst 13. At the time of the second SO_x release control, to make the SO_x which is released be exhausted from the exhaust purification catalyst 13 in this way, the air-fuel ratio (A/F) in of the exhaust gas is made considerably rich. Further, the air-fuel ratio (A/F) in of the exhaust gas is repeatedly made rich over a long period of time.

[0078] As will be understood if comparing FIG. 23A and FIG. 23B, in an embodiment of the present invention, the time during which the second SO_x release control is performed is made longer than the time during which the first SO_x release control is performed. Further, the targeted rich air-fuel ratio is made lower at the time of the

second SO_x release control compared with at the time of the first SO_x release control.

[0079] Note that, in the internal combustion engine shown in FIG. 1, at the time of deceleration operation, the throttle valve 10 is made to close. If the throttle valve 10 is made to close, the flow rate of the exhaust gas becomes slower. Therefore, at this time, if feeding hydrocarbons into the combustion chamber 2 or the exhaust passage to perform the temperature elevation action, heat will be applied concentratedly at the upstream-side end 13a of the exhaust purification catalyst 13, so the temperature of the upstream-side end 13a can be efficiently raised. Therefore, in another embodiment of the present invention, when the exhaust purification catalyst 13 should be raised in temperature for performing the first SO_x release control, at the time of a deceleration operation where the throttle valve 10 is made to close, hydrocarbons are fed into the combustion chamber 2 or upstream of the exhaust purification catalyst 13 in the engine exhaust passage.

[0080] Further, at the time of engine high load, high speed operation, the temperature of the exhaust purification catalyst 13 becomes the SO_x release temperature. Therefore, at this time, if performing the first SO_x release control, temperature elevation control of the exhaust purification catalyst 13 no longer is necessary. Therefore, in still another embodiment of the present invention, at the time of engine high load, high speed operation, the first SO_x release control is performed.

[0081] Further, in still another embodiment of the present invention, at the time of regeneration of the particulate filter 14, when the exhaust purification catalyst 13 is made to rise in temperature to raise the temperature of the particulate filter 14, the first SO_x release control is performed. If doing this, it is no longer necessary to perform temperature elevation control in the exhaust purification system 13 just for SO_x release control. FIG. 24 shows a time chart in the case of performing the first SO_x release control at the time of regeneration of the particulate filter 14 in this way, and FIG. 25 shows a exhaust purification control in this case.

[0082] In FIG. 24, ΔP indicates the differential pressure before and after the particulate filter 14 which is detected by the differential pressure sensor 24. As shown in FIG. 24, if the differential pressure ΔP before and after the particulate filter 14 exceeds the allowable value PX, for example, hydrocarbons are fed from the hydrocarbon feed valve 15 and temperature elevation control of the particulate filter 14 is performed. This temperature elevation control uses the heat of oxidation reaction of the fed hydrocarbons on the exhaust purification catalyst 13 so as to make the temperature of the exhaust gas rise and thereby make the temperature of the particulate filter 14 rise. If the temperature of the particulate filter 14 is made to rise, the particulate which is trapped on the particulate filter 14 will burn and therefore the front-back differential pressure ΔP will gradually fall.

[0083] On the other hand, at the time of temperature

elevation control of the particulate filter 14, as shown in FIG. 24, the temperature TC of the exhaust purification catalyst 13 also rises. Therefore, at this time, the first SO_x release control is performed. On the other hand, if the stored SO_x amount ΣSOX exceeds the allowable value SX, as shown in FIG. 23B, temperature elevation control is performed, then the second SO_x release control is performed. As shown in FIG. 23B, in this second SO_x release control, a rich air-fuel ratio and a lean air-fuel ratio are repeated, whereby the exhaust purification catalyst 13 is maintained at the SO_x release temperature.

[0084] The processing for regeneration of the particulate filter 14 is performed every time the vehicle driving distance reaches 100 km to 500 km. Therefore, the first SO_x release control is performed every time the vehicle driving distance reaches 100 km to 500 km. The total time during which the air-fuel ratio is made rich in this first SO_x release control is a maximum of 30 seconds. As opposed to this, the second SO_x release control is performed every time the vehicle driving distance reaches 1000 km to 5.000 km. In this second SO_x release control, the total time during which the air-fuel ratio is made rich is 5 minutes to 10 minutes. In this way, the period by which the second NO_x release control is performed is made longer than the period by which the first NO_x release control is performed.

[0085] Next, the exhaust purification control routine shown in FIG. 25 will be explained. This routine is executed by interruption every constant time.

[0086] Referring to FIG. 25, first, at step 60, the exhausted SO_x amount SOXA is calculated from the map shown in FIG. 22C. Next, at step 61, ΣSOX is increased by the exhausted SO_x amount SOXA to calculate the stored SO_x amount ΣSOX . Next, at step 62, it is judged from the output signal of the temperature sensor 23 if the temperature TC of the exhaust purification catalyst 13 exceeds the activation temperature TX. When $TC \geq TX$, that is, when the exhaust purification catalyst 13 is activated, the routine proceeds to step 63 where it is judged from the output signal of the differential pressure sensor 24 whether the differential pressure ΔP before and after the particulate filter 14 exceeds the allowable value PX.

[0087] When $\Delta P \leq PX$, the routine jumps to step 66. As opposed to this, when $\Delta P > PX$, the routine proceeds to step 64 where temperature elevation control of the particulate filter 14 is performed, then, at step 65, the first SO_x release control is performed. Next, the routine proceeds to step 66. At step 66, it is judged if the stored SO_x amount ΣSOX exceeds the allowable value SX. When $\Sigma SOX > SX$, the routine proceeds to step 67 where temperature elevation control of the exhaust purification catalyst 13 is performed. Next, step 68, the second SO_x release control is performed and ΣSOX is cleared.

[0088] On the other hand, when it is judged at step 62 that $TC \leq TC_0$, it is judged that the second NO_x purification method should be used, then the routine proceeds to step 69. At step 69, the NO_x amount NOXA of NO_x exhausted per unit time is calculated from the map shown

in FIG. 18. Next, step 70, ΣNO_x is increased by the exhausted NO_x amount NO_xA to calculate the stored NO_x amount ΣNO_x . Next, at step 71, it is judged if the stored NO_x amount ΣNO_x exceeds the allowable value NX . When $\Sigma\text{NO}_x > \text{NX}$, the routine proceeds to step 72 where the additional fuel amount WR is calculated from the map shown in FIG. 20 and an injection action of additional fuel is performed. Next, at step 73, ΣNO_x is cleared.

[0089] Note that, as another embodiment, in the engine exhaust passage upstream of the exhaust purification catalyst 13, an oxidation catalyst for reforming the hydrocarbons can be arranged.

Reference Signs List

[0090]

- 4 intake manifold
- 5 exhaust manifold
- 7 exhaust turbocharger
- 12 exhaust pipe
- 13 exhaust purification catalyst
- 14 particulate filter
- 15 hydrocarbon feed valve

Claims

1. A method of purifying exhaust gas exhausted from an internal combustion engine wherein an exhaust purification catalyst (13) for reacting NO_x contained in exhaust gas and reformed hydrocarbons to produce a reducing intermediate containing nitrogen and hydrocarbons is arranged in an engine exhaust passage, a precious metal catalyst (51, 52) is carried on an exhaust gas flow surface of the exhaust purification catalyst (13) and a basic exhaust gas flow surface part (54) is formed around the precious metal catalysts (51, 52), the exhaust purification catalyst (13) has a property of producing the reducing intermediate and reducing NO_x contained in exhaust gas by a reducing action of the produced reducing intermediate if a concentration of hydrocarbons flowing into the exhaust purification catalyst (13) is made to vibrate within a predetermined range of amplitude and within a predetermined range of period and has a property of being increased in storage amount of NO_x which is contained in exhaust gas if a vibration period of the hydrocarbon concentration is made longer than said predetermined range, wherein, at the time of engine operation, to reduce NO_x contained in the exhaust gas in the exhaust purification catalyst (13) according to a first NO_x purification method, the concentration of hydrocarbons flowing into the exhaust purification catalyst (13) is made to vibrate within said predetermined range of amplitude and within said predetermined range of period, wherein said vibration period (ΔT) of the hydrocarbon

concentration is between 0.3 second to 5 seconds, and,

wherein, when a stored SO_x should be released from the exhaust purification catalyst (13), an air-fuel ratio of the exhaust gas which flows into the exhaust purification catalyst (13) is lowered to a targeted rich air-fuel ratio to make the reducing intermediate built up on the exhaust purification catalyst (13) desorb in the form of ammonia and the desorbed ammonia is used to make the exhaust purification catalyst (13) release the stored SO_x .

2. A method of purifying exhaust gas exhausted from an internal combustion engine as claimed in claim 1, wherein a first SO_x release control which uses the desorbed ammonia to release the stored SO_x from an upstream-side end of the exhaust purification catalyst (13) and a second SO_x release control which release the stored SO_x from an entirety of the exhaust purification catalyst (13) are performed and wherein a time during which the second SO_x release control is performed is made longer than a time during which the first SO_x release control is performed.
3. A method of purifying exhaust gas exhausted from an internal combustion engine as claimed in claim 2, wherein a period in which the second SO_x release control is performed is longer than a period in which the first SO_x release control is performed.
4. A method of purifying exhaust gas exhausted from an internal combustion engine as claimed in claim 2, wherein the targeted rich air-fuel ratio is made lower at the time of the second SO_x release control compared with the time of the first SO_x release control.
5. A method of purifying exhaust gas exhausted from an internal combustion engine as claimed in claim 2, wherein a particulate filter (14) is arranged inside the engine exhaust passage downstream of the exhaust purification catalyst (13) and wherein the first SO_x release control is performed at the time when the exhaust purification catalyst (13) is made to rise in temperature to raise a temperature of the particulate filter (14) at the time of regeneration of the particulate filter (14).
6. A method of purifying exhaust gas exhausted from an internal combustion engine as claimed in claim 2, wherein the first SO_x release control is performed at the time of engine high load, high speed operation.
7. A method of purifying exhaust gas exhausted from an internal combustion engine as claimed in claim 2, wherein a throttle valve (10) is provided for control of an intake air amount and wherein when the exhaust purification catalyst (13) should rise in temper-

ature for the first SO_x release control, hydrocarbons are fed into a combustion chamber (2) or into the engine exhaust passage upstream of the exhaust purification catalyst (13) at the time of a deceleration operation where the throttle valve (10) is made to close.

8. A method of purifying exhaust gas exhausted from an internal combustion engine as claimed in claim 1, wherein said precious metal catalyst (51, 52) is comprised of platinum Pt and at least one of rhodium Rh and palladium Pd.
9. A method of purifying exhaust gas exhausted from an internal combustion engine as claimed in claim 1, wherein a basic layer (53) containing an alkali metal, an alkali earth metal, a rare earth, or a metal which can donate electrons to NO_x is formed on the exhaust gas flow surface of the exhaust purification catalyst (13) and wherein a surface of said basic layer (53) forms said basic exhaust gas flow surface part (54).

Patentansprüche

1. Verfahren zum Reinigen von Abgas, das von einer Verbrennungskraftmaschine ausgestoßen wird, wobei ein Abgasreinigungskatalysator (13) zum Reagieren von in dem Abgas enthaltenem NO_x und reformierten Kohlenwasserstoffen, um ein Reduktions-Zwischenprodukt zu erzeugen, das Stickstoff und Kohlenwasserstoffe enthält, in einem Maschinen-Abgastrakt angeordnet ist, ein Edelmetallkatalysator (51, 52) auf einer Abgasströmungsoberfläche des Abgasreinigungskatalysators (13) getragen ist und ein basischer Abgasströmungsoberflächenteil (54) um den Edelmetallkatalysator (51, 52) herum ausgebildet ist, wobei der Abgasreinigungskatalysator (13) eine Eigenschaft aufweist, das Reduktions-Zwischenprodukt zu erzeugen und das in dem Abgas enthaltene NO_x durch einen Reduktionsvorgang des erzeugten Reduktions-Zwischenprodukts zu reduzieren, falls eine Konzentration an Kohlenwasserstoffen, die in den Abgasreinigungskatalysator (13) strömen, veranlasst wird, innerhalb eines vorgegebenen Amplitudenbereichs und innerhalb eines vorgegebenen Periodenbereichs zu schwingen, und eine Eigenschaft aufweist, die Speicher- menge an in dem Abgas enthaltenem NO_x zu erhöhen, falls eine Schwingungsperiode der Kohlenwasserstoff-Konzentration über den vorgegebenen Bereich hinaus verlängert wird, wobei, zu der Zeit des Betriebs der Maschine, um in dem Abgas enthaltenes NO_x in dem Abgasreinigungskatalysator (13) nach einem ersten NO_x-Reinigungs- verfahren zu reduzieren, die Konzentration an Kohlenwasserstoffen, die in den Abgasreinigungskatalysator (13) strömen, veranlasst wird, in-

nerhalb des vorgegebenen Amplitudenbereichs und innerhalb des vorgegebenen Periodenbereichs zu schwingen, wobei die Schwingungsperiode (ΔT) der Kohlenwasserstoff-Konzentration zwischen 0,3 Sekunden und 5 Sekunden beträgt, und wobei, wenn gespeichertes SO_x aus dem Abgasreinigungskatalysator (13) freigesetzt werden soll, ein Luft-/Kraftstoff-Verhältnis des in den Abgasreinigungskatalysator (13) strömenden Abgases auf ein fettes Soll-Luft-/Kraftstoff-Verhältnis verringert wird, so dass das Reduktions-Zwischenprodukt, das sich an dem Abgasreinigungskatalysator (13) angesammelt hat, in der Form von Ammoniak desorbiert wird, und wobei das desorbierte Ammoniak verwendet wird, um den Abgasreinigungskatalysator (13) zu veranlassen, das gespeicherte SO_x freizusetzen.

2. Verfahren zum Reinigen von Abgas, das von einer Verbrennungskraftmaschine ausgestoßen wird, nach Anspruch 1, wobei eine erste SO_x-Freisetzungssteuerung, die das desorbierte Ammoniak verwendet, um das gespeicherte SO_x von einem stromaufwärtsseitigen Ende des Abgasreinigungskatalysators (13) freizusetzen, und eine zweite SO_x-Freisetzungssteuerung, die das gespeicherte SO_x von einer Gesamtheit des Abgasreinigungskatalysators (13) freizusetzt, durchgeführt werden, und wobei eine Zeit, während der die zweite SO_x-Freisetzungssteuerung durchgeführt wird, länger gemacht wird als eine Zeit, während der die erste SO_x-Freisetzungssteuerung durchgeführt wird.
3. Verfahren zum Reinigen von Abgas, das von einer Verbrennungskraftmaschine ausgestoßen wird, nach Anspruch 2, wobei eine Periode, während der die zweite SO_x-Freisetzungssteuerung durchgeführt wird, länger ist als eine Periode, während der die erste SO_x-Freisetzungssteuerung durchgeführt wird.
4. Verfahren zum Reinigen von Abgas, das von einer Verbrennungskraftmaschine ausgestoßen wird, nach Anspruch 2, wobei das fette Soll-Luft-/Kraftstoff-Verhältnis während der Zeit der zweiten SO_x-Freisetzungssteuerung im Vergleich zu der Zeit der ersten SO_x-Freisetzungssteuerung verringert wird.
5. Verfahren zum Reinigen von Abgas, das von einer Verbrennungskraftmaschine ausgestoßen wird, nach Anspruch 2, wobei ein Partikelfilter (14) im Inneren des Maschinen-Abgastrakts stromabwärts von dem Abgasreinigungskatalysator (13) angeordnet ist, und wobei die erste SO_x-Freisetzungssteuerung zu der Zeit durchgeführt wird, in der veranlasst wird, dass die Temperatur des Abgasreinigungskatalysators (13) steigt, um eine Temperatur des Par-

tikelfilters (14) zu der Zeit der Erholung des Partikelfilters (14) zu erhöhen.

6. Verfahren zum Reinigen von Abgas, das von einer Verbrennungskraftmaschine ausgestoßen wird, nach Anspruch 2, wobei die erste SO_x -Freisetzungsteuerung zu der Zeit durchgeführt wird, in der die Maschine mit hoher Last und hoher Drehzahl betrieben wird. 5
7. Verfahren zum Reinigen von Abgas, das von einer Verbrennungskraftmaschine ausgestoßen wird, nach Anspruch 2, wobei ein Drosselventil (10) vorhanden ist, um eine Ansaugluftmenge zu steuern, und wobei, wenn die Temperatur des Abgasreinigungskatalysators (13) für die erste SO_x -Freisetzungsteuerung steigen soll, zur Zeit eines Abbremsvorgangs, währenddessen das Drosselventil (10) veranlasst wird, sich zu schließen, Kohlenwasserstoffe in eine Brennkammer (2) oder in den Maschinen-Abgastrakt stromaufwärts von dem Abgasreinigungskatalysator (13) eingebracht werden. 10
8. Verfahren zum Reinigen von Abgas, das von einer Verbrennungskraftmaschine ausgestoßen wird, nach Anspruch 1, wobei der Edelmetallkatalysator (51, 52) aus Platin Pt und zumindest einem von Rhodium Rh und Palladium Pd besteht. 15
9. Verfahren zum Reinigen von Abgas, das von einer Verbrennungskraftmaschine ausgestoßen wird, nach Anspruch 1, wobei eine basische Schicht (53), die ein Alkalimetall, ein Erdalkalimetall, eine seltene Erde, oder ein Metall, das dem NO_x Elektronen zuführen kann, auf der Abgasströmungsoberfläche des Abgasreinigungskatalysators (13) ausgebildet ist, und wobei eine Oberfläche der basischen Schicht (53) den basischen Abgasströmungsoberflächenteil (54) bildet. 20

Revendications

1. Procédé de purification de gaz d'échappement évacués depuis un moteur à combustion interne où un catalyseur de purification de gaz d'échappement (13), pour provoquer une réaction des NO_x contenu dans un gaz d'échappement et des hydrocarbures reformés afin de produire un intermédiaire de réduction contenant de l'hydrogène et des hydrocarbures, est agencé dans une voie d'échappement de moteur, un catalyseur à base de métal précieux (51, 52) est retenu sur une surface de flux de gaz d'échappement du catalyseur de purification d'échappement (13) et une partie de surface de flux de gaz d'échappement de base (54) est formée autour des catalyseurs à base de métal précieux (51, 52), le catalyseur de purification de gaz d'échappement (13) ayant une 45

propriété consistant à produire l'intermédiaire de réduction et à réduire le NO_x contenu dans le gaz d'échappement à l'aide d'une action de réduction de l'intermédiaire de réduction produit si une concentration d'hydrocarbures s'écoulant à l'intérieur du catalyseur de purification de gaz d'échappement (13) est entraînée à vibrer selon une plage prédéterminée d'amplitude et pendant une plage temporelle prédéterminée et a une propriété consistant à être augmentée en quantité de stockage de NO_x contenu dans le gaz d'échappement si une période de vibration de la concentration d'hydrocarbures est rendue plus longue que ladite plage prédéterminée, où, au moment de l'opération du moteur, afin de réduire les NO_x contenus dans le gaz d'échappement dans le catalyseur de purification de gaz d'échappement (13), selon un premier procédé de purification des NO_x , la concentration des hydrocarbures s'écoulant à l'intérieur du catalyseur de purification de gaz d'échappement (13) est entraînée en vibration selon ladite plage prédéterminée d'amplitude et pendant ladite période prédéterminée, où ladite période de vibration (ΔT) de la concentration d'hydrocarbures est comprise entre 0,3 seconde et 5 secondes, et où, quand un SO_x stocké doit être libéré du catalyseur de purification de gaz d'échappement (13), un rapport air-carburant du gaz d'échappement qui s'écoule à l'intérieur du catalyseur de purification de gaz d'échappement (13) est réduit à un rapport air-carburant riche ciblé pour faire en sorte que l'intermédiaire de réduction accumulé sur le catalyseur de purification de gaz d'échappement (13) subisse une désorption sous la forme d'ammoniac et que l'ammoniac désorbé soit utilisé pour faire en sorte que le catalyseur de purification de gaz d'échappement (13) libère le SO_x stocké.

2. Procédé de purification de gaz d'échappement évacués depuis un moteur à combustion interne selon la revendication 1, où une première commande de libération de SO_x qui utilise l'ammoniac désorbé pour libérer le SO_x stocké à partir d'une extrémité du côté en amont du catalyseur de purification de gaz d'échappement (13) et une seconde commande de libération de SO_x qui libère le SO_x stocké à partir d'une intégralité du catalyseur de purification de gaz d'échappement (13) sont exécutées et où une période pendant laquelle la seconde commande de libération de SO_x est exécutée est rendue plus longue qu'une période pendant laquelle la première commande de libération de SO_x est exécutée. 40
3. Procédé de purification de gaz d'échappement évacués depuis un moteur à combustion interne selon la revendication 2, où une période pendant laquelle la seconde commande de libération de SO_x est exécutée est rendue plus longue qu'une période pendant laquelle la première commande de libération 45

de SO_x est exécutée.

4. Procédé de purification de gaz d'échappement évacués depuis un moteur à combustion interne selon la revendication 2, où le rapport air-carburant riche ciblé est rendu inférieur au moment de la seconde commande de libération de SO_x comparé au moment de la première commande de libération de SO_x . 5

5. Procédé de purification de gaz d'échappement évacués depuis un moteur à combustion interne selon la revendication 2, où un filtre de particules (14) est agencé à l'intérieur de la voie d'échappement du moteur en aval du catalyseur de purification de gaz d'échappement (13) et où la première commande de libération de SO_x est exécutée au moment où la température du catalyseur de purification de gaz d'échappement (13) est entraînée à augmenter pour augmenter une température du filtre de particules (14) au moment de régénération du filtre de particules (14). 10
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6. Procédé de purification de gaz d'échappement évacués depuis un moteur à combustion interne selon la revendication 2, où la première commande de libération de SO_x est exécutée au moment de l'opération du moteur à haute vitesse, à un taux de charge élevé. 25

7. Procédé de purification de gaz d'échappement évacués depuis un moteur à combustion interne selon la revendication 2, où une soupape d'étranglement (10) est fournie pour commander une quantité d'air d'amenée et où, quand la température du catalyseur de purification de gaz d'échappement (13) doit augmenter pour la première commande de libération de SO_x , des hydrocarbures sont fournis à l'intérieur d'une chambre de combustion (2) ou à l'intérieur de la voie d'échappement du moteur en amont du catalyseur de purification de gaz d'échappement (13) au moment d'une opération de décélération où la soupape d'étranglement (10) est amenée à fermer. 30
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8. Procédé de purification de gaz d'échappement évacués depuis un moteur à combustion interne selon la revendication 1, où ledit catalyseur à base de métal précieux (51, 52) est constitué de platine Pt et d'au moins un élément parmi le rhodium Rh et le palladium Pd. 45
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9. Procédé de purification de gaz d'échappement évacués depuis un moteur à combustion interne selon la revendication 1, où une couche de base (53) contenant un métal alcalin, un métal alcalino-terreux, un métal terrestre rare ou un métal qui peut donner des électrons aux NO_x est formée sur la surface de flux de gaz d'échappement du catalyseur de purification de gaz d'échappement (13) et où une surface de 55

ladite couche de base (53) forme ladite partie de surface de flux de gaz d'échappement de base (54).

Fig. 1

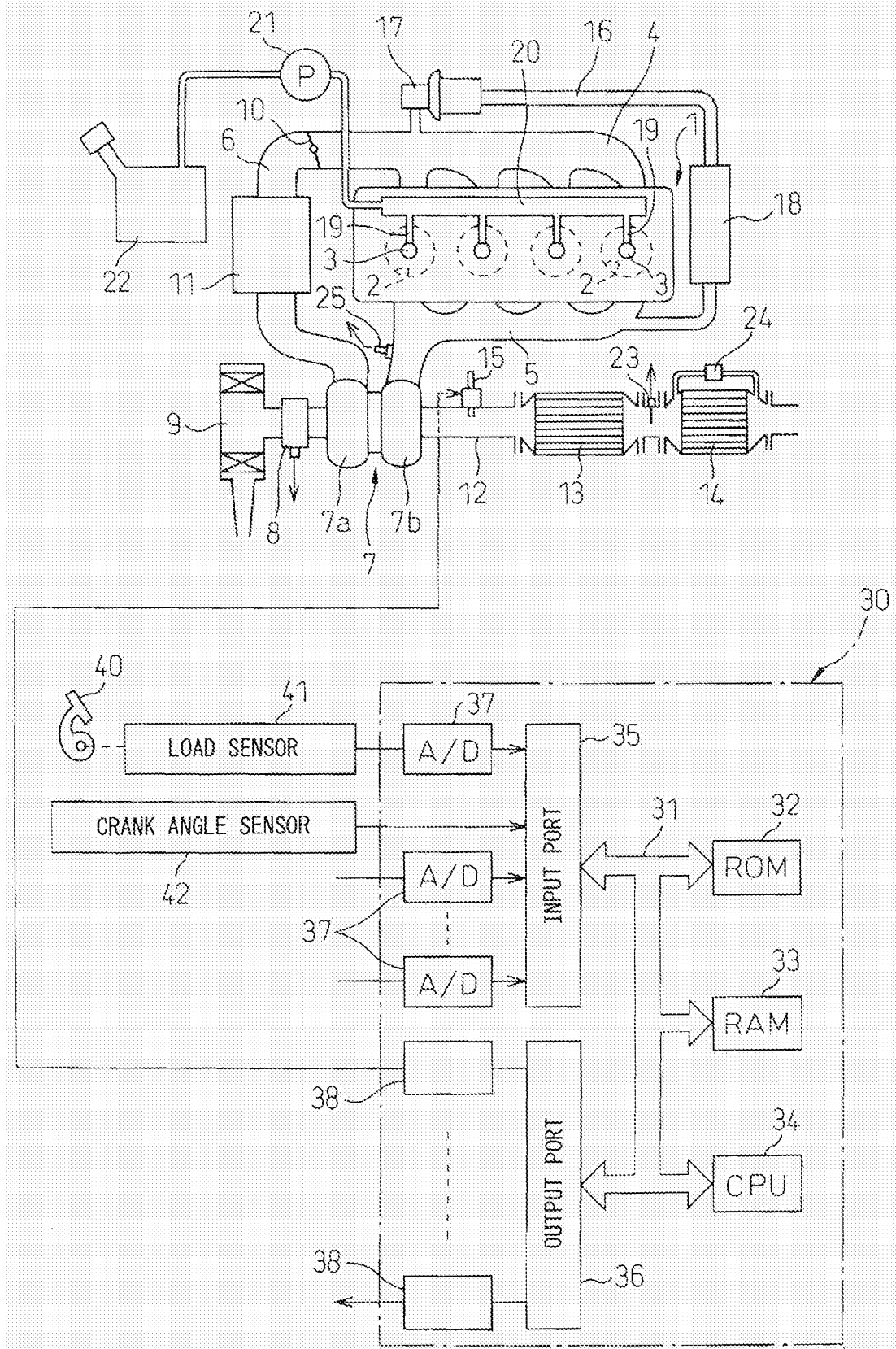


Fig.2

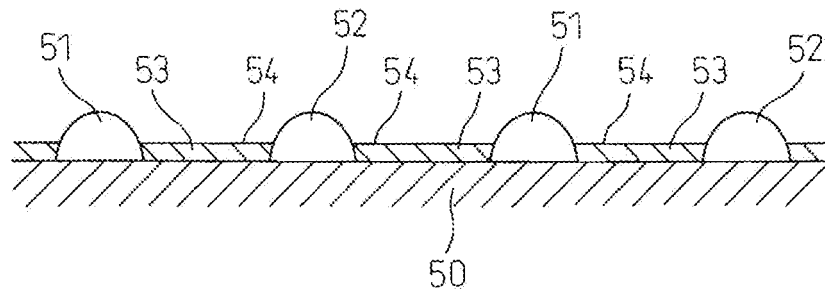


Fig.3

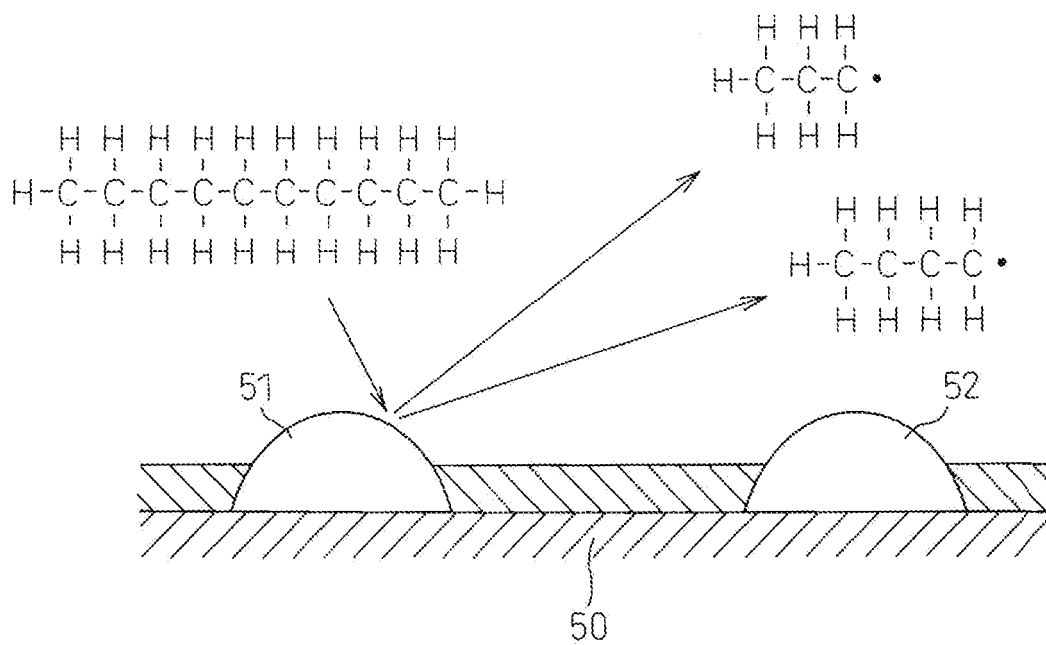


Fig.4

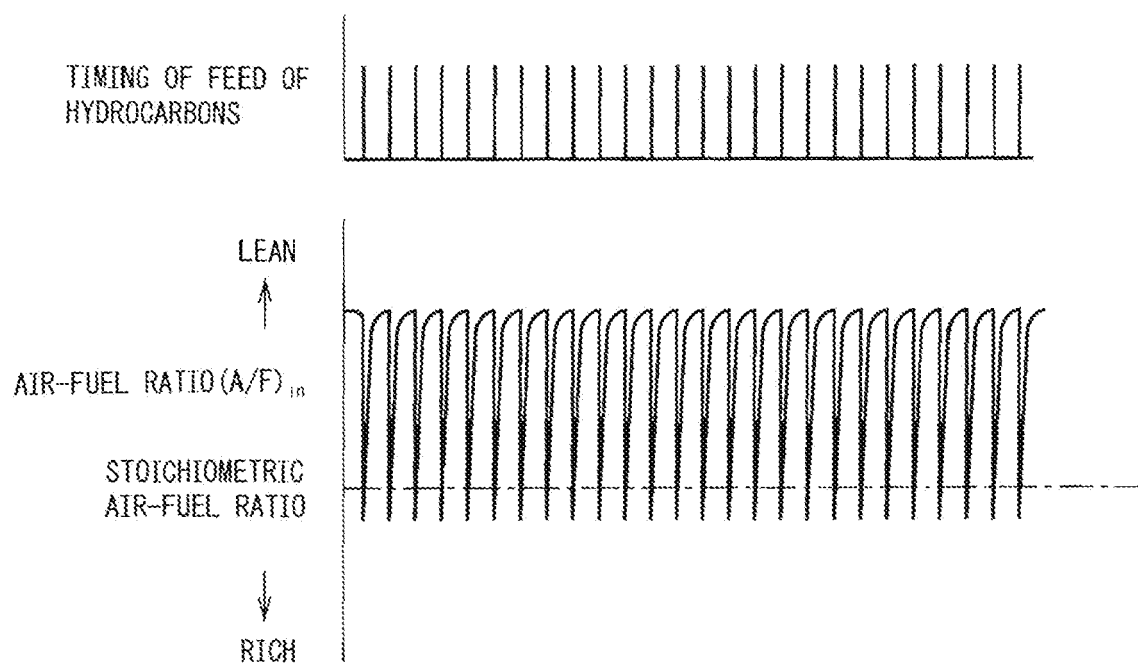


Fig.5

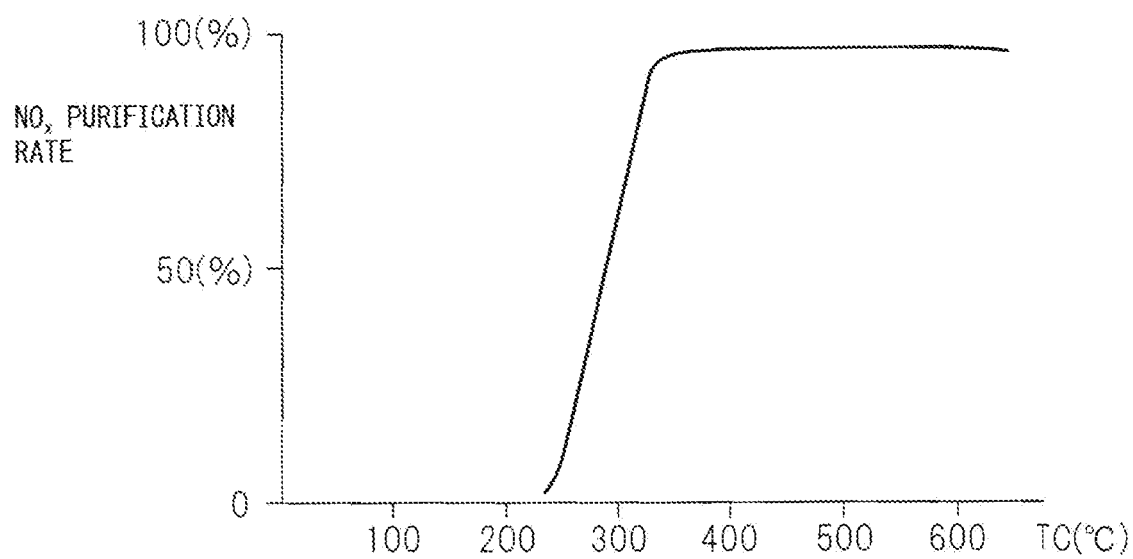


Fig.6A

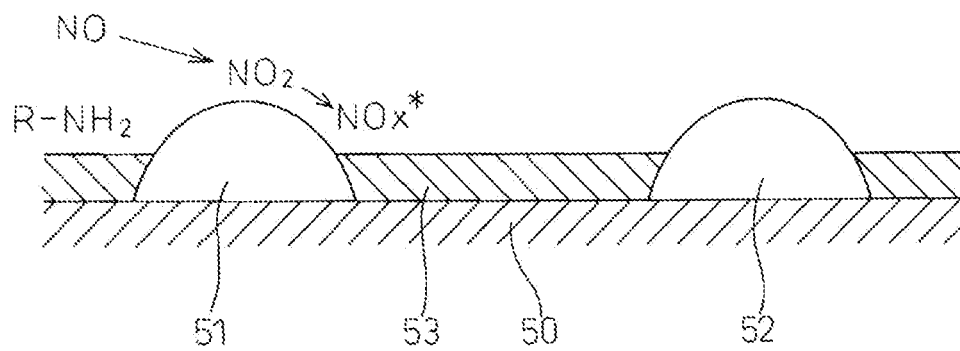


Fig.6B

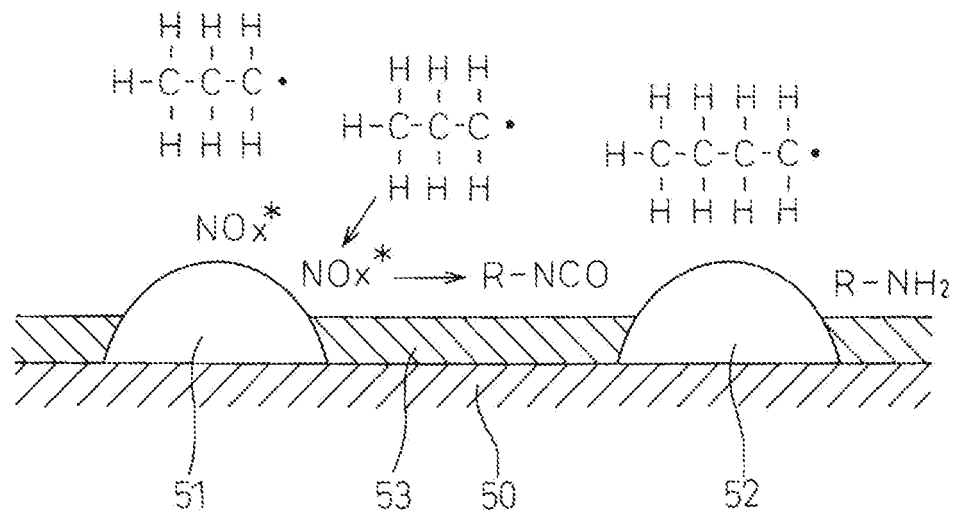


Fig.6C

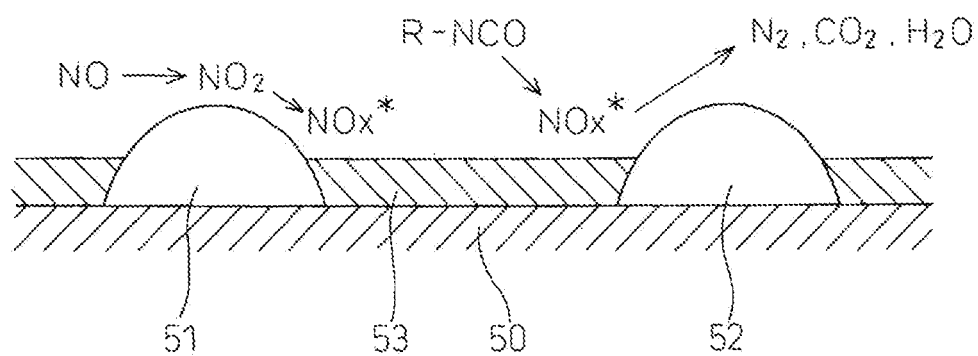


Fig.7A

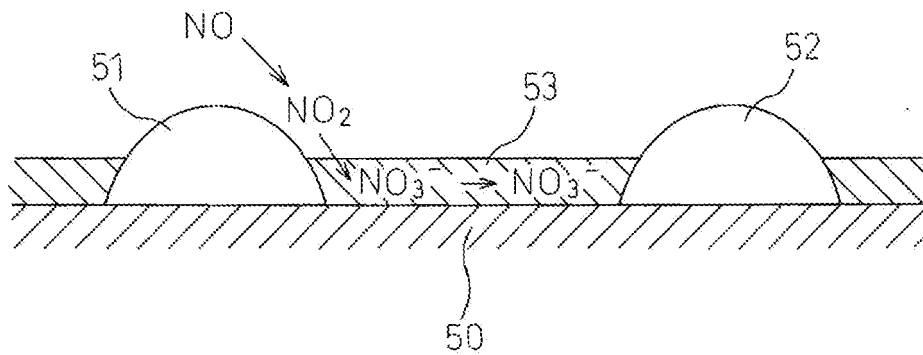


Fig.7B

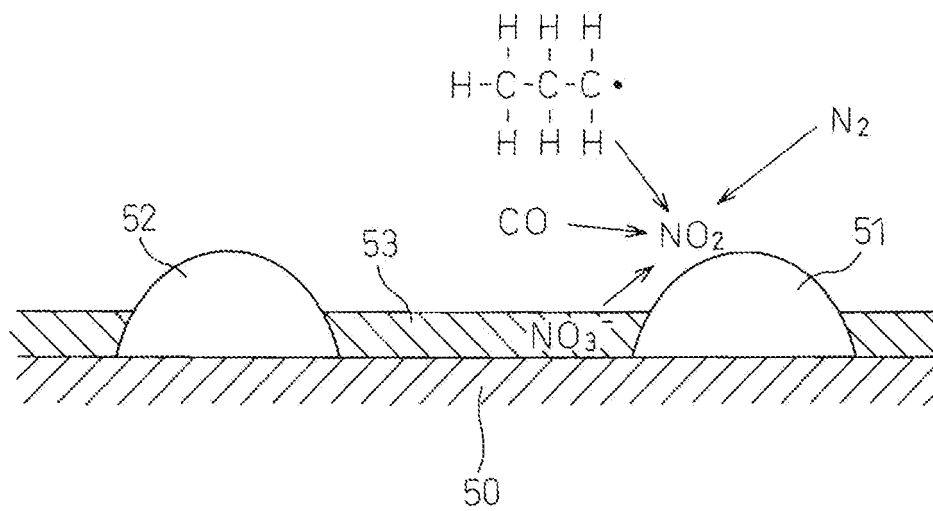


Fig.8

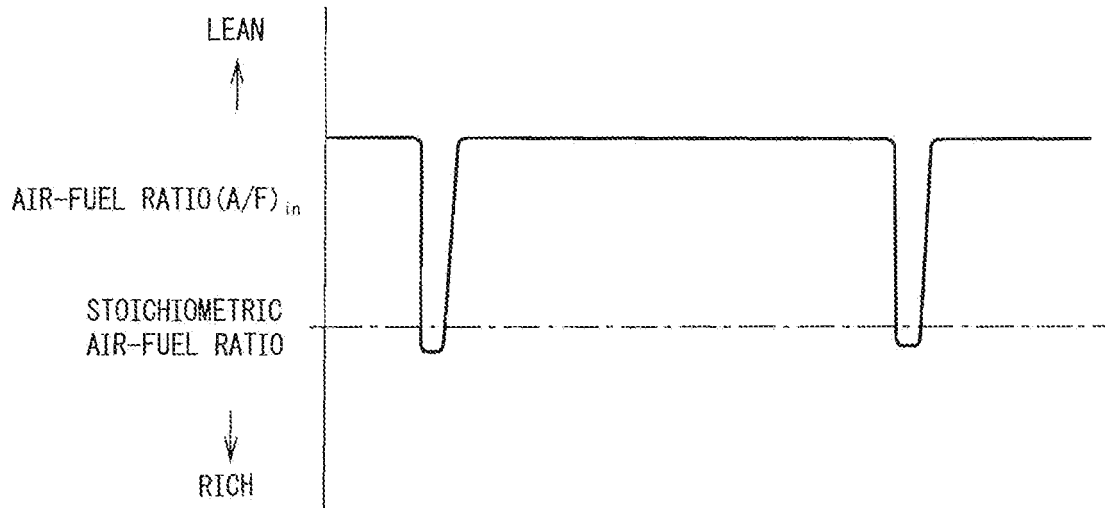


Fig.9

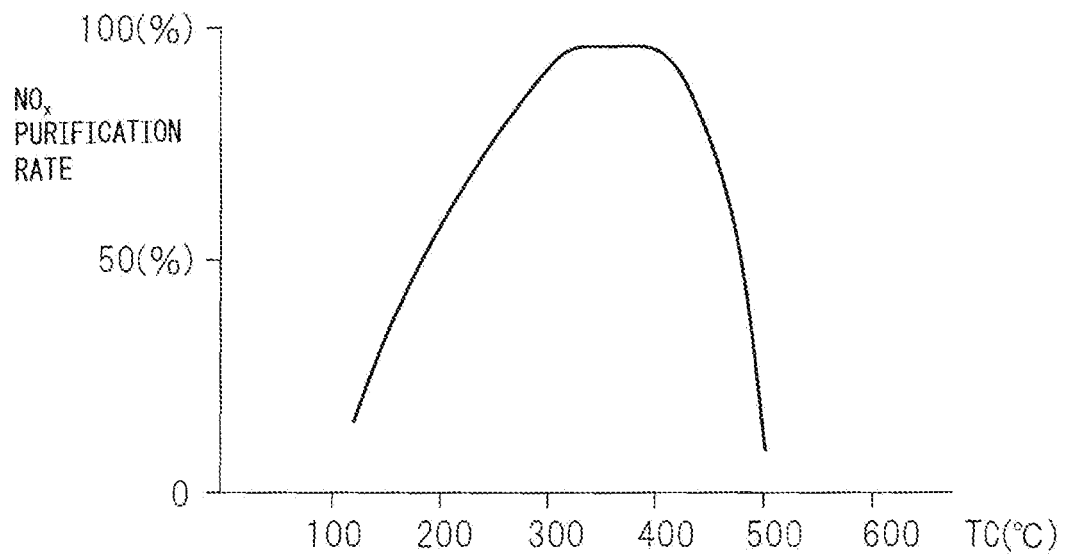


Fig.10

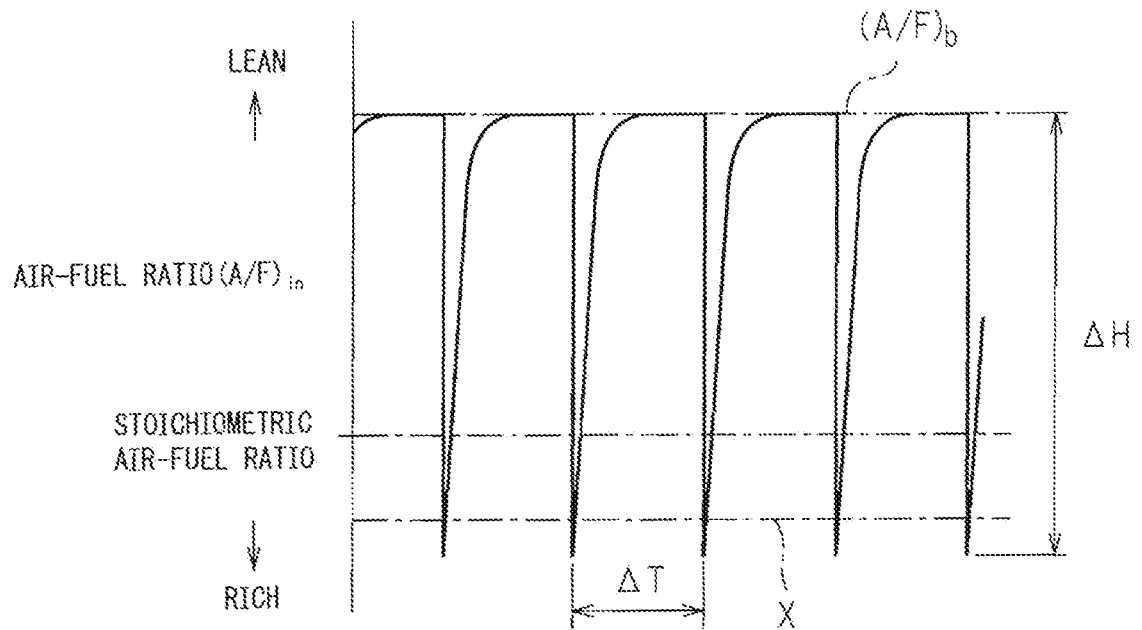


Fig.11

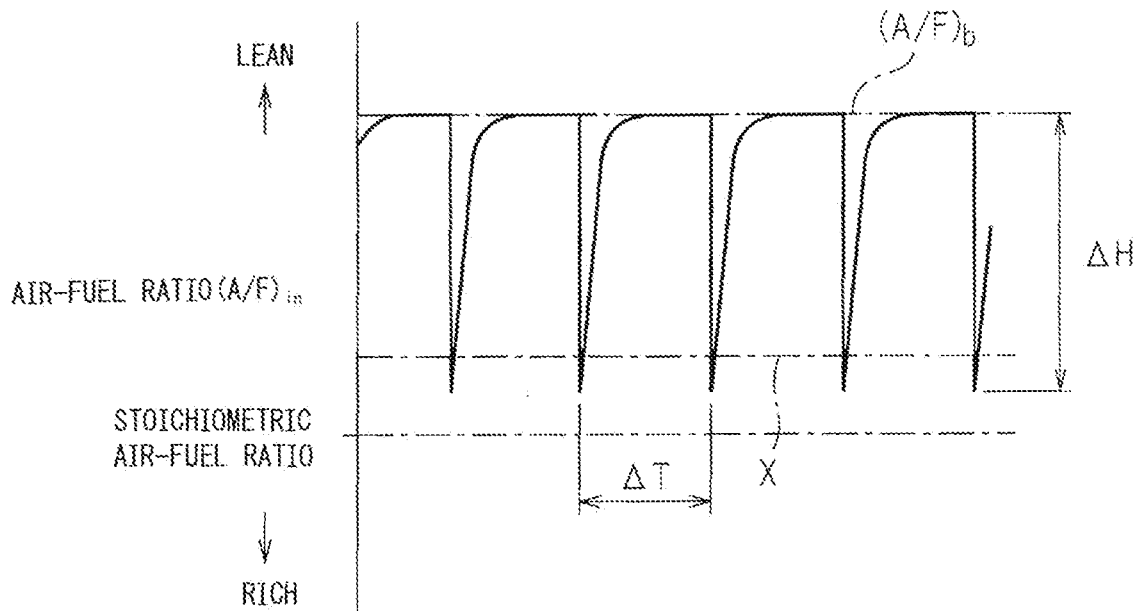


Fig.12

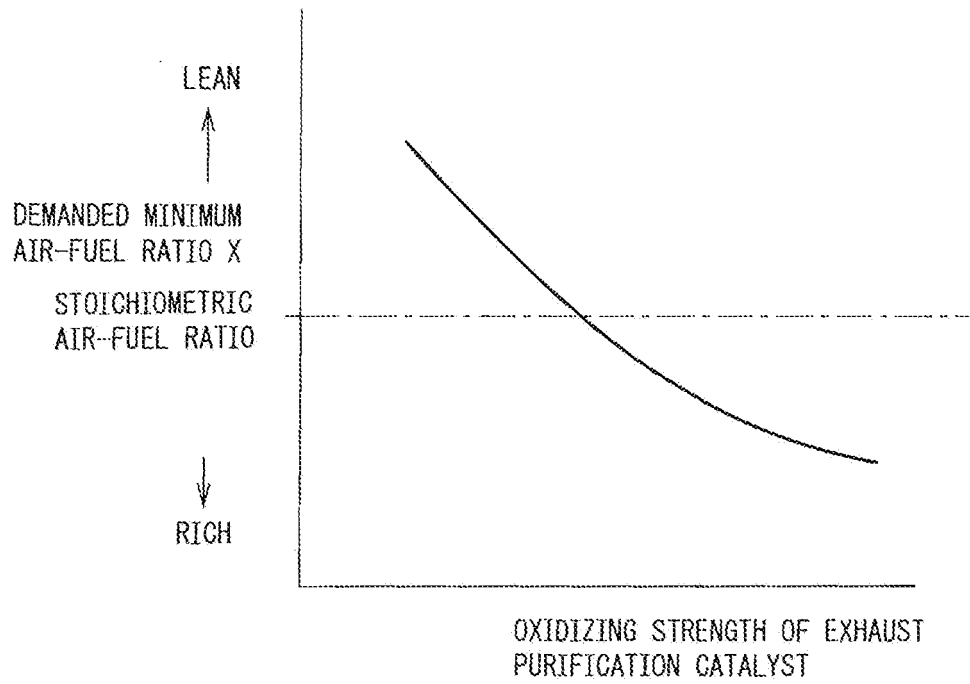


Fig.13

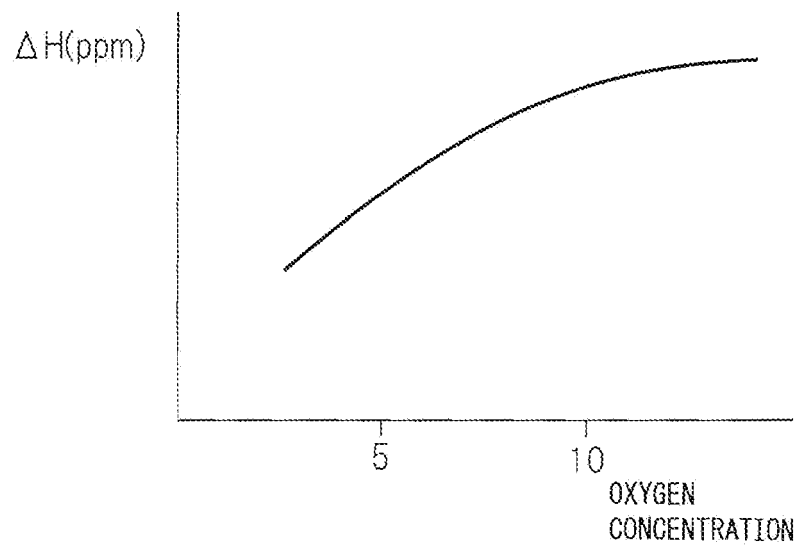


Fig.14

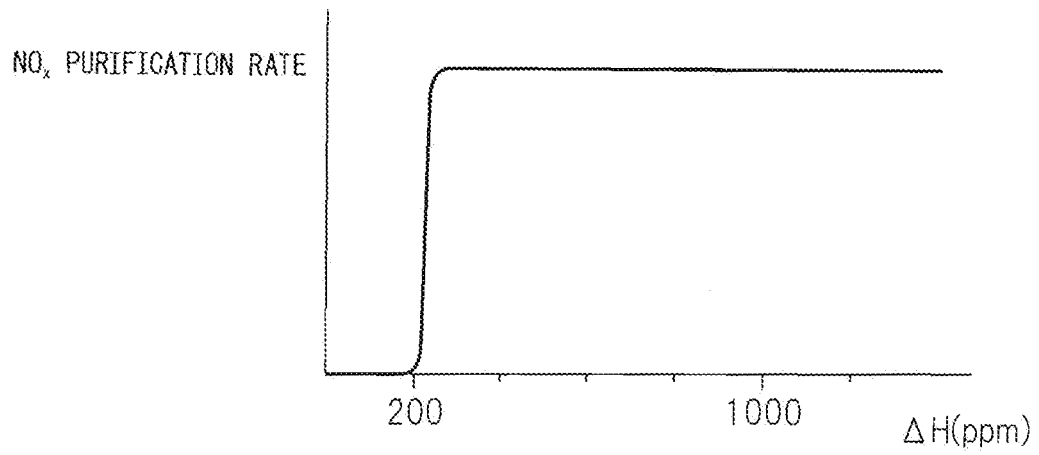


Fig.15

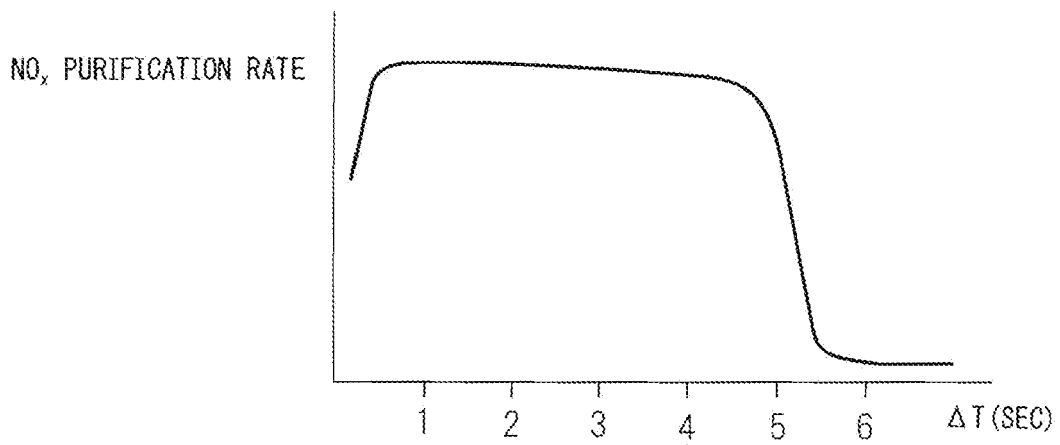


Fig.16

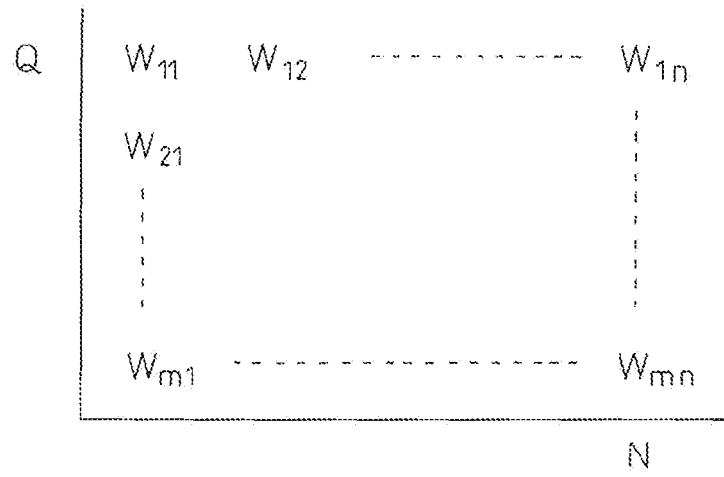


Fig.17

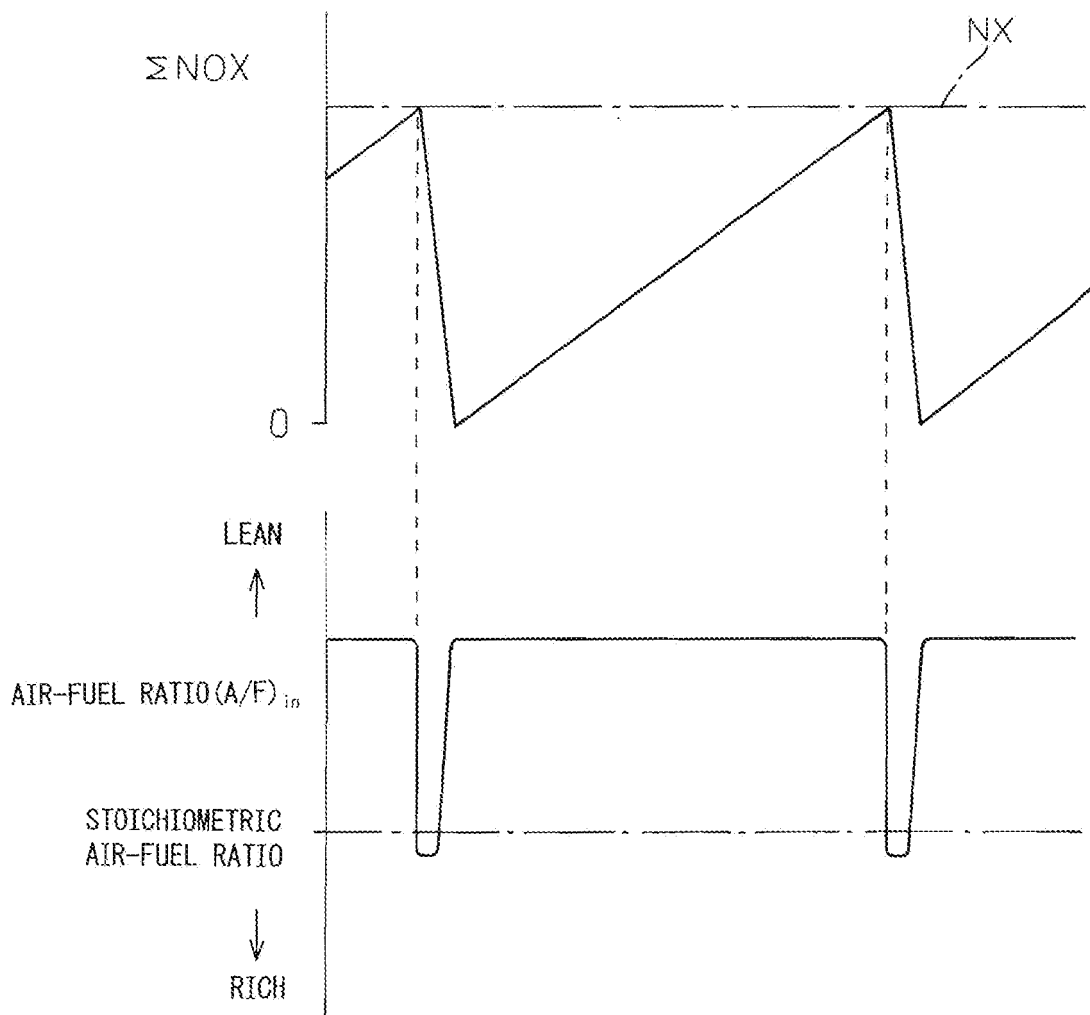


Fig.18

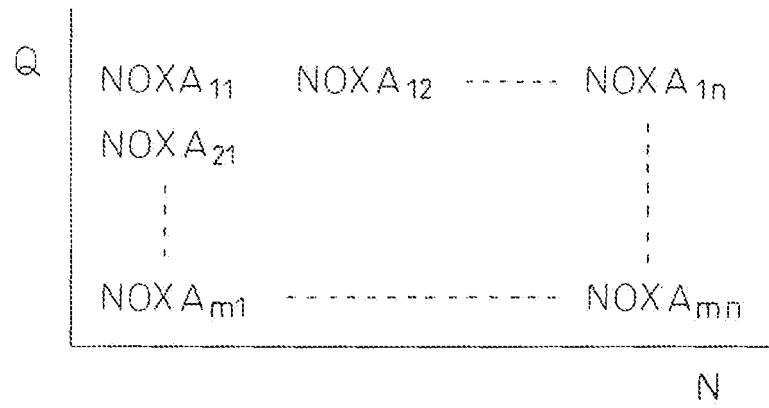


Fig.19

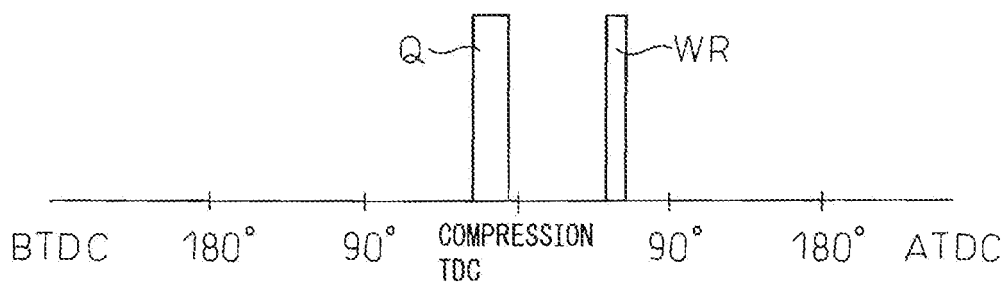


Fig.20

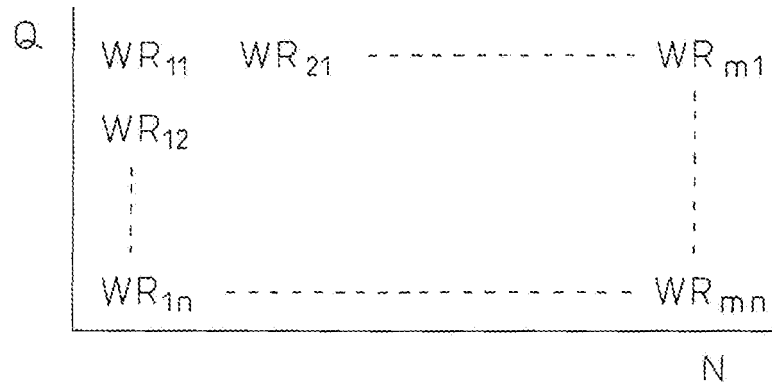


Fig.21A

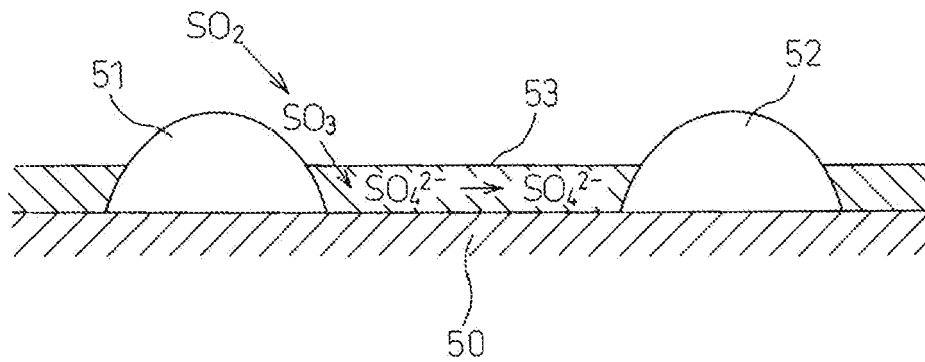


Fig.21B

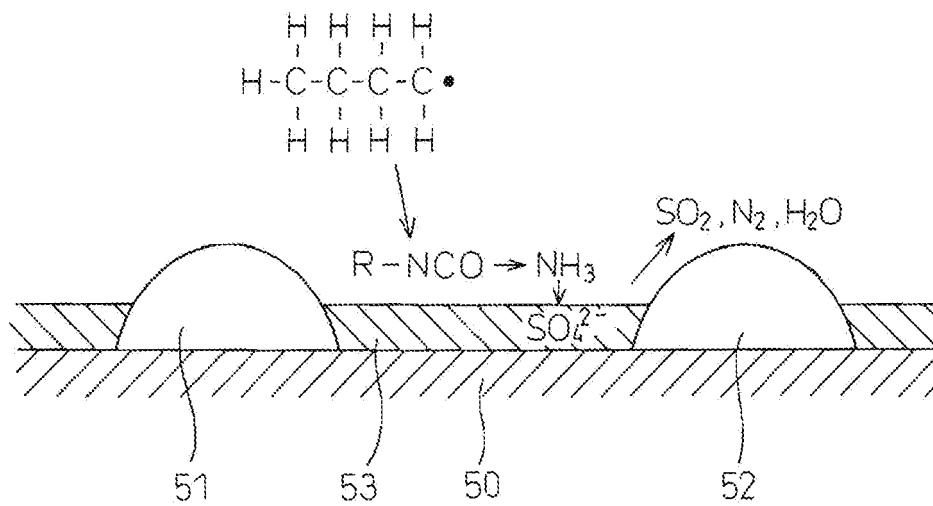


Fig.22A

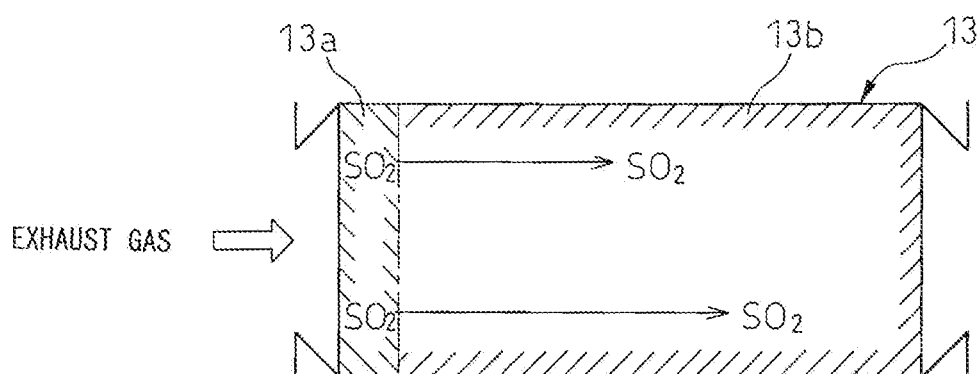


Fig.22B

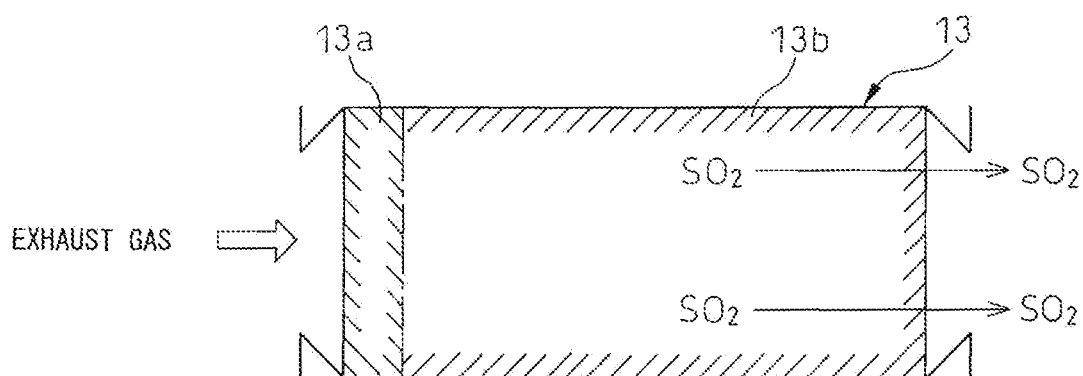


Fig.22C

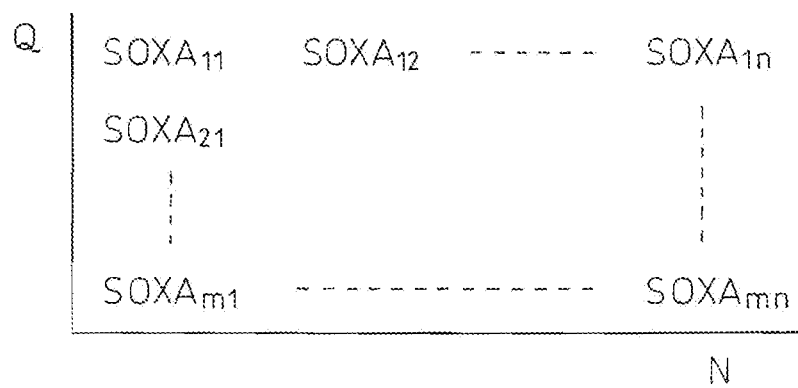


Fig.23A

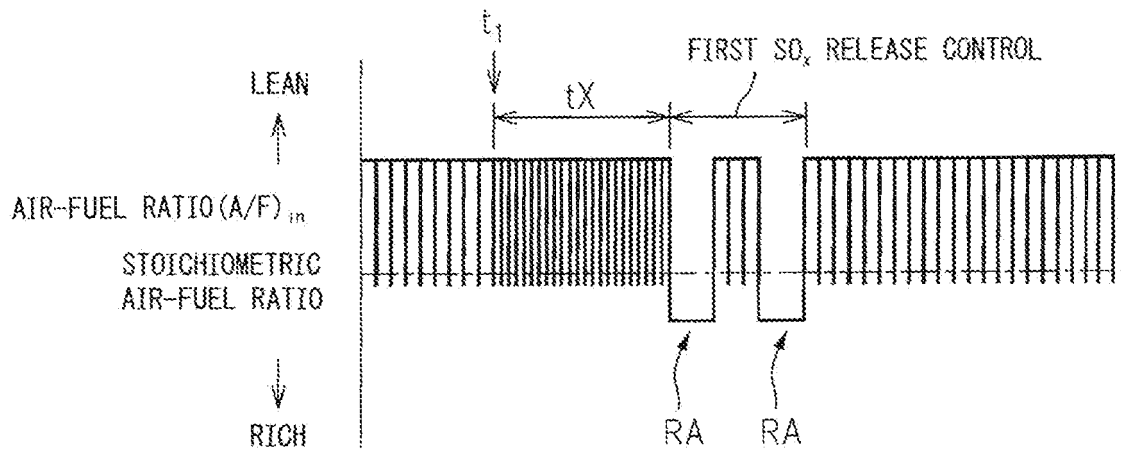


Fig.23B

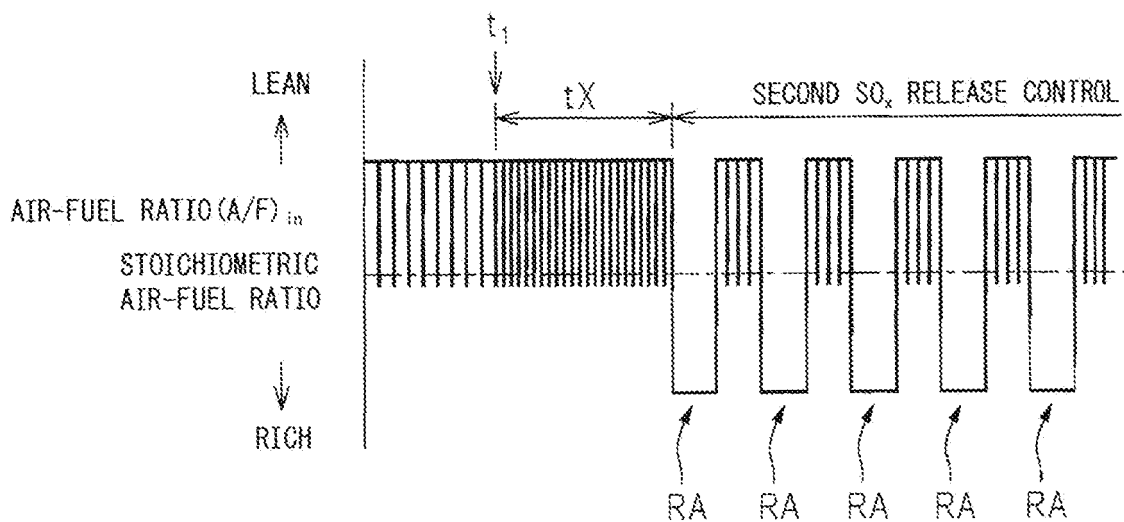


Fig.24

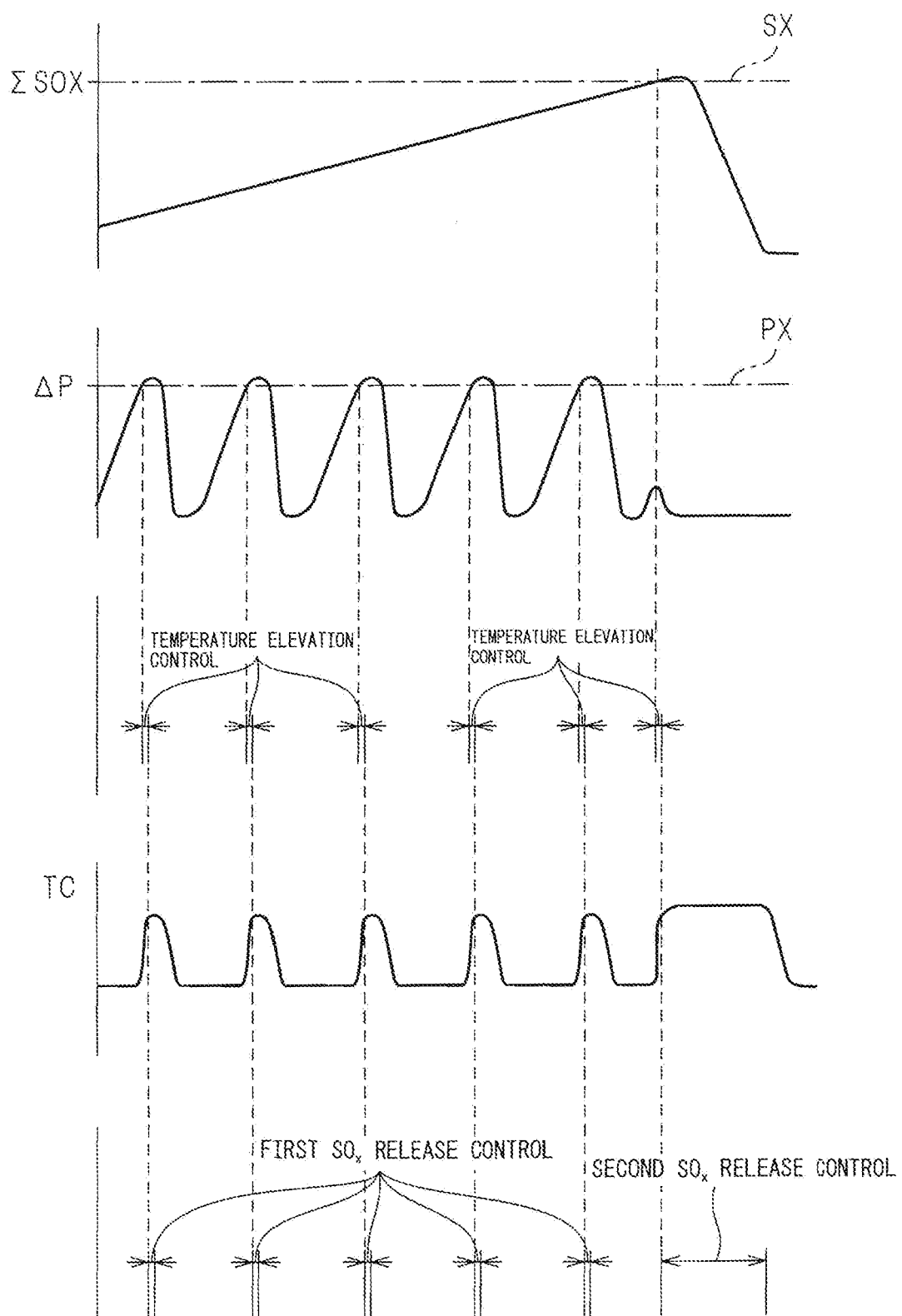
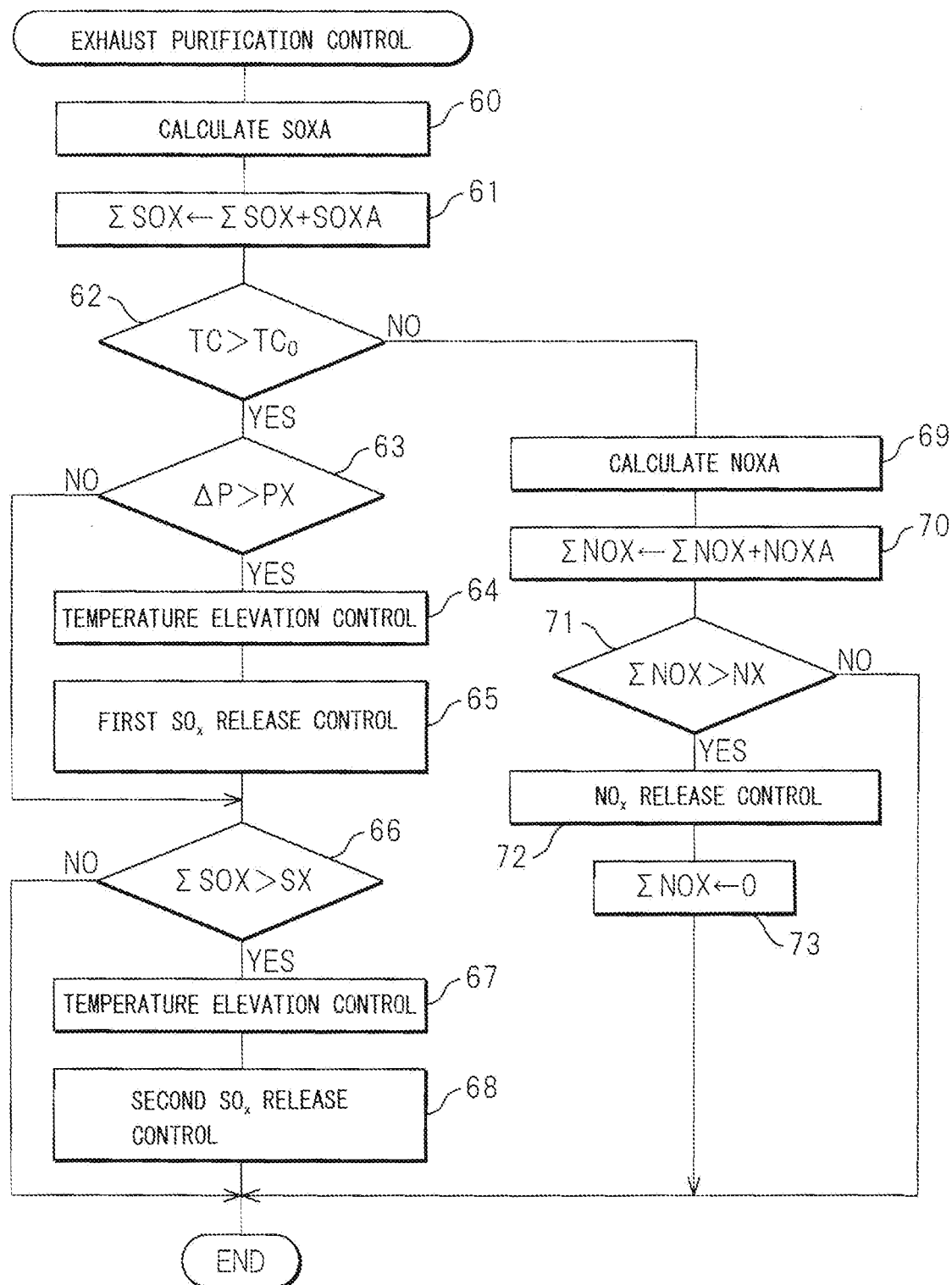


Fig.25



REFERENCES CITED IN THE DESCRIPTION

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