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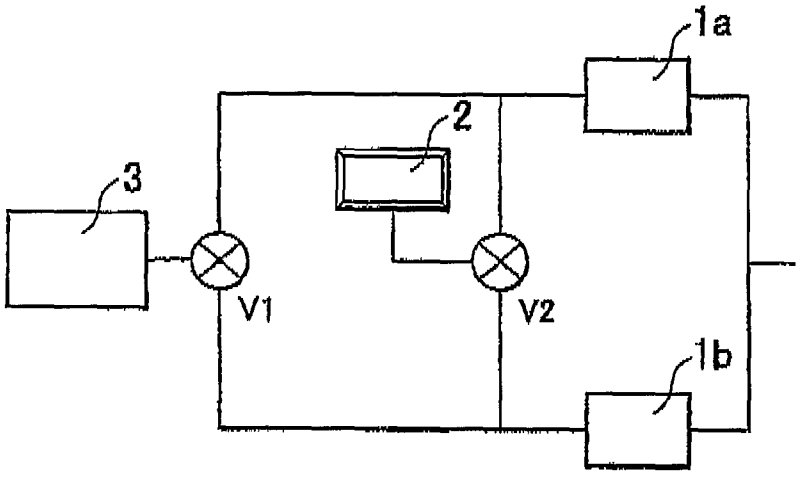
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(54) Title: EXHAUST GAS PURIFICATION SYSTEM FOR INTERNAL COMBUSTION ENGINE



(57) Abstract: An exhaust gas purification system includes: at least two catalysts (1a, 1b) disposed in parallel with each other on an exhaust gas passage of an internal combustion engine (3) and having a carrier containing a basic oxide and platinum carried on the carrier; and oxygen supply means (2) for supplying oxygen to the catalysts (1a, 1b).

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EXHAUST GAS PURIFICATION SYSTEM FOR INTERNAL COMBUSTION ENGINE

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to an exhaust gas purification system including a catalyst that is provided in an exhaust gas passage of an internal combustion engine and that can be regenerated by redispersing platinum particles having been sintered.

2. Description of the Related Art

In automobiles, an exhaust gas purifying catalyst is used to remove pollutants, such as HC, CO and NOx, contained in an exhaust gas from an engine. A known example of such an exhaust gas purifying catalyst is a three-way catalyst that simultaneously removes HC, CO and NOx from the exhaust gas after combustion at a theoretical air-fuel ratio. The three-way catalyst includes a honeycombed carrier base made of, for example, cordierite or a metal foil, a catalyst-carrying layer made of, for example, active alumina powders or silica powders and coated on the surface of the carrier base, and a precious metal such as platinum carried on the catalyst-carrying layer. The three-way catalyst removes HC and CO in the exhaust gas by oxidation, and reduces NOx.

An oxidation catalyst is also known, in which a precious metal is carried on a catalyst-carrying layer made of zeolite, which has excellent in absorption characteristics for HC contained in the exhaust gas. In the oxidation catalyst, HC contained in the exhaust gas is absorbed by the catalyst-carrying layer at low temperatures, and is released as the temperature of the catalyst increases. The released HC is oxidized by the precious metal when the precious metal is at or above its active temperature. In this way, HC emission can be suppressed at low temperatures, for example, when starting the engine and during in winter.

In addition, to mitigate variations in atmosphere of the exhaust gas, a catalyst having oxygen storage / releasing capacity and an NOx storage reduction catalyst are known. In the former, an element such as ceria is carried on a catalyst-carrying layer. In the latter, an NOx storage material such as alkali metals and alkali earth metals is carried on a

catalyst-carrying layer, along with a precious metal.

For the precious metal for use as an active component of such catalysts, platinum (Pt) is primarily used. When platinum is exposed to an oxidizing atmosphere at a high temperature for a long time, however, platinum particles become flocculated (platinum particles grow) and thus platinum sinters, unfavorably reducing the specific surface area of the platinum particles and hence the activity of the catalyst. Thus, various methods have been developed to regenerate exhaust gas purifying catalysts in which the platinum has been sintered.

For example, Japanese patent application publication No.JP-A-2000-202309 describes a method for regenerating an exhaust gas purifying catalyst. The catalyst is made up of a carrier containing at least one element selected from alkaline earth metal oxides and rare earth element oxides, and platinum carried on the carrier. The method includes an oxidation process in which the catalyst is heated in an oxidizing atmosphere containing oxygen, and a reduction process conducted after the oxidation process. In this regeneration method, platinum oxide is formed on the surface of platinum metal particles having been sintered and grown, in the oxidation process. The platinum oxide interacts strongly with the carrier containing the specific oxide mentioned above. Thus, the platinum oxide moves from the surface of the platinum metal particles to the surface of the carrier, allowing metal platinum to appear on the surface of the platinum metal particles. The metal platinum is oxidized into platinum oxide, which in turn moves to the surface of the carrier. By repeating these events, the platinum metal particles being carried become gradually smaller in diameter and dispersed over the surface of the carrier, resulting in platinum oxide being highly dispersed over the carrier. The catalyst is then subjected to the reduction process, in which the platinum oxide is reduced to metal platinum. The activity of the catalyst can be restored by the highly dispersed metal platinum.

The above-described regeneration method includes, as the oxidation process to regenerate platinum, increasing the air-fuel (A/F) ratio of an air-fuel mixture flowing into an engine to an extremely high degree. When the above-described regeneration method is used to regenerate a catalyst incorporated in an exhaust gas purification system, however,

the time when regeneration of platinum is required does not always coincide with the time when the air-fuel ratio is increased, depending on the operating conditions, making it difficult to reliably regenerate platinum.

When the concentration of oxygen is low, a sufficient amount of oxygen may not reach the downstream side of the catalyst, even if the air-fuel ratio is increased. In such a case, the regeneration process cannot be performed efficiently. Providing an air supply device on the upstream side of the catalyst is also proposed. With such an arrangement, however, it is difficult for an ordinary three-way catalyst to remove NOx in the exhaust gas with an excessive amount of oxygen supplied. As a result, NOx may unfavorably be emitted.

SUMMARY OF THE INVENTION

The present invention provides an exhaust gas purification system that regenerates the platinum and that maintains the exhaust gas purification performance even during the regeneration of the platinum.

An aspect of the present invention is directed to an exhaust gas purification system for an internal combustion engine. This exhaust gas purification system for an internal combustion engine includes: at least two catalysts disposed in parallel with each other on an exhaust gas passage of the internal combustion engine and having a carrier containing a basic oxide and platinum carried on the carrier; and oxygen supply means for supplying oxygen to the at least two catalysts.

In the above aspect, the oxygen supply means may not supply oxygen to all the catalysts at the same time during purification of an exhaust gas, and the exhaust gas may not be supplied to a first catalyst while it is supplied with oxygen, and the exhaust gas may be supplied to a second catalyst not being supplied with oxygen while the first catalyst is supplied with oxygen.

In the exhaust gas purification systems of the present invention, a first catalyst can be exposed to an oxidizing atmosphere by the oxygen supply means provided in the exhaust gas passage, allowing platinum having been sintered to be redispersed by oxidation / reduction. The at least two catalysts are disposed in parallel with each other on the

exhaust gas passage, and oxygen is supplied to not all but only some of the catalysts at the same time. Thus, even during the regeneration of a catalyst, the exhaust gas can be purified at another catalyst not being subjected to the regeneration process, preventing a decrease in NOx purification rate during the regeneration.

BRIEF DESCRIPTION OF THE DRAWINGS

The foregoing and further objects, features and advantages of the invention will become apparent from the following description of preferred embodiments with reference to the accompanying drawings, wherein like numerals are used to represent like elements and wherein:

FIG. 1 is a schematic diagram showing the configuration of an exhaust gas purification system according to an embodiment of the present invention.

FIG. 2 is a flowchart of a process to control the regeneration of a catalyst 1a in the exhaust gas purification system according to the embodiment of the present invention.

FIG. 3 is a flowchart of a process to control the regeneration of a catalyst 1b in the exhaust gas purification system according to the embodiment of the present invention.

FIG. 4 is a schematic diagram showing the configuration of an exhaust gas purification system in Comparative Example 1.

FIG. 5 is a schematic diagram showing the configuration of an exhaust gas purification system in Comparative Example 2.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

An exhaust gas purification system according to first and second embodiments of the present invention includes: a catalyst (hereinafter referred to as "platinum-carrying catalyst") provided in an exhaust gas passage of an internal combustion engine and having a carrier containing a basic oxide and platinum carried on the carrier; a three-way catalyst or an NOx storage reduction catalyst; and oxygen supply means.

The basic oxide contained in the carrier of the platinum-carrying catalyst may be an oxide of at least one element selected from the alkaline earth metals and the rare earth

elements. Alternatively, the carrier may contain a complex oxide of zirconia and/or almina and at least one element selected from the group including the alkaline earth metals, the rare earth elements and the group 3A elements.

The alkaline earth metal oxide may be an oxide of Mg, Ca, Sr, Ba and Ra of various valence numbers, and may be selected from at least one of magnesium oxide (MgO), calcium oxide (CaO) and barium oxide (BaO), which interact strongly with and hence have a high affinity to metal Pt and Pt oxide.

The rare earth oxide may be an oxide of a metal, such as Sc, Y, La, Ce, Pr, Nd, Sm, Tb, Dy, Yb and Lu, of various valence numbers, and is preferably at least one kind selected from lanthanum oxide (La_2O_3), ceric oxide (CeO_2), yttrium oxide (Y_2O_3) and neodymium oxide (Nd_2O_3), which interact strongly with and hence have a high affinity to metal Pt and Pt oxide.

The complex oxide of zirconia (ZrO_2) and/or alumina (Al_2O_3) and at least one of elements selected from the group including alkali earth metals, rare earth elements and group 3A elements may be a complex oxide of zirconia and/or alumina and at least one of elements selected from the above-mentioned alkali metals Mg, Ca, Sr, Ba and Ra and the above-mentioned rare earth elements such as Sc, Y, La, Ce, Pr, Nd, Sm, Tb, Dy, Yb and Lu, and may be a complex oxide with Mg, Ca, Ba, La, Ce, Y or Nd, which interacts strongly with and hence has a high affinity to metal Pt and Pt oxide. Such complex oxides include CeO_2-ZrO_2-Y_2O_3, ZrO_2-La_2O_3, CeO_2-ZrO_2 and CeO_2-ZrO_2-La_2O_3-Pr_2O_3. The proportion (composite ratio) of zirconia and/or alumina to at least one of elements selected from the group including alkali earth metals, rare earth elements and group 3A elements is not specifically limited. From the viewpoint of the effect, the proportion of zirconia and/or alumina in the complex oxide may be 10 to 90 wt%, and may be 30 to 90 wt%.

The carrier of the platinum-carrying catalyst needs only to contain the above-mentioned basic oxide, even a small amount, in order to be effective. The carrier may contain 50 wt%, for example, of the basic oxide, or may be entirely composed of the basic oxide. In the case where the basic oxide is used as a part of the carrier, the rest of the carrier may be silica, alumina, zirconia, titania and silica-alumina.

The production method of the carrier is not specifically limited. For example, the method may include allowing a precipitate of the above-mentioned basic oxide to be produced from an aqueous solution containing a metal salt (for example, nitrate) as a raw material of the basic oxide, and as necessary a surface-active agent (for example, nonion surface-active agent), in the presence of ammonia, and filtering, washing, drying and then calcining the obtained precipitate.

The platinum-carrying catalyst includes at least powders in which platinum is carried on the carrier. The amount of platinum carried on the carrier may be in a range of 0.01 to 10 wt%, and may be in a range of 0.1 to 5 wt%. If the amount of platinum carried is less than the lower limit, the activity of the catalyst as an exhaust gas purifying catalyst tends to be insufficient. On the other hand, if the amount of platinum carried is more than the upper limit, the activity of the catalyst does not improve, and only increases the cost.

The method of causing platinum to be carried on the carrier is not specifically limited. For example, the method may include causing an aqueous solution containing a platinum salt (for example, dinitrodiamine salt) or a platinum complex (for example, tetraammine complex) to contact the carrier, and drying and then calcining the carrier.

The form of the platinum-carrying catalyst is not specifically limited. The platinum-carrying catalyst may be a monolithic catalyst in the form of a honeycomb, or a pellet catalyst in the form of a pellet, for example. The base is also not specifically limited, and may be selected appropriately according to the purpose of use, for example, of the catalyst to be obtained. The base may be a DPF base, a monolithic base, a pellet base and a plate-like base, for example. The material of the base is also not specifically limited. The base may be made of ceramics such as cordierite, silicone carbide and mullite, and metals such as stainless steel containing chromium and almunium. In addition, the method of producing such a catalyst is not specifically limited. For example, a monolithic catalyst may be produced by forming a coating layer of the above-mentioned carrier powders on a honeycombed base made of cordierite or a metal foil, and causing platinum to be carried on the coating layer. Another method of producing a catalyst includes first causing platinum to be carried on the above-mentioned carrier powders, and

then forming a coating layer on the base using the platinum-carrying powders.

The oxygen supply means for use in the exhaust gas purification system according to this embodiment is not specifically limited as long as it can supply oxygen or air, and may be implemented as an air valve, for example. Ambient air may be supplied directly. In order to efficiently regenerate the catalyst, air warmed beforehand using a heat exchanger mounted on an engine exhaust pipe, for example, may be supplied.

In the exhaust gas purification systems according to the embodiments of the present invention, when the platinum in the platinum-carrying catalyst is determined to have been sintered, an oxidation process and a reduction process are performed to redisperse fine platinum particles over the carrier and recover the activity of the catalyst. The carrier of the platinum-carrying catalyst for use in the exhaust gas purification systems according to the embodiments of the present invention contains a basic oxide that interacts strongly with metal platinum. Thus, the surface of platinum particles carried on the carrier have increased in size and coarsened can be oxidized easily, allowing platinum oxide to be formed easily on the surface of the coarsened platinum particles, by heating the platinum-carrying catalyst at 500 to 1000 °C in an oxidizing atmosphere containing oxygen.

Then, the platinum oxide, which has a high affinity to the carrier, moves from the surface of the coarsened platinum particles to the surface of the carrier, exposing metal platinum at the surface of the coarsened platinum particles. The exposed metal platinum is oxidized by the oxygen present in the oxidizing atmosphere to become platinum oxide, which in turn moves to the surface of the carrier. By repeating these events, the platinum particles being carried and having coarsened become gradually smaller in diameter and dispersed over the surface of the carrier as if wet, resulting in platinum oxide being highly dispersed over the carrier.

Then, a reduction process is performed, which easily reduces the platinum oxide into metal platinum. Thus, fine metal platinum particles are highly dispersed over the carrier, whereby the activity of the catalyst is recovered.

The temperature of the catalyst during the regeneration process of the platinum-carrying

catalyst is initiated by an oxidation process, which includes supplying oxygen to the catalyst by means of the oxygen supply means disposed upstream of the catalyst, and heating the catalyst in an oxidizing atmosphere containing oxygen. The oxidizing atmosphere need only contain oxygen, even a small amount, that will oxidize a corresponding number of moles of platinum. The concentration of oxygen may be 1 % or more by volume, or further limited to 1 to 20 % by volume. Other than oxygen, the oxidizing atmosphere should contain no reducing gas, but may contain a nitrogen gas or an inert gas.

The temperature of the catalyst during the oxidation process may be any temperature at which the metal platinum carried by the catalyst is oxidized, and may be in a range of 500 to 1000 °C. The duration of the oxidation process is determined according to the temperature of the oxidation process. A lower temperature requires a longer duration, and a higher temperature requires a shorter duration. In the case where the temperature of the catalyst during the oxidation process is in a range of 500 to 1000 °C, the duration of the oxidation process may be between about two seconds and one hour. The catalyst may be heated by reaction heat at the catalyst. However, if the temperature of the catalyst is below the lower limit of the above-mentioned range, the catalyst may be heated by a heating means.

The reduction process may be performed by heating in the presence of a reducing gas, such as hydrogen and carbon oxide. For example, the reduction process can be performed while supplying, to the platinum-carrying catalyst, an exhaust gas in a stoichiometric atmosphere which is at a stoichiometric balance, or in a rich atmosphere where the oxygen concentration is low. In this way, the oxidation process and the reduction process can be performed on the platinum-carrying catalyst inside the exhaust gas passage, allowing the regeneration process to be performed on the catalyst as a part of the air-fuel ratio control for the engine.

The temperature of the catalyst during the reduction process may be any temperature at which the platinum oxide is reduced, and may be 200 °C or more, and may be in a range of 400 to 1000 °C. The duration of the reduction process is selected appropriately according

to the temperature of the reduction process. A lower catalyst temperature requires a longer duration, and a higher catalyst temperature requires a shorter duration. In the case where the temperature of the catalyst during the reduction process is 300 °C or more, the duration of the reduction process may be between about two seconds and five minutes. The catalyst may be heated by reaction heat at the catalyst. However, if the temperature of the catalyst is below the lower limit of the above-mentioned range, the catalyst may be heated by a heating means.

The platinum-carrying catalyst, which is disposed in the exhaust gas passage of the internal combustion engine, may be subjected to the regeneration process in real time as the performance of the catalyst deteriorates. The regeneration process may be performed regularly, for example according to the operating duration or the travel distance of the vehicle. Alternatively, an NOx sensor or a CO sensor may be provided downstream of the platinum-carrying catalyst to detect the performance of the catalyst, so that the regeneration process can be performed when the detected NOx and/or CO concentration exceeds a reference value.

During the regeneration process, the NOx reduction purification performance decreases under the influence of the oxidizing atmosphere in the oxidation process. However, the exhaust gas purification systems of the present invention are provided with a three-way catalyst or an NOx storage reduction catalyst in addition to the catalyst to be regenerated, and thus can prevent NOx emission, even during the regeneration.

FIG. 1 is a schematic diagram of an exhaust gas purification system according to an embodiment of the present invention. The exhaust gas purification system includes oxygen supply means 2, and two platinum-carrying catalysts 1a, 1b disposed in parallel with each other. The oxygen supply means 2 and the platinum-carrying catalysts 1a, 1b are disposed in the stated order from the upstream side of an exhaust gas passage from an internal combustion engine 3. When either platinum-carrying catalyst 1a or 1b is determined to have deteriorated, the oxygen supply means 2 supplies oxygen to the platinum-carrying catalyst determined to have deteriorated, so that the platinum-carrying catalyst supplied with oxygen can be regenerated. At this time, a valve V1 is switched to

supply the exhaust gas to the one of the platinum-carrying catalysts 1a and 1b determined to have deteriorated (for example, 1a), while a valve V2 is switched to supply oxygen to the other platinum-carrying catalyst (for example, 1b). In this way, the catalyst 1b can be subjected to the regeneration process, during which the exhaust gas is not supplied to the catalyst 1b but purified solely by the catalyst 1a. Thus, NOx emission during the regeneration of the platinum-carrying catalysts can be avoided.

FIGs. 2 and 3 show a routine of a process to control the regeneration of the catalysts 1a and 1b, respectively, in the exhaust gas purification system of the present invention. In the regeneration control, the oxygen supply means (AI) 2 is controlled based on the degree of deterioration (accumulated deterioration time) of the platinum-carrying catalysts 1a and 1b derived from the temperature of the platinum-carrying catalysts 1a and 1b, as described below, in order to perform a regeneration process on the platinum-carrying catalysts 1a and 1b. The following describes oxygen control by the oxygen supply means (AI) 2, in which air is supplied to either catalyst 1a or 1b. In FIGs. 2 and 3, "V" is a variable indicating the switching state of the valves V1 and V2. When "V" is 0, the valve V1 is switched to supply the exhaust gas to both the platinum-carrying catalysts 1a and 1b. When "V" is Va, the valves V1 and V2 are switched to supply air to the platinum-carrying catalyst 1a and the exhaust gas to the platinum-carrying catalyst 1b. When "V" is Vb, the valves V1 and V2 are switched to supply the exhaust gas to the platinum-carrying catalyst 1a and air to the platinum-carrying catalyst 1b. In addition, in FIGs. 2 and 3, "Ta" represents the temperature of the platinum-carrying catalyst 1a detected by a temperature sensor provided to the platinum-carrying catalyst 1a, and "Tb" represents that of the platinum-carrying catalyst 1b. "f(Ta)" is a map for converting the temperature (Ta) of the platinum-carrying catalyst 1a into the deterioration time, and "f(Tb)" is the corresponding map for the platinum-carrying catalyst 1b. "ta" represents the accumulated deterioration time of the platinum-carrying catalyst 1a, and "tb" represents that of the platinum-carrying catalyst 1b. "t1a" represents the deterioration temperature time of the platinum-carrying catalyst 1a, and "t1b" represents that of the platinum-carrying catalyst 1b. "t0" represents the regeneration starting time of the platinum-carrying catalysts 1a and 1b. "f'(Ta)" is a map

for converting the temperature (Ta) of the platinum-carrying catalyst 1a into the regeneration time, and "f'(Tb)" is the corresponding map for the platinum-carrying catalyst 1b. "t2a" represents the regeneration temperature time of the platinum-carrying catalyst 1a, and "t2b" represents that of the platinum-carrying catalyst 1b. "t3a" represents the accumulated regeneration time of the platinum-carrying catalyst 1a, and "t3b" represents that of the platinum-carrying catalyst 1b.

(1) An ECU for controlling the oxygen supply means (AI) 2 records the accumulated deterioration time (ta, tb) of each of the platinum-carrying catalysts 1a and 1b using the temperature (Ta, Tb) of the platinum-carrying catalysts 1a and 1b detected by the temperature sensor each provided to the platinum-carrying catalysts 1a and 1b and the prescribed map (f(Ta), f(Tb)) defining the deterioration of the platinum-carrying catalysts 1a and 1b.

(2) The ECU predicts the current degree of deterioration (diameter of platinum particles) of the platinum-carrying catalysts 1a and 1b based on the accumulated deterioration time (ta, tb) of the platinum-carrying catalysts 1a and 1b and the deterioration temperature time (t1a, t1b) derived from the map defining the deterioration of the platinum-carrying catalysts 1a and 1b. When platinum of either of the platinum-carrying catalysts 1a and 1b is detemined to have been sintered ($ta + t1a > t0$ or $tb + t1b > t0$), the ECU sends an air induction signal to the oxygen supply means (AI) 2. When the AI inducts air to either of the platinum-carrying catalysts 1a and 1b, the valve V1 needs to be switched to allow the exhaust gas from the internal combustion engine to pass through both the platinum-carrying catalysts 1a and 1b (V=0 in FIGs.2 and 3). Thus, when the exhaust gas from the internal combustion engine is allowed to pass through only either of the platinum-carrying catalysts 1a and 1b, the process returns to the step (1) above.

(3) The platinum is regenerated (redispersed) when the temperature of the catalyst is in a range of 500 to 1000 °C, but regeneration of the platinum is minimal outside of this range. Thus, in the case where the platinum-carrying catalyst having deteriorated reaches the temperature range of 500 to 1000 °C, where the catalyst can be regenerated, after the air induction signal is sent in step (2) above, the ECU controls the valves V1 and V2 so as

to induct air to the platinum-carrying catalyst having deteriorated, by means of the oxygen supply means (AI) 2, and only the exhaust gas to the other platinum-carrying catalyst. This allows regeneration of the platinum-carrying catalyst having deteriorated. When the temperature of the platinum-carrying catalyst having deteriorated is not in the range, air is not inducted and the process returns to the step (1) above. Assuming that the platinum-carrying catalyst 1a has deteriorated, for example, in the case where the platinum-carrying catalysts 1a reaches the temperature range of 500 to 1000 °C, where the catalyst can be regenerated, after the air induction signal is sent in step (2) above, the ECU controls the valves V1 and V2 so as to induct air to the platinum-carrying catalyst 1a, by means of the oxygen supply means (AI) 2, and only the exhaust gas to the platinum-carrying catalyst 1b (V=Va in FIG. 2). This allows regeneration of the platinum-carrying catalyst 1a. When the temperature of the platinum-carrying catalyst 1a is not in the range, air is not inducted and the process returns to the step (1) above.

(4) The oxygen supply means (AI) 2 continues inducting air in step (3) above, until the platinum-carrying catalyst having deteriorated is determined to have been regenerated sufficiently, based on the degree of regeneration of the platinum-carrying catalyst having deteriorated of the platinum-carrying catalysts 1a and 1b, predicted based on the accumulated regeneration time (t3a or t3b) of the platinum-carrying catalyst having deteriorated and the regeneration temperature time (t2a or t2b) derived from the prescribed map (f'(Ta) or f'(Tb)) defining the regeneration (redispersion of platinum) of the platinum-carrying catalyst having deteriorated. When the temperature of at least one of the platinum-carrying catalysts 1a and 1b has come out of the range of 500 to 1000 °C, the oxygen supply means (AI) 2 stops inducting air and the process returns to the step (1) above.

(5) After the regeneration of the platinum-carrying catalyst having deteriorated is determined to have finished in the step (4) above, the oxygen supply means (AI) 2 stops inducting air and the process starts over again from the step (1) above, allowing reliable regeneration of platinum and maintaining the exhaust gas purification performance.

Example 1

A honeycombed base made of cordierite was coated with CeO_2-ZrO_2 complex oxide (with a molar ratio of Ce/Zr = 6/4) carrying 1 wt% of platinum at a coating concentration of 120 g/L, and dried at 250 °C. After drying, the base was calcined at 600 °C for one hour to obtain a platinum-carrying catalyst. Two platinum-carrying catalysts obtained in this way are used, as platinum-carrying catalysts 1a and 1b. A part of the coating layer of the platinum-carrying catalysts was sampled, and subjected to the CO chemisorption method described in JP-A-2005-164391 to determine the average diameter of platinum particles, which was 1 nm.

Oxygen supply means and the platinum-carrying catalysts 1a and 1b described above were disposed on an exhaust pipe from a 3.0-L gasoline engine as shown in FIG. 1.

Catalyst Durability Test

The engine was operated at an approximately stoichiometric ratio for five hours such that the catalyst bed temperature of the platinum-carrying catalyst 1a or 1b is at 900 °C in the above-described exhaust gas purification system. During the operation, the valve V1 was opened such that the exhaust gas would flow through both the platinum-carrying catalysts 1a and 1b for ten minutes. After that, the valve V1 was set such that the exhaust gas would flow only through the platinum-carrying catalyst 1b for two minutes, while the valve V2 was also set such that the oxygen supply means 2 would supply oxygen only to the platinum-carrying catalyst 1a for two minutes. After that, the valve V1 was opened such that the exhaust gas would flow through both platinum-carrying catalysts 1a and 1b for ten minutes. For the next two minutes, the valves V1 and V2 and the oxygen supply means 2 were set such that the exhaust gas and oxygen would be supplied to the platinum-carrying catalysts 1a and 1b, respectively. These steps were repeated for five hours. After the five-hour durability test, part of the coating layer of the platinum-carrying catalysts 1a and 1b was sampled, and subjected to the same CO absorption process as mentioned above to determine the average diameter of platinum particles. The NOx purification rate during the operation of five hours was obtained by comparing the amount of NOx emission when using a catalyst to that when using no catalyst.

Comparative Example 1

Only one platinum-carrying catalyst was used, as shown in FIG. 4. The durability test was conducted by causing the exhaust gas to flow for five hours while inducting air to the platinum-carrying catalyst 1a for two minutes at intervals of ten minutes.

Comparative Example 2

The catalysts 1a and 1b, but not oxygen supply means or valves, were disposed as shown in FIG. 5 so that the exhaust gas from the 3.0-L gasoline engine would flow through both catalysts 1a and 1b. The durability test was conducted by causing the exhaust gas to flow for five hours without inducting air.

The durability test results are shown in Table 1 below.

[Table 1]

	Platinum particle diameter of catalyst before durability test	Platinum particle diameter of catalyst after durability test	NOx purification rate during durability test
Example 1	1a: 1nm 1b: 1nm	1a: 3nm 1b: 3nm	95 %
Comparative Example 1	1a: 1nm	1a: 4nm	66 %
Comparative Example 2	1a: 1nm 1b: 1nm	1a: 11nm 1b: 11nm	78 %

As shown in the table, the exhaust gas purification system of the present invention allows regeneration of catalysts without reducing the NOx purification rate.

While the invention has been described with reference to example embodiments thereof, it is to be understood that the invention is not limited to the example embodiments or constructions. To the contrary, the invention is intended to cover various modifications and equivalent arrangements. In addition, while the various elements of the preferred embodiments are shown in various example combinations and configurations, other combinations and configurations, including more, less or only a single element, are also within the spirit and scope of the invention.

CLAIMS

1. An exhaust gas purification system for an internal combustion engine, comprising:

at least two catalysts (1a, 1b) disposed in parallel with each other in an exhaust gas passage of the internal combustion engine (3) and having a carrier containing a basic oxide and platinum carried on the carrier; and

oxygen supply means (2) for supplying oxygen to the at least two catalysts (1a, 1b).

2. The exhaust gas purification system for an internal combustion engine according to Claim 1, wherein the oxygen supply means (2) does not supply oxygen to all the catalysts (1a, 1b) at the same time during purification of an exhaust gas, and the exhaust gas is not supplied to a first catalyst while it is supplied with oxygen, and the exhaust gas is supplied to a second catalyst not being supplied with oxygen while the first catalyst is supplied with oxygen.

3. The exhaust gas purification system for an internal combustion engine according to Claim 1, wherein the oxygen supply means (2) supplies oxygen to a point on the exhaust gas passage upstream of the catalysts (1a, 1b).

4. The exhaust gas purification system for an internal combustion engine according to Claim 1, wherein the basic oxide is an oxide of at least one element selected from the group consisting of alkaline earth metals and rare earth elements, or is a complex oxide of zirconia and/or almina and at least one of elements selected from alkaline earth metals and rare earth elements.

5. The exhaust gas purification system for an internal combustion engine according to Claim 1, further comprising:

a first switching valve (V1) for switching the supply of the exhaust gas between the at least two catalysts (1a, 1b);

a second switching valve (V2) for switching the supply of oxygen from the oxygen

supply means (2) between the at least two catalysts (1a, 1b);

a temperature sensor for detecting a temperature of each of the at least two catalysts (1a, 1b); and

a controller for controlling the first switching valve (V1), the second switching valve (V2) and the oxygen supply means (2) to determine whether either of the at least two catalysts (1a, 1b) has deteriorated based on the detected temperature of the catalysts (1a, 1b).

6. The exhaust gas purification system for an internal combustion engine according to Claim 5, wherein the controller controls the first switching valve (V1), the second switching valve (V2) and the oxygen supply means (2) to stop supplying oxygen to the first catalyst and supply the exhaust gas to the at least two catalysts when the first catalyst, which was determined to have deteriorated, is regenerated.

7. The exhaust gas purification system for an internal combustion engine according to Claim 6, wherein the controller controls the oxygen supply means (2) to supply oxygen to the catalyst determined to have deteriorated when a catalyst is determined to have deteriorated and is in a temperature range of 500 °C to 1000 °C.

8. The exhaust gas purification system for an internal combustion engine according to Claim 7, wherein the controller controls the oxygen supply means (2) to stop supplying oxygen to the catalyst determined to have deteriorated when the catalyst that is determined to thave deteriorated is in a temperature range of 500 °C to 1000 °C.

9. The exhaust gas purification system for an internal combustion engine according to Claim 5, wherein the controller controls, each predetermined duration of operation of the internal combustion engine (1), the oxygen supply means (2) and the second switching valve (V2) to supply oxygen to at least one of the catalysts, and the first switching valve (V1) to supply the exhaust gas only to the catalyst that is not being supplied with oxygen.

10. The exhaust gas purification system for an internal combustion engine according to Claim 1, wherein an amount of the basic oxide contained in the carrier is 50 wt% or more.

FIG. 1

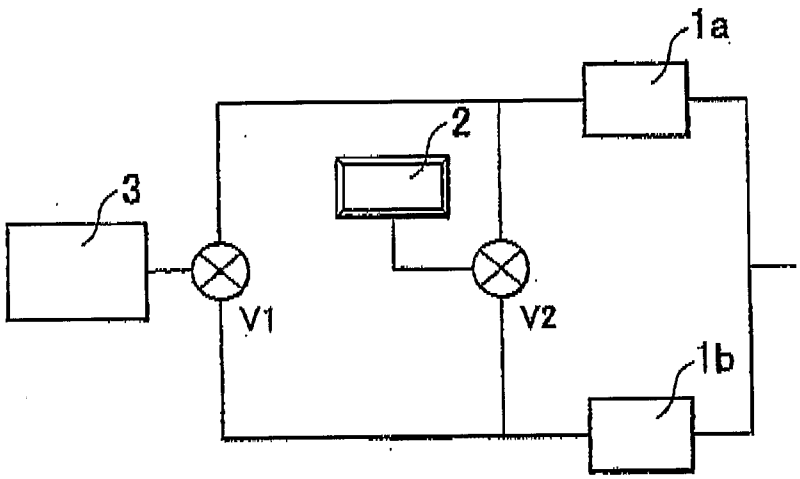


FIG. 2

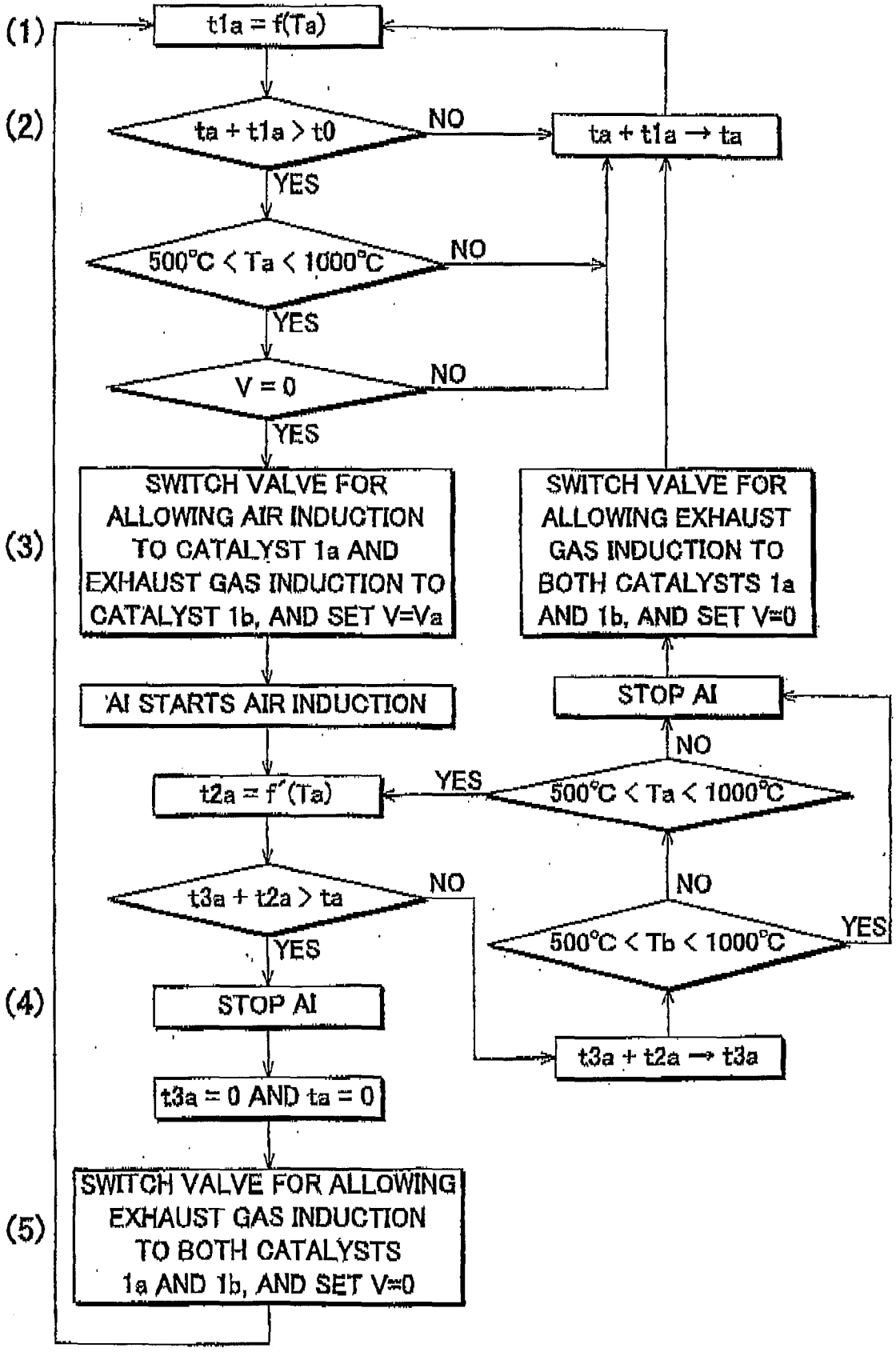

(1)
t1a = f(Ta)
(2)
ta + t1a > t0
NO
ta + t1a → ta
YES
500°C < Ta < 1000°C
NO
YES
V = 0
NO
YES
(3)
SWITCH VALVE FOR ALLOWING AIR INDUCTION TO CATALYST 1a AND EXHAUST GAS INDUCTION TO CATALYST 1b, AND SET V=Va
SWITCH VALVE FOR ALLOWING EXHAUST GAS INDUCTION TO BOTH CATALYSTS 1a AND 1b, AND SET V=0
AI STARTS AIR INDUCTION
STOP AI
NO
t2a = f'(Ta)
YES
500°C < Ta < 1000°C
t3a + t2a > ta
NO
NO
YES
500°C < Tb < 1000°C
YES
(4)
STOP AI
t3a + t2a → t3a
t3a = 0 AND ta = 0
(5)
SWITCH VALVE FOR ALLOWING EXHAUST GAS INDUCTION TO BOTH CATALYSTS 1a AND 1b, AND SET V=0

FIG. 3

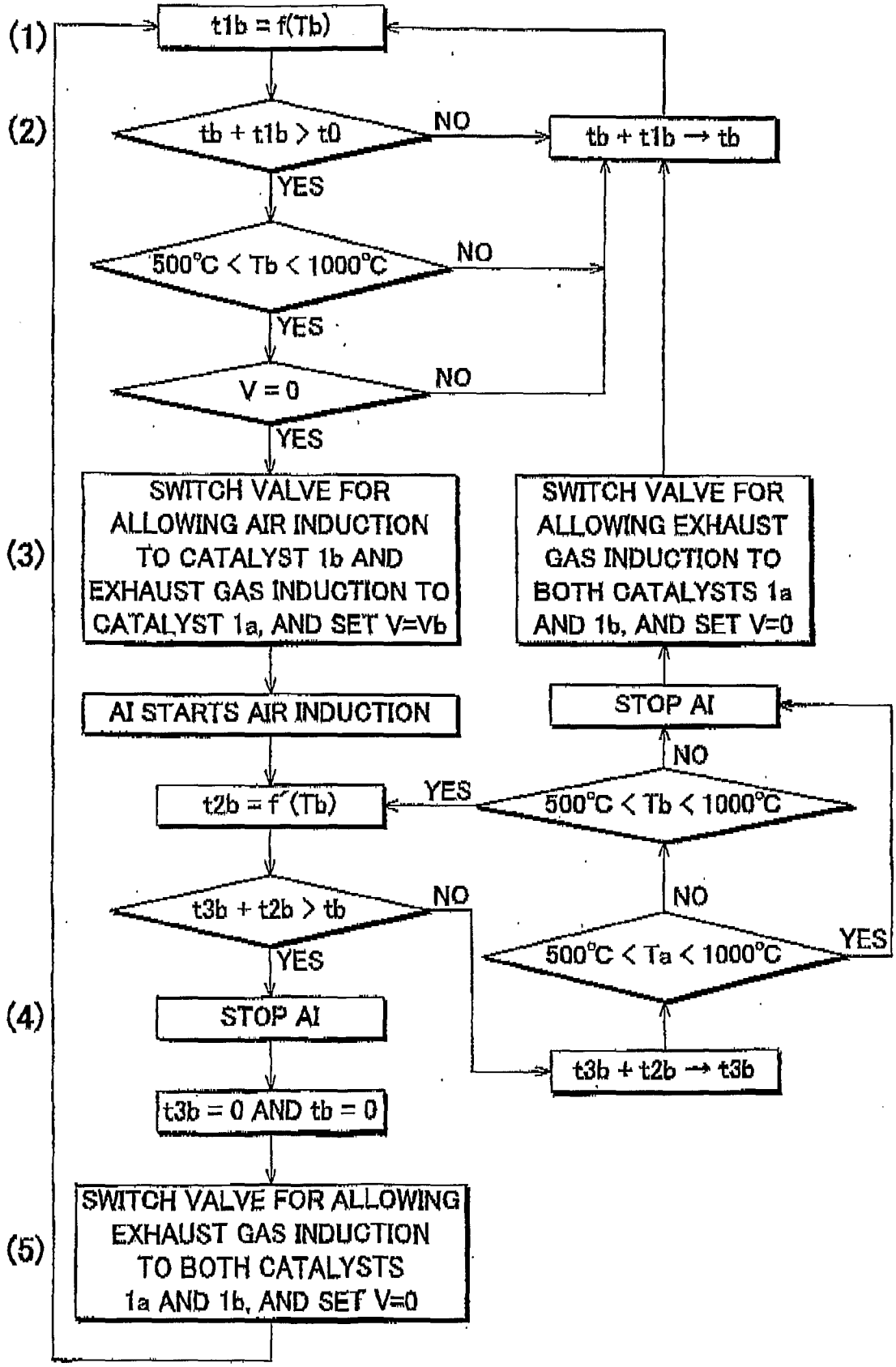

(1)
t1b = f(Tb)
(2)
tb + t1b > t0
NO
tb + t1b → tb
YES
500°C < Tb < 1000°C
NO
YES
V = 0
NO
YES
(3)
SWITCH VALVE FOR ALLOWING AIR INDUCTION TO CATALYST 1b AND EXHAUST GAS INDUCTION TO CATALYST 1a, AND SET V=Vb
SWITCH VALVE FOR ALLOWING EXHAUST GAS INDUCTION TO BOTH CATALYSTS 1a AND 1b, AND SET V=0
AI STARTS AIR INDUCTION
STOP AI
NO
t2b = f'(Tb)
YES
500°C < Tb < 1000°C
t3b + t2b > tb
NO
NO
YES
500°C < Ta < 1000°C
YES
(4)
STOP AI
t3b + t2b → t3b
t3b = 0 AND tb = 0
(5)
SWITCH VALVE FOR ALLOWING EXHAUST GAS INDUCTION TO BOTH CATALYSTS 1a AND 1b, AND SET V=0

FIG. 4

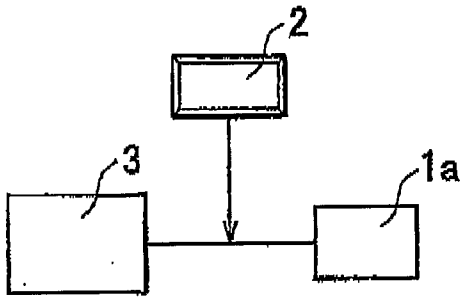


FIG. 5

