A catalyst monitoring system diagnoses deterioration of an NOx catalyst (18) which is arranged in an exhaust passage (12) of an internal combustion engine (10). An NOx sensor (25) is arranged downstream of the NOx catalyst (18). An output integrated value of the NOx sensor (25) is calculated by integrating an output from the NOx sensor (25) during at least a period near the end of air-fuel ratio control. Deterioration of the NOx catalyst (18) is diagnosed based on the output integrated value of the NOx sensor (25).
FIG. 4

START

READ NOx IN

NOxIN ≥ α?

YES

END INTEGRATION OF LAST NOxS
CALCULATE NOxSCNT_R

INTEGRATE NOxS

START RICH SPIKE CONTROL

START TO INTEGRATE NOxS

IS OUTPUT FROM O2 SENSOR DOWNSTREAM OF CATALYST RICH?

YES

END RICH SPIKE CONTROL

IS DETERIORATION DETERMINING CONDITION SATISFIED?

YES

NOxSCNT_R ≥ β?

NO

YES

DETERMINE THAT CATALYST IS DETERIORATED

NO

DETERMINE THAT CATALYST IS NORMAL

END
FIG. 5A

FIG. 5B

FIG. 5C

FIG. 5D

FIG. 5E

FIG. 5F

FIG. 5G
FIG. 7

REDUCING AGENT AMOUNT INTEGRATED VALUE (RFCNT)

A/F SENSOR OUTPUT (AFS_2)

STOICHIOMETRIC

TIME
FIG. 12

RELATIONSHIP BETWEEN EMISSIONS REGULATIONS AND OBD REGULATIONS

<table>
<thead>
<tr>
<th></th>
<th>EURO STEPIV</th>
<th>US SULEV</th>
</tr>
</thead>
<tbody>
<tr>
<td>EMISSIONS REGULATION</td>
<td>0.08g/km</td>
<td>0.013g/km (0.02g/mile)</td>
</tr>
<tr>
<td>VALUE</td>
<td></td>
<td></td>
</tr>
<tr>
<td>OBD REGULATION VALUE</td>
<td>0.28g/km (EMISSIONS REGULATION VALUE + 0.2 g/km)</td>
<td>0.022g/km (EMISSIONS REGULATION VALUE × 1.75)</td>
</tr>
</tbody>
</table>

FIG. 13
**FIG. 14A**

Differential in catalyst performance due to NOx that passes through.

- NOx (downstream of catalyst)

**FIG. 14B**

Differential in catalyst performance due to NOx that is discharged.

- NOx (downstream of catalyst)

1. NOx that passes through during lean burn operation
2. NOx that is discharged during rich spike control
CATALYST MONITORING SYSTEM AND MONITORING METHOD

BACKGROUND OF THE INVENTION

[0001] 1. Field of the Invention
[0002] The invention relates to a catalyst monitoring system and monitoring method.
[0003] 2. Description of the Related Art
[0004] Emissions regulations that regulate an amount of harmful substances discharged from vehicles are currently being imposed from the standpoint of environmental protection. Moreover, so-called “on-board diagnostic (OBD) regulations” are also being imposed which mandate that vehicles must be equipped with an OBD system that automatically performs a diagnostic on an exhaust gas purifying apparatus to check for failure or deterioration of the exhaust gas purifying apparatus.

[0005] A three-way catalyst is unable to sufficiently purify NOx when the air-fuel ratio of the inflowing exhaust gas is leaner than the stoichiometric air-fuel ratio. Therefore, a lean burn engine, for example, that is able to operate at a leaner air-fuel ratio than the stoichiometric air-fuel ratio is equipped with a NOx catalyst in the exhaust passage. This NOx catalyst is able to store NOx when the air-fuel ratio of the exhaust gas is lean.

[0006] Japanese Patent No. 3316066 describes a diagnostic system for an exhaust gas purifying apparatus as one type of OBD system for a lean burn engine. This diagnostic system is provided with a NOx sensor downstream of a NOx catalyst and integrates the amount of NOx emission for a predetermined period of time based on the actual NOx concentration detected by the NOx sensor. The diagnostic system then checks whether the NOx catalyst has failed based on that integrated value.

[0007] In a lean burn engine, in order to reduce and purify the NOx stored in the NOx catalyst, so-called “rich spike control” which temporarily switches the air-fuel ratio of the exhaust gas from the lean air-fuel ratio to the rich or the stoichiometric air-fuel ratio is executed in cycles. Therefore, the NOx discharged from a lean burn engine into the atmosphere may be classified into two categories, i.e., NOx that passes through the NOx catalyst during lean burn operation and NOx that is discharged from the NOx catalyst during the rich spike control. The former NOx that passes through the NOx catalyst during lean burn operation is NOx that was discharged from the engine and passed through the NOx catalyst without being trapped by the NOx catalyst. The latter NOx that is discharged from the NOx catalyst during the rich spike control is NOx that was stored in the NOx catalyst but then discharged from the NOx catalyst without completely being reduced during the rich spike control.

[0008] A limiting current NOx sensor that is used in recent years responds to NH3 as well as NOx. When the air-fuel ratio of the exhaust gas is rich, a reducing agent (such as unburned fuel) reacts with nitrogen gas in the catalyst, thereby producing NH3. Accordingly, when the air-fuel ratio of the exhaust gas is rich (such as during the rich spike control), the NOx sensor is unable to detect the concentration of only the NOx because the NOx sensor also responds to the NH3 in the exhaust gas. Therefore, a NOx sensor is unable to detect the amount of NOx that is discharged from the NOx catalyst during the rich spike control. Due to this problem, OBD systems provided with NOx sensors, including the diagnostic system described in Japanese Patent No. 3316066, are designed to detect the NOx concentration with a NOx sensor only during the lean burn operation, when the exhaust gas does not contain NH3.

[0009] However, under recent strict regulations, there are instances where it is difficult to detect deterioration of an NOx catalyst by only detecting NOx that passes through during the lean burn operation. This will be described below.

[0100] FIGS. 12 and 13 show the NOx emissions regulation values and the OBD regulation values according to NIST IV in Europe and SULEV (Super Ultra-Low Emission Vehicle) in the United States. As shown in FIG. 13, SULEV not only has a stringent NOx emissions regulation value, but also has an extremely stringent OBD regulation value such as 1.75 times the NOx emissions regulation value. That is, the deterioration detection range is extremely small so deterioration of a NOx catalyst is required to be diagnosed with extremely high accuracy.

[0101] FIGS. 14A and 14B each show experimental data about NOx discharged from a lean burn engine system on a graph in which the horizontal axis represents time and the vertical axis represents the amount of NOx emission. FIG. 14A shows a case using a NOx catalyst for Euro STEP IV and FIG. 14B shows a case using a NOx catalyst for US SULEV. In FIGS. 14A and 14B, the solid lines on the graphs represent data obtained using catalysts that correspond to the NOx emissions regulation values, i.e., catalysts that are not deteriorated. On the other hand, the broken lines in the graphs represent data obtained using catalysts that correspond to the OBD regulation value, i.e., catalysts that have deteriorated to a level where deterioration of the NOx catalyst must be detected according to OBD regulations. That is, in order to clear the OBD regulations set forth in the Euro STEP IV emissions standards, deterioration of the NOx catalyst must be detected when the amount of NOx emission has increased to the level of the broken line in FIG. 14A. Meanwhile, in order to clear the OBD regulations set forth in the US SULEV emissions standards, deterioration of the NOx catalyst must be detected when the amount of NOx emission has increased to the level of the broken line in FIG. 14B.

[0102] As can be seen in FIG. 14A, with the Euro STEP IV emissions standards, there is a relatively large difference between the amount of NOx that passes through the NOx catalyst corresponding to the emissions regulation value during the lean burn operation and the amount of NOx that passes through the NOx catalyst corresponding to the OBD regulation value during the lean burn operation. Therefore, with the OBD regulation in the Euro STEP IV emissions standards, the NOx sensor detects the amount of NOx that passes through the NOx catalyst during the lean burn operation, and deterioration of the NOx catalyst may be determined by comparing the detected NOx value with a predetermined determining value.

[0103] On the other hand, as can be seen in FIG. 14B, with the even more stringent US SULEV emissions standards, during lean burn operation almost no NOx passes through either the NOx catalyst corresponding to the emissions regulation value or the NOx catalyst corresponding to the OBD regulation value so there is only a slight difference between the two NOx catalysts. Therefore, with the US SULEV emission standards, even if the NOx sensor detects the amount of NOx that passes through the NOx catalyst during lean burn operation, it is difficult to determine deterioration of the NOx catalyst. On the other hand, there is a relatively large difference between the amount of NOx that is discharged from the
NO\textsubscript{X} catalyst corresponding to the emissions regulation value during the rich spike control and the amount of NO\textsubscript{X} that is discharged from the NO\textsubscript{X} catalyst corresponding to the OBD regulation value during the rich spike control. However, as described above, when the air-fuel ratio of the exhaust gas is rich, it is difficult to accurately detect the concentration of only NO\textsubscript{X} with the NO\textsubscript{X} sensor because the NO\textsubscript{X} sensor also responds to the NH\textsubscript{3} in the exhaust gas. Therefore, it is also difficult to determine deterioration of the NO\textsubscript{X} catalyst with the difference in the amount of NO\textsubscript{X} that is discharged from the NO\textsubscript{X} catalyst during the rich spike control.

In this way, increasingly stringent OBD regulations make it difficult to determine deterioration of the NO\textsubscript{X} catalyst by a method that uses a NO\textsubscript{X} sensor to detect the NO\textsubscript{X} concentration in the exhaust gas.

**SUMMARY OF THE INVENTION**

The invention thus provides a catalyst monitoring system and monitoring method that accurately diagnoses deterioration of a NO\textsubscript{X} catalyst which is arranged in an exhaust passage of an internal combustion engine.

A catalyst monitoring system according to the first aspect of the invention includes a NO\textsubscript{X} catalyst which is arranged in an exhaust passage of an internal combustion engine; an NO\textsubscript{X} sensor which is arranged downstream of the NO\textsubscript{X} catalyst and detects a concentration of NO\textsubscript{X}; air-fuel ratio controlling means for temporarily switching an air-fuel ratio of exhaust gas during operation of the internal combustion engine from a lean air-fuel ratio to a rich or stoichiometric air-fuel ratio; calculating means for calculating an output integrated value of the NO\textsubscript{X} sensor by integrating an output from the NO\textsubscript{X} sensor at least during a period near the end of air-fuel ratio control; and diagnosing means for diagnosing deterioration of the NO\textsubscript{X} catalyst based on the output integrated value of the NO\textsubscript{X} sensor.

Also, the NO\textsubscript{X} sensor may be capable of detecting a concentration of NH\textsubscript{3} as well as the concentration of NO\textsubscript{X}.

Further, the NO\textsubscript{X} sensor may be a limiting current NO\textsubscript{X} sensor.

Moreover, the period near the end of the air-fuel ratio control may be a period during which the output from the NO\textsubscript{X} sensor temporarily increases abruptly.

Also, the catalyst monitoring system may also include reducing agent amount calculating means for calculating an amount of reducing agent that has flowed into the NO\textsubscript{X} catalyst during the air-fuel ratio control. The air-fuel ratio controlling means may end the air-fuel ratio control when the reducing agent amount reaches a predetermined amount.

Further, the diagnosing means may diagnose deterioration of the NO\textsubscript{X} catalyst based on the output integrated value of the NO\textsubscript{X} sensor and the reducing agent amount.

Moreover, the catalyst monitoring system may also include reducing time measuring means for measuring a reducing time of NO\textsubscript{X} according to the air-fuel ratio control. The diagnosing means may diagnose deterioration of the NO\textsubscript{X} catalyst based on the output integrated value of the NO\textsubscript{X} sensor and the reducing time.

Also, the air-fuel ratio controlling means may start the air-fuel ratio control when the amount of NO\textsubscript{X} that has flowed into the NO\textsubscript{X} catalyst reaches a predetermined value.

Further, the catalyst monitoring system may also include an O\textsubscript{2} sensor which is arranged downstream of the NO\textsubscript{X} catalyst and detects a concentration of O\textsubscript{2}. The air-fuel ratio controlling means may end the air-fuel ratio control when an output from the O\textsubscript{2} sensor while the air-fuel ratio control is being executed becomes the rich air-fuel ratio.

Moreover, the diagnosing means may start to diagnose deterioration of the NO\textsubscript{X} catalyst when a predetermined executing condition for determining deterioration is satisfied. The predetermined executing condition for determining deterioration may include: i) a condition that the internal combustion engine operate at a predetermined operating condition while the air-fuel ratio control is executed; and ii) a condition that a temperature of the NO\textsubscript{X} catalyst be within a predetermined temperature range while the air-fuel ratio control is executed.

Also, the predetermined operating condition may include a condition that at least one from among a speed of the internal combustion engine, a throttle opening amount of the internal combustion engine, and an intake air amount of the internal combustion engine be within a predetermined range.

The period near the end of the air-fuel ratio control may include a period during which the output from the NO\textsubscript{X} sensor temporarily increases abruptly due to NH\textsubscript{3} that is discharged from the NO\textsubscript{X} catalyst.

The calculating means may calculate the output integrated value of the NO\textsubscript{X} sensor by integrating the product of a physical quantity corresponding to an amount of intake air flowing into the NO\textsubscript{X} catalyst multiplied by the output from the NO\textsubscript{X} sensor.

The air-fuel ratio controlling means may end the air-fuel ratio control when the output current from the NO\textsubscript{X} sensor while the air-fuel ratio control is being executed corresponds to the rich air-fuel ratio.

A catalyst monitoring method according to a second aspect of the invention includes steps of: performing air-fuel ratio control that temporarily switches an air-fuel ratio of exhaust gas during operation of an internal combustion engine from a lean air-fuel ratio to a rich or stoichiometric air-fuel ratio; calculating an output integrated value of an NO\textsubscript{X} sensor which is arranged downstream of an NO\textsubscript{X} catalyst in an exhaust passage of the internal combustion engine by integrating an output from the NO\textsubscript{X} sensor at least during a period near the end of the air-fuel ratio control; and diagnosing deterioration of the NO\textsubscript{X} catalyst based on the output integrated value of the NO\textsubscript{X} sensor.

**BRIEF DESCRIPTION OF THE DRAWINGS**

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

FIG. 1 is a schematic view of a system configuration according to a first example embodiment of the invention;

FIG. 2 is a sectional view of the structure of a NO\textsubscript{X} sensor provided in the system shown in FIG. 1;

FIG. 3 is a timing chart, with FIG. 3A showing the output from an A/F sensor;

FIG. 3B showing the NO\textsubscript{X} concentration downstream of a NO\textsubscript{X} catalyst, and FIG. 3C showing the output from a NO\textsubscript{X} sensor;

FIG. 4 is a flowchart illustrating a routine executed in the first example embodiment of the invention;

FIG. 5 is a timing chart illustrating the various operations of the first example embodiment of the invention, with FIG. 5A showing an integrated amount of NO\textsubscript{X} that
flows into a NOx catalyst, FIG. 5B showing an air-fuel ratio control execution flag, FIG. 5C showing output from a downstream O2 sensor, FIG. 5D showing output from an A/F sensor, FIG. 5E showing a reducing agent amount integrated value, FIG. 5F showing output from a NOx sensor, and FIG. 5G showing a NOx sensor output integrated value.

FIG. 6 is a chart showing a reference determining value in the first example embodiment of the invention;

FIG. 7 is a timing chart illustrating a method for calculating the reducing agent amount integrated value;

FIG. 8 is a chart showing a reference determining value in a second example embodiment of the invention;

FIG. 9 is a chart showing a reference determining value in a third example embodiment of the invention;

FIG. 10 is a schematic view of a system configuration according to a modified example of the first example embodiment of the invention;

FIG. 11 is a timing chart illustrating a method for obtaining the reducing agent amount integrated value and a reducing time in the modified example;

FIG. 12 is a chart showing the NOx emissions regulation values and the OBD regulation values according to the US STEP IV emissions standards and the US SULEV emissions standards;

FIG. 13 is a graph showing the NOx emissions regulation values and the OBD regulation values according to the US STEP IV emissions standards and the US SULEV emissions standards;

FIG. 14A is a graph showing experimental data of the amount of NOx discharged from a lean burn engine system when a NOx catalyst for the US STEP IV emissions standards is used; and

FIG. 14B is a graph showing experimental data of the amount of NOx discharged from a lean burn engine system when a NOx catalyst for the US SULEV emissions standards is used.

**DETAILED DESCRIPTION OF EMBODIMENTS**

FIG. 1 is a view of a schematic view of a system configuration according to a first example embodiment of the invention. The system shown in FIG. 1 is provided with an internal combustion engine 10. The internal combustion engine 10 shown in the drawing is an in-line four cylinder type internal combustion engine having four cylinders "#1" to "#4". However, the invention is not limited to this, i.e., the number and arrangement of cylinders are not limited to this.

The internal combustion engine 10 may operate by burning fuel at an air-fuel ratio that is leaner than the stoichiometric air-fuel ratio (i.e., hereinafter, this air-fuel ratio will be referred to as "lean-air-fuel ratio"). The internal combustion engine 10 may be any one of a port injection type internal combustion engine in which fuel is injected into an intake port, an in-cylinder direct injection type internal combustion engine in which fuel is injected directly into the cylinder, or a combination of the two types internal combustion engines which employs both port injection and in-cylinder direct injection.

Also, in the first example embodiment, the internal combustion engine 10 is a spark ignition type internal combustion engine but the invention may also be applied to a catalyst monitoring system of a compression ignition type internal combustion engine.

Provided midway in an exhaust passage 12 of the internal combustion engine 10 are two start catalysts (upstream catalysts) 14 and 16, and a single NOx catalyst (NSR) 18. Exhaust gas from the #1 and #4 cylinders flows into the start catalyst 14 while exhaust gas from the #2 and #3 cylinders flows into the start catalyst 16. The exhaust gas that has passed through the start catalyst 14 merges with the exhaust gas that has passed through the start catalyst 16 and together they flow into the NOx catalyst 18.

The start catalysts 14 and 16 function as three-way catalysts that may simultaneously purify HCs, CO, and NOx with the storage and release of oxygen when the air-fuel ratio of the inflowing exhaust gas is near the stoichiometric air-fuel ratio. It is to be understood that "storage" used herein means retention of a substance (solid, liquid, gas molecules) in the form of at least one of adsorption, adsorption, absorption, trapping, occlusion, and others.

The NOx catalyst converter 18 functions as a NOx storage-reduction catalyst that stores NOx when the air-fuel ratio of the inflowing exhaust gas is lean, and reduces the stored NOx to N2 when the air-fuel ratio of the inflowing exhaust gas is rich, thereby purifying NOx after which is then released. This NOx storage-reduction catalyst 18 also has the ability to store oxygen and may function as a three-way catalyst when the internal combustion engine 10 operates at the stoichiometric air-fuel ratio.

The NOx catalyst 18 according to the first example embodiment is a high performance NOx catalyst that is compatible with the stringent exhaust gas regulations.

In the exhaust passage 12, an A/F sensor 20 is arranged upstream of the start catalyst 14, an A/F sensor 22 is arranged upstream of the start catalyst 16, an A/F sensor 24 is arranged upstream of the NOx catalyst 18, and a NOx sensor 26 and an O2 sensor 28 are arranged downstream of the NOx catalyst 18.

The A/F sensors 20, 22, and 24 are air-fuel ratio sensors that produce linear output signals which indicate the air-fuel ratio of the exhaust gas. Also, the O2 sensor 26 is an oxygen sensor that produces an output signal that abruptly changes depending on whether the air-fuel ratio of the exhaust gas becomes richer or leaner than the stoichiometric air-fuel ratio.

The NOx sensor 25 detects not only the concentration of NOx concentration in the exhaust gas, but also the concentration of NH3 (ammonia) in the exhaust gas. This NOx sensor 25 will be described in detail later.

A temperature sensor 28 that detects a temperature (bed temperature) TCAT of the NOx catalyst 18 is arranged in the NOx catalyst 18. Incidentally, the temperature TCAT of the NOx catalyst 18 may not be directly detected, i.e., it may be estimated from the exhaust gas temperature detected by an exhaust gas temperature sensor provided upstream or downstream of the NOx catalyst 18. Alternatively, the temperature TCAT of the NOx catalyst 18 may be estimated based on the operating state of the internal combustion engine 10.

Also, an intake system, not shown, which draws in air and distributes the air to the cylinders is connected to the internal combustion engine 10.

The system according to the first example embodiment includes an ECU (Electronic Control Unit) 30. This ECU 30 is electrically connected to, in addition to the sensors described above, various sensors that detect the engine speed NE, the intake air pressure PM, the intake air amount GA, and the throttle opening amount TH, and the like. The ECU 30 is also electrically connected to various actuators, such as fuel injectors, spark plugs, and a throttle valve.
The internal combustion engine 10 according to the first example embodiment operates by combustion at a lean air-fuel ratio within a predetermined operating range (hereinafter this operation will be referred to as “lean burn operation”). During lean burn operation, NOx is difficult to be puriﬁed in the start catalysts 14 and 16 so it is temporarily stored in the NOx catalyst 18. When NOx accumulates in the NOx catalyst 18, the ECU 30 executes rich spike control which temporarily switches the air-fuel ratio of the exhaust gas that ﬂows into the NOx catalyst 18 from a lean to a rich or the stoichiometric air-fuel ratio. As a result, NOx that has stored in the NOx catalyst 18 may be released from the NOx catalyst 18 and thus reduced (i.e., puriﬁed).

The method for temporarily switching the air-fuel ratio of the exhaust gas that ﬂows into the NOx catalyst 18 from the lean to the rich or the stoichiometric air-fuel ratio may be any one of the following methods: i.e., a method that switches the combustion air-fuel ratio of the internal combustion engine 10 from the lean to the rich or the stoichiometric air-fuel ratio, a method that injects additional fuel from an in-cylinder fuel injector during the latter half of the expansion stroke or during the exhaust stroke, or a method that injects fuel into the exhaust passage 12 upstream of the NOx catalyst 18. In this example embodiment, rich spike control is executed by switching the combustion air-fuel ratio of the internal combustion engine 10 from the lean to the rich or the stoichiometric air-fuel ratio.

FIG. 2 is a sectional view of the structure of a sensor portion of the NOx sensor 25 provided in the system shown in FIG. 1. As will be described below, the NOx sensor 25 in this example embodiment is a limiting current NOx sensor. As shown in FIG. 2, the sensor portion of the NOx sensor 25 is made of six oxygen ion conducting solid electrolyte layers such as oxidized zirconia, which have been laminated together. These six solid electrolyte layers will hereinafter be referred to, in order from the top, as the ﬁrst layer L1, the second layer L2, the third layer L3, the fourth layer L4, the ﬁfth layer L5, and the sixth layer L6.

A porous ﬁrst diffusion-controlling member 50 and porous second diffusion-controlling member 51, for example, are arranged between the ﬁrst layer L1 and the third layer L3. A ﬁrst catalyst 52 is formed between these diffusion-controlling members 50 and 51, and a second catalyst 53 is formed between the second diffusion-controlling member 51 and the second layer L2. Also, an atmospheric chamber 54 that is communicated with ambient air is formed between the third layer L3 and the ﬁfth layer L5. Meanwhile, an outer end surface of the ﬁrst diffusion-controlling member 50 contacts the exhaust gas. Accordingly, the exhaust gas ﬂows into the ﬁrst catalyst 52 via the ﬁrst diffusion-controlling member 50 such that the ﬁrst catalyst 52 ﬁlls up with exhaust gas.

Meanwhile, a negative electrode side ﬁrst pump electrode 55 is formed on an inner peripheral surface of the ﬁrst layer L1, that faces the ﬁrst catalyst 52, and a positive electrode side ﬁrst pump electrode 56 is formed on an outer peripheral surface of the ﬁrst layer L1. Voltage is applied by a ﬁrst pump voltage supply 57 between these ﬁrst pump electrodes 55 and 56. When voltage is applied between the ﬁrst pump electrodes 55 and 56, oxygen in the exhaust gas inside the ﬁrst catalyst 52 contacts the negative electrode side ﬁrst pump electrode 55 and turns into oxygen ions. These oxygen ions ﬂow inside the ﬁrst layer L1 toward the positive electrode side ﬁrst pump electrode 56. Accordingly, the oxygen in the exhaust gas inside the ﬁrst catalyst 52 moves inside the ﬁrst layer L1 and is drawn out to the outside. The amount of oxygen drawn out to the outside at this time increases as the voltage of the ﬁrst pump voltage supply 57 increases.

Meanwhile, a reference electrode 58 is formed on an inner peripheral surface of the third layer L3 that faces the atmospheric chamber 54. When there is a difference in the oxygen concentration on one side with respect to the other side of the solid electrolyte layer in an oxygen ion conducting solid electrolyte, oxygen ions move inside the solid electrolyte layer from the side where the oxygen concentration is high toward the side where the oxygen concentration is low. In the example shown in FIG. 2, the oxygen concentration in the atmospheric chamber 54 is higher than the oxygen concentration in the ﬁrst catalyst 52 so the oxygen inside the atmospheric chamber 54 receives a charge from contacting the reference electrode 58 and as a result, turns into oxygen ions. These oxygen ions move inside the third layer L3, the second layer L2, and the ﬁrst layer L1, and release a charge in the negative electrode side ﬁrst pump electrode 55. As a result, a voltage Vn indicated by reference numeral 59 is generated between the reference electrode 58 and the negative electrode side ﬁrst pump electrode 55. This voltage Vn is proportional to the difference between the oxygen concentration in the atmospheric chamber 54 and the oxygen concentration in the ﬁrst catalyst 52.

In the example shown in FIG. 2, the voltage of the ﬁrst pump voltage supply 57 is feedback controlled so that this voltage Vn becomes equal to the voltage generated when the oxygen concentration in the ﬁrst catalyst 52 is 1 ppm. That is, the oxygen in the ﬁrst catalyst 52 is drawn out through the ﬁrst layer L1 so that the oxygen concentration in the ﬁrst catalyst 52 becomes 1 ppm. This enables the oxygen concentration in the ﬁrst catalyst 52 to be maintained at 1 ppm.

The negative electrode side ﬁrst pump electrode 55 is made of material with low NOx reducing ability, such as an alloy of gold Au and platinum Pt, for example. Therefore, almost none of the NOx in the exhaust gas is reduced in the ﬁrst catalyst 52 so the NOx ﬂows into the second catalyst 53 through the second diffusion-controlling member 51. Meanwhile, a negative electrode side second pump electrode 60 is formed on the inner peripheral surface of the ﬁrst layer L1, that faces the second catalyst 53. Voltage is applied by a second pump voltage supply 61 between the negative electrode side second pump electrode 60 and the positive electrode side ﬁrst pump electrode 56. When voltage is applied between these pump electrodes 60 and 56, the oxygen in the exhaust gas inside the second catalyst 53 contacts the negative electrode side second pump electrode 60 and turns into oxygen ions. These oxygen ions ﬂow inside the ﬁrst layer L1 toward the positive electrode side ﬁrst pump electrode 56. Accordingly, the oxygen in the exhaust gas inside the second catalyst 53 moves inside the ﬁrst layer L1, and is drawn out to the outside. The amount of oxygen that is drawn out to the outside at this time increases as the voltage of the second pump voltage supply 61 increases.

Meanwhile, as described above, when there is a difference in the oxygen concentration on one side with respect to the other side of the solid electrolyte layer in an oxygen ion conducting solid electrolyte, oxygen ions move inside the solid electrolyte layer from the side where the oxygen concentration is high toward the side where the oxygen concentration is low. In the example shown in FIG. 2, the oxygen concentration in the atmospheric chamber 54 is
higher than the oxygen concentration in the second chamber 53 so the oxygen inside the atmospheric chamber 54 receives a charge from contacting the reference electrode 58 and as a result, turns into oxygen ions. These oxygen ions move inside the third layer L₃, the second layer L₂, and the first layer L₁, and release a charge in the negative electrode side second pump electrode 60. As a result, a voltage Vᵢ, indicated by reference numeral 62 is generated between the reference electrode 58 and the negative electrode side second pump electrode 60. This voltage Vᵢ is proportional to the difference between the oxygen concentration in the atmospheric chamber 54 and the oxygen concentration in the second chamber 53.

[0070] In the example shown in FIG. 2, the voltage of the second pump voltage supply 61 is feedback controlled so that this voltage Vᵢ becomes equal to the voltage generated when the oxygen concentration in the second chamber 53 is 0.01 ppm. That is, the oxygen in the second chamber 53 is drawn out through the first layer L₁ so that the oxygen concentration in the second chamber 53 becomes 0.01 ppm. This enables the oxygen concentration in the second chamber 53 to be maintained at 0.01 ppm.

[0071] The negative electrode side second pump electrode 60 is made of material with low NOₓ reducing ability, such as an alloy of gold Au and platinum Pt, for example. Therefore, almost none of the NOₓ in the exhaust gas is reduced even if the NOₓ contacts the negative electrode side second pump electrode 60. Meanwhile, a negative electrode side pump electrode 63 for detecting NOₓ is formed on the inner peripheral surface of the third layer L₃ that faces the second chamber 53. This negative electrode side pump electrode 63 is made of material with high NOₓ reducing ability, such as rhodium Rh or platinum Pt, for example. Accordingly, the NOₓ inside the second chamber 53, that is, the NO that actually makes up a substantial portion in the NOₓ, is separated into N₂ and O₂ on the negative electrode side pump electrode 63. A constant voltage 64 is applied between this negative electrode side pump electrode 63 and the reference electrode 58, and as a result, the resultant O₂ on the negative electrode side pump electrode 63 turns into oxygen ions which move inside the third layer L₃ toward the reference electrode 58. At this time, a current I₁, indicated by reference numeral 65 which is proportional to the amount of oxygen ions, flows between the negative electrode side pump electrode 63 and the reference electrode 58.

[0072] As described above, almost no NOₓ is reduced in the first chamber 52, and almost no oxygen is present in the second chamber 53. Therefore, the current I₁ is proportional to the NOₓ concentration in the exhaust gas so the NOₓ concentration in the exhaust gas is detected from the current I₁.

[0073] Meanwhile, the ammonia NH₃ in the exhaust gas is separated into NO and H₂O (4NH₃+5O₂→4NO+6H₂O) in the first chamber 52, and the resultant NO flows into the second chamber 53 through the second diffusion-controlling member 51. This NO is separated into N₂ and O₂ on the negative electrode side pump electrode 63, and the resultant O₂ turns into oxygen ions that move in the third layer L₃ toward the reference electrode 58. Also at this time, the current I₁ is proportional to the NH₃ concentration in the exhaust gas so the NH₃ concentration in the exhaust gas is detected from the current I₁.

[0074] In this way, the NOₓ sensor 25 according to the first example embodiment simultaneously detects both NOₓ and NH₃ in the exhaust gas in principle. Therefore, when NH₃ is present in the exhaust gas, the current I₁ of the NOₓ sensor 25 (hereinafter, this current I₁ will simply be referred to as the “output of the NOₓ sensor 25”) is the combined value of the output according to NOₓ and the output according to NH₃.

[0075] On the other hand, a higher oxygen concentration in the exhaust gas, i.e., a leaner air-fuel ratio, results in more oxygen being drawn out from the first chamber 52 to the outside and thus an current I₁ represented by reference numeral 66 increases. Accordingly, the air-fuel ratio of the exhaust gas may be detected from this current I₁.

[0076] Incidentally, an electric heater 67 for heating the sensor portion of the NOₓ sensor 25 is provided between the fifth layer L₅ and the sixth layer L₆. This electric heater 67 heats the sensor portion of the NOₓ sensor 25 up to between 700° C. and 800° C.

[0077] Next, the concentration of ammonia NH₃ in the exhaust gas will be described with reference to FIG. 3. FIG. 3 is a timing chart, with FIG. 3A showing the output from the A/F sensor 24, FIG. 3B showing the NOₓ concentration downstream of the NOₓ catalyst 18, and FIG. 3C showing the output from the NOₓ sensor 25.

[0078] In FIG. 3, before time t₁ the internal combustion engine 10 is operating with a lean air-fuel ratio, i.e., is in lean burn operation. When the air-fuel ratio is lean, i.e., when the atmosphere is oxidant, almost no ammonia NH₃ is produced. Also, as described above, the amount of NOₓ that passes through downstream of the NOₓ catalyst 18 during lean burn operation is extremely small (see FIG. 3B). Therefore, during lean burn operation, the output from the NOₓ sensor 25 is substantially zero because almost no NOₓ and no ammonia NH₃ pass through downstream of the NOₓ catalyst 18.

[0079] Meanwhile, when the air-fuel ratio of the exhaust gas is switched from lean to rich, i.e., when the exhaust gas is turned to a reducing atmosphere, by executing rich spike control, nitrogen N₂ in the exhaust gas is reduced by hydrocarbons HC in the start catalysts 14 and 16, thus producing ammonia NH₃. However, when the air-fuel ratio of the exhaust gas becomes rich, NOₓ that was stored in the NOₓ catalyst 18 is released. The ammonia NH₃ that was produced is used to reduce this NOₓ. Therefore, while NOₓ is being released from the NOₓ catalyst 18, or more accurately, while the ammonia NH₃ is being used to release and reduce the NOₓ, almost no ammonia NH₃ is discharged from the NOₓ catalyst 18. Accordingly, as shown in FIG. 3C, the output from the NOₓ sensor 25 remains substantially zero for a while even after the rich spike control has started (i.e., after time t₁).

[0080] In contrast, when the air-fuel ratio is still rich even after NOₓ has finished being released from the NOₓ catalyst 18, the ammonia NH₃ is no longer consumed to reduce the NOₓ so the ammonia NH₃ is discharged from the NOₓ catalyst 18 at this time.

[0081] Incidentally, a similar phenomenon occurs even when the start catalysts 14 and 16 are not provided upstream of the NOₓ catalyst 18. That is, the NOₓ catalyst 18 is also provided with a catalyst such as platinum Pt which has a reducing function so when the air-fuel ratio becomes rich, ammonia NH₃ may be produced in the NOₓ catalyst 18. However, even if ammonia NH₃ is produced at the rich air-fuel ratio, the ammonia NH₃ is used to reduce the NOₓ that is released from the NOₓ catalyst 18 so almost no ammonia NH₃ is discharged from the NOₓ catalyst 18. However, when the air-fuel ratio is still rich even after the NOₓ has finished being released from the NOₓ catalyst 18, ammonia NH₃ is no longer
consumed to reduce the NO\textsubscript{X} so ammonia NH\textsubscript{3} is discharged from the NO\textsubscript{X} catalyst 18 at this time. [0082] For this reason, ammonia NH\textsubscript{3} flows to the downstream side of the NO\textsubscript{X} catalyst 18 near the time when the rich spike control ends (i.e., time t2). This ammonia NH\textsubscript{3} is detected by the NO\textsubscript{X} sensor 25 somewhat late due to the delay in movement of the exhaust gas. Therefore, as shown in FIG. 3C, the output from the NO\textsubscript{X} sensor 25 temporarily increases abruptly near the time when the rich spike control ends. As shown in FIG. 3B, the NO\textsubscript{X} concentration also increases near the time that the rich spike control ends due to the effect from the NO\textsubscript{X} that is discharged, as described above. However, at this time the NO\textsubscript{X} concentration rises only slightly compared to the rise in the output from the NO\textsubscript{X} sensor 25. That is, it may be said that the percentage of an output due to NO\textsubscript{X} (discharged NO\textsubscript{X}) of the entire output from the NO\textsubscript{X} sensor 25 near the time that the rich spike control ends, is small, while the majority of the output from the NO\textsubscript{X} sensor 25 is due to ammonia NH\textsubscript{3}. [0083] As described above, under the stringent OBD regulations, the difference between the amount of NO\textsubscript{X} that has passed through the NO\textsubscript{X} catalyst 18 that has not yet deteriorated during lean burn operation and the amount of NO\textsubscript{X} that has passed through the NO\textsubscript{X} catalyst 18 that has deteriorated corresponding to the OBD regulation value (hereinafter simply referred to as the “deteriorated NO\textsubscript{X} catalyst 18”) is extremely low. Therefore, even if the NO\textsubscript{X} that has passed through an NO\textsubscript{X} catalyst 18 is detected by the NO\textsubscript{X} sensor 25, it is difficult to detect deterioration of the NO\textsubscript{X} catalyst 18. Accordingly, deterioration of the NO\textsubscript{X} catalyst 18 is required to be detected from the difference in the amounts of NO\textsubscript{X} that has discharged from the NO\textsubscript{X} catalyst 18 during rich spike control. However, as described above, ammonia NH\textsubscript{3} flows out downstream of the NO\textsubscript{X} catalyst 18 following rich spike control so it is not easy to obtain the discharged amount of only NO\textsubscript{X} from the output of the NO\textsubscript{X} sensor 25. [0084] Accordingly, the inventors have discovered that deterioration of the NO\textsubscript{X} catalyst 18 may be accurately diagnosed based on a value which indicates the integrated output of the NO\textsubscript{X} sensor 25 near the time that the rich spike control ends (hereinafter this value will be referred to as the “NO\textsubscript{X} sensor output integrated value NO\textsubscript{X}SCNT”). [0085] The discharged amount of NO\textsubscript{X} increases as the NO\textsubscript{X} catalyst 18 deteriorates, but this is due to a decrease in reducing efficiency. As described above, as long as the ammonia NH\textsubscript{3} that was produced in the exhaust gas is being consumed to reduce the NO\textsubscript{X} that has been released from the NO\textsubscript{X} catalyst 18, the ammonia NH\textsubscript{3} will not flow downstream of the NO\textsubscript{X} catalyst 18. In other words, as the reducing efficiency decreases, ammonia NH\textsubscript{3} becomes difficult to be consumed to reduce NO\textsubscript{X}. As a result, more ammonia NH\textsubscript{3} becomes to flow downstream of the NO\textsubscript{X} catalyst 18. Accordingly, it may be said that the discharged amount of NO\textsubscript{X} increases as the amount of ammonia NH\textsubscript{3} that flows downstream of the NO\textsubscript{X} catalyst 18 increases. As described above, the majority of the output from the NO\textsubscript{X} sensor 25 near the time when the rich spike control ends is due to the ammonia NH\textsubscript{3} so there is a correlation between the amount of ammonia NH\textsubscript{3} that flows downstream of the NO\textsubscript{X} catalyst 18 and the NO\textsubscript{X} sensor output integrated value NO\textsubscript{X}SCNT near the time when the rich spike control ends. Accordingly, it may be estimated that the discharged amount of NO\textsubscript{X} increases as the NO\textsubscript{X} sensor output integrated value NO\textsubscript{X}SCNT increases near the time when the rich spike control ends.

[0086] In this way, according to the first example embodiment, deterioration of the NO\textsubscript{X} catalyst 18 may be diagnosed based on the NO\textsubscript{X} sensor output integrated value NO\textsubscript{X}SCNT that deeply correlates with the discharged amount of NO\textsubscript{X} during rich spike control, which makes it possible to more accurately diagnose deterioration. [0087] FIG. 4 is a flowchart of a routine executed by the ECU 30 in the first example embodiment in order to diagnose deterioration of the NO\textsubscript{X} catalyst 18. This routine is executed repeatedly at predetermined intervals of time. FIGS. 5A to 5G is a timing chart that illustrates the various operations of the first example embodiment. The operations including the rich spike controls which are executed three times are shown in FIGS. 5A to 5G.

[0088] According to the routine shown in FIG. 4, first, the value of NO\textsubscript{X}IN that indicates the integrated amount of NO\textsubscript{X} flowing into the NO\textsubscript{X} catalyst 18 is read (step 100). FIG. 5A shows this NO\textsubscript{X}IN. In the first example embodiment, the relationship between the load and speed of the internal combustion engine 10 and the amount of NO\textsubscript{X} generated per unit time is checked beforehand by experimentation. This relationship is stored in the ECU 30 in advance. The ECU 30 then calculates the amount of NO\textsubscript{X} generated per unit time at the actual load and speed of the internal combustion engine 10 based on that relationship, and calculates the integrated value of that amount of NO\textsubscript{X} generated per unit time as NO\textsubscript{X}IN. [0089] FIG. 5B shows a rich spike control execution flag FR. When rich spike control is being executed, FR equals 1. When rich spike control is not being executed, FR equals 0. NO\textsubscript{X}IN is reset after NO\textsubscript{X} that has been stored in the NO\textsubscript{X} catalyst 18 is released by execution of rich spike control. That is, NO\textsubscript{X}IN represents an (estimated value of the) amount of NO\textsubscript{X} that has flowed into the NO\textsubscript{X} catalyst 18 between after rich spike control ended and before the next rich spike control ends.

[0090] Incidentally, the method for calculating the NO\textsubscript{X}IN is not limited to the method of estimating the NO\textsubscript{X}IN from the operating state of the internal combustion engine 10. That is, an NO\textsubscript{X} sensor capable of detecting the NO\textsubscript{X} concentration may be arranged upstream of the NO\textsubscript{X} catalyst 18 and the NO\textsubscript{X}IN may be calculated based on the output from this NO\textsubscript{X} sensor.

[0091] In the first example embodiment, rich spike control starts when NO\textsubscript{X}IN, i.e., the amount of NO\textsubscript{X} that has flowed into the NO\textsubscript{X} catalyst 18, reaches a predetermined value \( \alpha \). Therefore, when NO\textsubscript{X}IN is read in step 100, it is determined whether NO\textsubscript{X}IN is equal to or greater than the predetermined value \( \alpha \) (step 102). If NO\textsubscript{X}IN has not yet reached the predetermined value \( \alpha \) in step 102, then the NO\textsubscript{X} sensor output integrated value NO\textsubscript{X}SCNT is updated by integrating the output NO\textsubscript{X}S from the NO\textsubscript{X} sensor 25 detected in this cycle of the routine (step 104). Then, this cycle of the routine ends.

[0092] FIG. 5E shows the output NO\textsubscript{X}S from the NO\textsubscript{X} sensor 25 and FIG. 5G shows the NO\textsubscript{X} sensor output integrated value NO\textsubscript{X}SCNT. As shown in FIG. 5G, in this first example embodiment, the NO\textsubscript{X} sensor output integrated value NO\textsubscript{X}SCNT is calculated by integrating the NO\textsubscript{X} sensor output NO\textsubscript{X}S from the time that rich spike control starts until the time that next rich spike control starts. Therefore, when it is determined in step 102 that the NO\textsubscript{X}IN has reached the predetermined value \( \alpha \), integration of the last NO\textsubscript{X}S ends (step 106).
[0093] Also, as shown in FIG. 5G, in this first example embodiment, the NOₓ sensor output integrated value NOₓ SCNTₘ is separated into NOₓSCNTₘₓ and NOₓSCNTₘₑ. NOₓ SCNTₘₑ indicates a value that NOₓ sensor output NOₓS has been integrated for the period during which the majority of the NOₓ sensor output NOₓS is due to the ammonia NH₃ produced during the rich spike control. On the other hand, NOₓSCNTₘₓ indicates a value that NOₓ sensor output NOₓS has been integrated for the period during which the majority of the NOₓ sensor output NOₓS is due to the ammonia NH₃ produced during the lean burn operation. In step 106, a process for calculating the NOₓSCNTₘₑ is also executed. More specifically, as shown in FIG. 5G, it may be determined that the majority of the NOₓ sensor output NOₓS is due to the ammonia NH₃ during the period when the NOₓ sensor output NOₓS temporarily increases abruptly. Therefore, the integrated value of the NOₓ sensor output NOₓS during this period may be made NOₓSCNTₘₓ and the integrated value of the NOₓ sensor output NOₓS during a period other than this period may be made NOₓSCNTₘₑ.

[0094] When NOₓIN has reached the predetermined value α, rich spike control for this cycle starts (step 108), following the step 106 and then the NOₓ sensor output NOₓS starts to be integrated for this cycle (step 110).

[0095] FIG. 5C shows the output O₂S from the O₂ sensor downstream of the NOₓ catalyst 18. In this first example embodiment, the rich spike control ends when the output O₂S from the O₂ sensor 26 becomes a rich output. Therefore, while the rich spike control is being executed, it is determined whether the output O₂S from the O₂ sensor 26 has become a rich output (step 112). When it is determined that the output O₂S from the O₂ sensor 26 has become a rich output, the rich spike control for this cycle ends (step 114).

[0096] When the rich spike control ends, it is then determined whether a condition for determining deterioration of the NOₓ catalyst 18 is satisfied (step 116). This deterioration determining condition more specifically consists of the two conditions. These conditions are: (1) that an operating condition (such as the engine speed NE, the throttle opening amount TTH, or the intake air amount GA) when rich spike control is executed be within a predetermined range; and (2) that the temperature TCAT of the NOₓ catalyst 18 when the rich spike control is executed be within a predetermined temperature range.

[0097] Condition (1) above is a condition provided so that only data obtained when the rich spike control is executed under predetermined operating conditions in which there is no sudden acceleration or deceleration or the like is used as the basis for the catalyst deterioration determination in order to prevent an erroneous determination due to a calculation error of the NOₓIN or the like. Condition (2) above is a condition to prevent an erroneous determination due to the effect of the temperature of the NOₓ catalyst 18. That is, the storage-reduction ability of the NOₓ catalyst 18 changes depending on its temperature. Therefore, condition (2) above is provided so that only data obtained when the rich spike control is executed in a temperature range in which the storage-reduction ability of the NOₓ catalyst 18 is regarded as being constant is used as the basis for the catalyst deterioration determination.

[0098] If it is determined in step 116 that the deterioration determining condition is not satisfied, then it may be determined that catalyst deterioration determination should not be performed. Therefore, in this case, the routine for this cycle directly ends. On the other hand, if it is determined in step 116 that the deterioration determining condition is satisfied, catalyst deterioration determination is performed as follows. First, the NOₓSCNTₘₑ that was calculated in step 106 is compared with a predetermined reference deterioration value β (step 118). As described above, it may be determined that the larger NOₓSCNTₘₑ, which indicates the integrated NOₓ sensor output NOₓS near the time that the rich spike control ends, the more ammonia NH₃ has flowed out downstream of the NOₓ catalyst 18. Also, it may be determined that the more ammonia NH₃ flowing out downstream of the NOₓ catalyst 18, the larger amount of NOₓ is discharged during rich spike control. Accordingly, when the NOₓSCNTₘₑ is equal to or greater than the reference deterioration value β in step 118, it is determined that the NOₓ catalyst 18 is deteriorated (step 120). On the other hand, when the NOₓSCNTₘₑ is less than the reference deterioration value β, it is determined that the NOₓ catalyst 18 is normal (i.e., not deteriorated) (step 122).

[0099] Next, the reference determining value β will be described. FIG. 6 is a graph showing a plurality of experimental data plotted on a coordinate system in which the horizontal axis represents the temperature TCAT of the NOₓ catalyst 18 and the vertical axis represents the NOₓ sensor output integrated value NOₓSCNTₘₑ. In FIG. 6, the black squares represent experimental data obtained with an NOₓ catalyst 18 in which level of the discharged amount of NOₓ corresponds to the emissions regulation value (hereinafter this catalyst will be referred to as “normal catalyst (X)”). In contrast, the black diamonds represent experimental data obtained with an NOₓ catalyst 18 in which level of the amount of NOₓ discharged corresponds to the OBD regulation value (hereinafter this catalyst will be referred to as “deteriorated catalyst (Y)”). As can be seen from FIG. 6, the normal catalyst (X) may be reliably differentiated from the deteriorated catalyst (Y) by setting the reference determining value β to a value such as that shown by the straight line in FIG. 6.

[0100] In this way, according to this first example embodiment, extremely high diagnostic accuracy may be obtained by diagnosing deterioration of the NOₓ catalyst 18 based on the NOₓ sensor output integrated value NOₓSCNTₘₑ which correlates with the amount of NOₓ that has been discharged during rich spike control.

[0101] Incidentally, in the example shown in FIG. 6, the reference determining value β is constant regardless of the temperature TCAT of the NOₓ catalyst 18. Alternatively, however, the reference determining value β may be changed according to the TCAT. Also, the reference determining value β may be changed according to another operating condition of the internal combustion engine 10.

[0102] Also, in the routine shown in FIG. 4, the NOₓ sensor output integrated value NOₓSCNTₘₑ is separated into NOₓSCNTₘₓ and NOₓSCNTₘₑ and catalyst deterioration determination of the NOₓ catalyst 18 is performed based on the NOₓSCNTₘₑ. However, the invention is not limited to this method of determination. Alternatively, catalyst deterioration determination may be performed based on the NOₓ sensor output integrated value NOₓSCNTₘₑ before the NOₓSCNT is separated into NOₓSCNTₘₓ and NOₓSCNTₘₑ because the value of NOₓSCNTₘₑ is small compared with the value of NOₓSCNTₘₓ and thus has little effect. Also, it is also possible to calculate only the NOₓSCNTₘₓ from the start. That is, in the invention, the integration period of the NOₓ sensor output NOₓS on which the catalyst deterioration determination is based need only include the period of time during which the
output of the NOx sensor 25 abruptly increases temporarily due to the ammonia NH3 near the time when the rich spike control ends.

[0103] Also, in the first example embodiment described above, the NOx sensor output integrated value NOx\_SCN\_T is calculated by integrating the NOx sensor output NOx\_S. However, the method for calculating the NOx sensor output integrated value NOx\_SCN\_T is not limited to this. Alternatively, for example, the NOx sensor output integrated value NOx\_SCN\_T may also be calculated by integrating the product of a physical quantity corresponding to the amount of air flowing into the NOx catalyst 18 (i.e., corresponding to the inflow gas amount) multiplied by the NOx sensor output NOx\_S. Incidentally, the air amount flowing into the NOx catalyst 18 (hereinafter also referred to as the “inflow air amount”) may be calculated based on, for example, the intake air amount GA detected by an airflow meter, the fuel injection quantity, or the output from the A/F sensor 24.

[0104] Also, in the first example embodiment, the rich spike control ends when the output from the O2 sensor 26 downstream of the NOx catalyst 18 becomes a rich output. Alternatively, the rich spike control may be ended using the O2 sensor function or the A/F sensor function of the NOx sensor 25. For example, with the NOx sensor 25 in the first example embodiment, the air-fuel ratio of the exhaust gas may be detected from the current I2 of the NOx sensor 25 as described with reference to FIG. 2. Accordingly, the rich spike control may be ended when this current I2 corresponds to a rich air-fuel ratio. In this case, it is no longer necessary to provide the O2 sensor 26 downstream of the NOx catalyst 18 so costs may be reduced.

[0105] Next, a modified example of the first example embodiment will be described. In the routine shown in FIG. 4 described above, the rich spike control ends when the output from the O2 sensor 26 downstream of the NOx catalyst 18 becomes a rich output. Alternatively, in this modified example, the rich spike control ends when the amount of reducing agent that has flowed into the NOx 18 reaches a predetermined value \( \gamma \) after the rich spike control starts.

[0106] The method used to calculate the amount of reducing agent that has flowed into the NOx catalyst 18 is not particularly limited. For example, the following method may be used. FIG. 7 is a timing chart illustrating a method for calculating a reducing agent amount integrated value RFCNT. More specifically, the upper drawing in FIG. 7 shows the change in the reducing agent amount integrated value RFCNT, as well as the lower drawing in FIG. 7 shows the output AFS \_2 from the A/F sensor 24, i.e., the air-fuel ratio AFS \_2 of the exhaust gas that flows into the NOx catalyst 18.

[0107] The reducing agent amount integrated value RFCNT is a value indicative of the amount of reducing agent that has flowed into the NOx catalyst 18 due to the rich spike control, and is calculated according to the following expression.

\[ \text{RFCNT} = \Sigma (\text{amount of reducing agent per unit time multiplied by the ECU calculation cycle}) \]  

[0108] Of the fuel that has flowed into the NOx catalyst 18 during the rich spike control, the fuel of an amount that exceeds the amount necessary to achieve the stoichiometric air-fuel ratio (14.6 in this case) (i.e., excess fuel) acts as the reducing agent. Therefore, the amount of reducing agent per unit time may be calculated according to the following expression.

\[ \text{Amount of reducing agent} = \frac{\text{amount of fuel that flows into the NOx catalyst}}{\text{amount of air that flows into the NOx catalyst divided by 14.6}} \]

[0109] While rich spike control is being executed, the reducing agent amount integrated value RFCNT may be successively calculated by the ECU 30 based on the foregoing Expressions (1) and (2). In this modified example, the rich spike control ends when the reducing agent amount integrated value RFCNT that is calculated as described above reaches the predetermined value \( \gamma \). Therefore, the total amount of reducing agent supplied during rich spike control may be constant each time.

[0110] Meanwhile, when the rich spike control is made to end when the output from the O2 sensor 26 downstream of the NOx catalyst 18 becomes a rich output, the amount of the reducing agent may change depending on the deterioration level of the NOx catalyst 18. For example, when the deterioration level of the NOx catalyst 18 is extremely high and the NOx storage amount is extremely small, all of NOx that was stored is soon reduced so the output from the O2 sensor 26 soon becomes the rich output. As a result, the rich spike control soon ends so the amount of reducing agent becomes extremely small. When the amount of reducing agent is small, the amount of ammonia NH3 produced is also small. In the case described above, the NOx sensor output integrated value NOx\_SCN\_T is calculated to be small regardless of whether the deterioration level of the NOx catalyst 18 is extremely high so there is a possibility that the NOx catalyst 18 will be erroneously determined to be normal.

[0111] In contrast, according to this modified example, the amount of reducing agent during rich spike control may be made constant so the amount of ammonia NH3 produced may also be made constant. When the amount of ammonia NH3 is made constant, the amount of ammonia NH3 that flows downstream of the NOx catalyst 18, i.e., the NOx sensor output integrated value NOx\_SCN\_T, may be made to more accurately correlate with the discharged amount of NOx, i.e., with the reducing efficiency. Therefore, according to this modified example, an erroneous determination such as that described above may be more reliably prevented, which makes it possible to more accurately diagnose deterioration of the NOx catalyst 18.

[0112] Also, in the first example embodiment, the “air-fuel ratio controlling means” of the invention may be realized by the ECU 30 executing steps 108 and 114, the “calculating means” of the invention may be realized by the ECU 30 executing steps 104, 106, and 110, and the “diagnosing means” of the invention may be realized by the ECU 30 executing steps 118 and 120, and 122.

[0113] Also, in the modified example of the first example embodiment, the reducing agent amount integrated value RFCNT may be regarded as the “reducing agent amount” of the invention. Also, the “reducing agent amount calculating means” of the invention may be realized by the ECU 30 calculating the reducing agent amount integrated value RFCNT based on Expressions (1) and (2) above. Further, the “air-fuel ratio controlling means” of the invention may be also realized by the ECU 30 ending the rich spike control when the reducing agent amount integrated value RFCNT reaches the predetermined value \( \gamma \).

[0114] Next, a second example embodiment of the invention will be described with reference to FIG. 8. However, the following description will focus on those points that differ
from the first example embodiment described above. Descriptions that are similar to that in the first example embodiment will be simplified or omitted.

[0115] In the first example embodiment described above, deterioration determination of the NOx catalyst 18 is performed by comparing the NOx sensor output integrated value NOxSCNT_R with the reference determining value \( \beta \) (step 118 of the routine in FIG. 4). In contrast, in this second example embodiment, deterioration determination of the NOx catalyst 18 is performed by comparing the quotient NOxSCNT_P/RCNT of the NOx sensor output integrated value NOxSCNT_P divided by the amount of reducing agent that has flowed into the NOx catalyst 18 (i.e., the reducing agent amount integrated value RFCNT), with the reference determining value.

[0116] FIG. 8 is a graph in which experimental data using the same catalyst as in FIG. 6 is plotted on a coordinate system in which the horizontal axis represents the temperature TCAT of the NOx catalyst 18 and the vertical axis represents the quotient of NOxSCNT_P/RCNT. That is, in FIG. 8, the black squares represent experimental data of the normal catalyst (X) while the black diamonds represent experimental data of the deteriorated catalyst (Y). Incidentally, the rich spike control end condition was set such that the output from the O2 sensor 26 downstream of the NOx catalyst 18 be rich output. As can be seen from FIG. 8, in this second example embodiment, the normal catalyst (X) may be reliably differentiated from the deteriorated catalyst (Y) by setting the reference determining value as shown by the sloped straight line in FIG. 8.

[0117] The quotient of NOxSCNT_P/RCNT is a value that represents the percentage of reducing agent that has passed through the NOx catalyst 18 without being consumed to reduce the NOx that has been released from the NOx catalyst 18, with respect to the entire amount of the reducing agent that flowed into the NOx catalyst 18. Therefore, it may be said that the quotient of NOxSCNT_P/RCNT is a value that more accurately represents the reducing efficiency of the NOx catalyst 18. Therefore, according to this second example embodiment, even greater diagnostic accuracy is able to be obtained by diagnosing deterioration of the NOx catalyst 18 by comparing the quotient of NOxSCNT_P/RCNT with the reference determining value.

[0118] Incidentally, in FIG. 8, the reference determining value becomes lower as the temperature TCAT of the NOx catalyst 18 during rich spike control increases. This is thought to be because the temperature TCAT of the NOx catalyst 18 is high when the internal combustion engine 10 is operating at a high load. When the internal combustion engine 10 is operating at a high load, the intake air amount GA is large so even if the amount of ammonia NH3 that passes through the NOx catalyst 18 is the same, the concentration of the ammonia NH3 is lower. As a result, the NOx sensor output NOxS is smaller so the NOx sensor output integrated value NOxSCNT_R is also smaller. Therefore, the reference determining value is thought to become lower as the temperature TCAT of the NOx catalyst 18 increases.

[0119] However, when this kind of tendency is not detected in the experimental results, the reference determining value may be a constant value regardless of the temperature TCAT of the NOx catalyst 18.

[0120] The specific process of the second example embodiment is as follows. The ECU 30 successively calculates the reducing agent amount integrated value RFCNT according to the same method that is used in the modified example of the first example embodiment described above while the rich spike control is being executed. Referring to step 118 of the routine in FIG. 4, the quotient of NOxSCNT_P/RCNT is calculated by dividing the NOx sensor output integrated value NOxSCNT_P by the reducing agent amount integrated value RFCNT at the time that the rich spike control ends. Next, a reference determining value is obtained according to the relationship shown in FIG. 8 based on the temperature TCAT of the NOx catalyst 18. This reference determining value is then compared with the quotient of NOxSCNT_P/RCNT. If the quotient of NOxSCNT_P/RCNT is equal to or greater than the reference determining value, it is determined that the NOx catalyst 18 is deteriorated (step 120). Meanwhile, if the quotient of NOxSCNT_P/RCNT is less than the reference determining value, it is determined that the NOx catalyst 18 is normal (step 122).

[0121] In all other regards, the second example embodiment is similar to the first example embodiment so further description will be omitted. In the second example embodiment, the reducing agent amount integrated value RFCNT may be regarded as the "reducing agent amount" of the invention. Also, the "reducing agent amount calculating means" of the invention may be also realized by the ECU 30 calculating the reducing agent amount integrated value RFCNT, and the "diagnosing means" of the invention may also be realized by the ECU 30 comparing the quotient of NOxSCNT_P/RCNT with the reference determining value and diagnosing deterioration of the NOx catalyst 18.

[0122] Next, a third example embodiment of the invention will be described with reference to FIG. 9. However, the following description will focus on those points that differ from the first example embodiment described above. Descriptions that are similar to that in the first example embodiment will be simplified or omitted.

[0123] In the third example embodiment, deterioration determination of the NOx catalyst 18 is performed by comparing the quotient of NOxSCNT_P/T_R5 with the quotient of NOxSCNT_P/RCNT, which is the quotient of the NOx sensor output integrated value NOxSCNT_P divided by the reducing time T_R5 according to rich spike control, with a reference determining value.

[0124] In this third example embodiment, the reducing time T_R5 is the time for which the rich spike control is continued, as shown in FIG. 5D, but the reducing time T_R5 is not limited to this. For example, the reducing time T_R5 may also be the time for which the output from the A/F sensor 24 upstream of the NOx catalyst 18 is maintained at a rich output.

[0125] FIG. 9 is a graph in which experimental data using the same catalyst as in FIG. 6 is plotted on a coordinate system in which the horizontal axis represents the temperature TCAT of the NOx catalyst 18 and the vertical axis represents the quotient of NOxSCNT_P/T_R5. That is, in FIG. 9 the black squares represent experimental data obtained with the normal catalyst (X) and the black diamonds represent experimental data obtained with the deteriorated catalyst (Y). Incidentally, the rich spike control end condition was set such that the output from the O2 sensor 26 downstream of the NOx catalyst 18 be a rich output. As can be seen from FIG. 9, in this third example embodiment, the normal catalyst (X) may be reliably differentiated from the deteriorated catalyst (Y) by setting the reference determining value as shown by the sloped straight line in FIG. 9.

[0126] Typically, it may be said that the amount of reducing agent that flows into the NOx catalyst 18 (i.e., the reducing
agent amount integrated value RFCNT) increases as the reducing time \( T_{KS} \) increases. Accordingly, the quotient of \( NO_x SCNT, \) \( \frac{FC}{T_{KS}} \), may be used as the similar indicator to the quotient of \( NO_x SCNT, \frac{RFCNT}{RFCNT} \) in the second example embodiment. Therefore, greater diagnostic accuracy may be also obtained according to the third example embodiment, just as in the second example embodiment.

[0127] The specific process of the third example embodiment is as follows. The ECU 30 measures the reducing time \( T_{KS} \) while the rich spike control is being executed. Referring to step 118 of the routine in FIG. 4, the quotient of \( NO_x SCNT, \frac{T_{KS}}{RFCNT} \), is calculated by dividing the \( NO_x \) sensor output integrated value \( NO_x SCNT, \) by the reducing time \( T_{KS} \). Next, a reference determining value is obtained according to the relationship shown in FIG. 9 based on the temperature \( TCAT \) of the \( NO_x \) catalyst 18. This reference determining value is then compared with the quotient of \( NO_x SCNT, \frac{T_{KS}}{RFCNT} \), as indicated in FIG. 4. If the quotient of \( NO_x SCNT, \frac{T_{KS}}{RFCNT} \) is equal to or greater than the reference determining value, it is determined that the \( NO_x \) catalyst 18 is normal (step 122).

[0128] In all other regards, the third example embodiment is similar to the first example embodiment so further description will be omitted. In the third example embodiment, the “reducing time measuring means” of the invention may be realized by the ECU 30 measuring the reducing time \( T_{KS} \). Also, the “determining means” of the invention may be also realized by the ECU comparing the quotient of \( NO_x SCNT, \frac{T_{KS}}{RFCNT} \) with the reference determining value and diagnosing deterioration of the \( NO_x \) catalyst 18.

[0129] In each of the foregoing example embodiments, a system is described in which the \( A/F \) sensor 24 is arranged upstream of the \( NO_x \) catalyst 18 and the \( O_2 \) sensor 26 is arranged downstream of the \( NO_x \) catalyst 18. However, the system configuration of the invention is not limited to this. For example, it may also be modified as described below.

[0130] FIG. 10 is a schematic view of a system configuration according to a modified example of the first example embodiment of the invention. In the system shown in FIG. 10, an \( O_2 \) sensor 27 that produces an output signal which suddenly changes when the air-fuel ratio of the exhaust gas becomes richer or leaner than the stoichiometric air-fuel ratio, is arranged upstream of the \( NO_x \) catalyst 18 instead of the \( A/F \) sensor 24. In all other regards, the system shown in FIG. 10 is similar to the system shown in FIG. 1. Hereinafter, for the sake of simplifying the description, the \( O_2 \) sensor 27 arranged upstream of the \( NO_x \) catalyst 18 will be referred to as the “upstream \( O_2 \) sensor 27” and the \( O_2 \) sensor 26 arranged downstream of the \( NO_x \) catalyst 18 will be referred to as the “downstream \( O_2 \) sensor 26”.

[0131] FIG. 11 is a timing chart illustrating a method for obtaining the reducing agent amount integrated value RFCNT and the reducing time \( T_{KS} \) in this modified example. More specifically, the upper drawing in FIG. 11 shows the output from the downstream \( O_2 \) sensor 26, the intermediate drawing in FIG. 11 shows the output from the upstream \( O_2 \) sensor 27, and the lower drawing in FIG. 11 shows an output which is either the output from one of the \( A/F \) sensors 20 or 22 arranged upstream of the start catalysts 14 and 16, or the output which is the average of both outputs from the \( A/F \) sensors 20 and 22 (hereinafter referred to as “\( A/F \) sensor output”).

[0132] As shown in FIG. 11, when the rich spike control is started, and exhaust gas of a rich air-fuel ratio starts to be discharged from the internal combustion engine 10, the \( A/F \) sensor output is switched from lean to rich (time 1). Then, when all of the oxygen that has been stored in the start catalysts 14 and 16 is used up by the reducing agent that flows into the start catalysts 14 and 16, exhaust gas of a rich air-fuel ratio starts to pass through to the downstream side of the start catalysts 14 and 16. As a result, the output of the upstream \( O_2 \) sensor 27 changes from lean to rich (time 2).

[0133] From time 2, the reducing agent starts to flow into the \( NO_x \) catalyst 18. Then when all of the oxygen and \( NO_x \) that have been stored in the \( NO_x \) catalyst 18 are used up by the reducing agent, exhaust gas of a rich air-fuel ratio starts to pass through to the downstream side of the \( NO_x \) catalyst 18. As a result, the output of the downstream \( O_2 \) sensor 26 changes from lean to rich (time 3).

[0134] In this modified example, the amount of reducing agent that has flowed into the \( NO_x \) catalyst 18 (i.e., the reducing agent amount integrated value RFCNT) may be calculated based on the \( A/F \) sensor output from time 2 to time 3 (the portion with hatching in FIG. 11). Also, the reducing time \( T_{KS} \) may be obtained by measuring the time from time 2 to time 3.

[0135] As another modified example of the first example embodiment in the invention, the amount of oxygen and \( NO_x \) stored in the \( NO_x \) catalyst 18 may be calculated from the reducing agent amount integrated value RFCNT. In the invention, deterioration determination may also be performed with extremely high accuracy by combining the deterioration determination results of the \( NO_x \) catalyst 18, which was obtained based on the amount of oxygen and \( NO_x \) stored in the \( NO_x \) catalyst 18, with deterioration determination results which was obtained using the \( NO_x \) sensor 25 described above.

[0136] 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 described 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 example embodiments are shown in various 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.

1. (canceled)
2. The catalyst monitoring system according to claim 16, wherein the \( NO_x \) sensor is capable of detecting a concentration of \( NH_3 \) as well as the concentration of \( NO_x \)
3. The catalyst monitoring system according to claim 16, wherein the \( NO_x \) sensor is a limiting current \( NO_x \) sensor.
4. The catalyst monitoring system according to claim 16, wherein the period near the end of the air-fuel ratio control is a period during which the output from the \( NO_x \) sensor temporarily increases abruptly.
5. The catalyst monitoring system according to claim 16, further comprising reducing agent amount calculating portion that calculates an amount of reducing agent that has flowed into the \( NO_x \) catalyst during the air-fuel ratio control,
wherein the air-fuel ratio controlling means ends the air-fuel ratio control when the reducing agent amount reaches a predetermined amount.

6. The catalyst monitoring system according to claim 16, further comprising
reducing agent amount calculating portion that calculates an amount of reducing agent that has flowed into the NOX catalyst during the air-fuel ratio control, wherein the diagnosing portion diagnoses deterioration of the NOX catalyst based on the output integrated value of the NOX sensor and the reducing agent amount.

7. The catalyst monitoring system according to claim 16, further comprising
reducing time measuring portion that measures a reducing time of NOX according to the air-fuel ratio control, wherein the diagnosing portion diagnoses deterioration of the NOX catalyst based on the output integrated value of the NOX sensor and the reducing time.

8. The catalyst monitoring system according to claim 16, wherein
the air-fuel ratio controlling portion starts the air-fuel ratio control when the amount of NOX that has flowed into the NOX catalyst reaches a predetermined value.

9. The catalyst monitoring system according to claim 16, further comprising
an O2 sensor which is arranged downstream of the NOX catalyst and detects a concentration of O2, wherein the air-fuel ratio controlling portion ends the air-fuel ratio control when an output from the O2 sensor while the air-fuel ratio control is being executed becomes the rich air-fuel ratio.

10. The catalyst monitoring system according to claim 16, wherein
the diagnosing means starts to diagnose deterioration of the NOX catalyst when a predetermined executing condition for determining deterioration is satisfied, and the predetermined executing condition for determining deterioration includes: i) a condition that the internal combustion engine operate at a predetermined operating condition while the air-fuel ratio control is executed; and ii) a condition that a temperature of the NOX catalyst be within a predetermined temperature range while the air-fuel ratio control is executed.

11. The catalyst monitoring system according to claim 10, wherein
the predetermined operating condition includes a condition that at least one from among a speed of the internal combustion engine, a throttle opening amount of the internal combustion engine, and an intake air amount of the internal combustion engine be within a predetermined range.

12. The catalyst monitoring system according to claim 4, wherein the period near the end of the air-fuel ratio control includes a period during which the output from the NOX sensor temporarily increases abruptly due to NH3 that is discharged from the NOX catalyst.

13. The catalyst monitoring system according to claim 16, wherein
the calculating portion calculates the output integrated value of the NOx sensor by integrating the product of a physical quantity corresponding to an amount of intake air flowing into the NOX catalyst multiplied by the output from the NOX sensor.

14. The catalyst monitoring system according to claim 16, wherein
the air-fuel ratio controlling portion ends the air-fuel ratio control when the output current from the NOX sensor while the air-fuel ratio control is being executed corresponds to the rich air-fuel ratio.

15. A catalyst monitoring method comprising:
performing air-fuel ratio control that temporarily switches an air-fuel ratio of exhaust gas during operation of the internal combustion engine at a lean air-fuel ratio to a rich or a stoichiometric air-fuel ratio;
calculating an output integrated value of an NOX sensor which is arranged downstream of an NOX catalyst in an exhaust passage of the internal combustion engine by integrating an output from the NOX sensor at least during a period near the end of the air-fuel ratio control; and
diagnosing deterioration of the NOX catalyst based on the output integrated value of the NOX sensor.

16. A catalyst monitoring system comprising:
an NOX catalyst which is arranged in an exhaust passage of an internal combustion engine;
an NOX sensor which is arranged downstream of the NOX catalyst and detects a concentration of NOx;
an air-fuel ratio controlling portion that temporarily switches an air-fuel ratio of exhaust gas during operation of the internal combustion engine from a lean air-fuel ratio to a rich or a stoichiometric air-fuel ratio;
a calculating portion that calculates an output integrated value of the NOX sensor by integrating an output from the NOX sensor at least during a period near the end of the air-fuel ratio control; and
diagnosing deterioration of the NOX catalyst based on the output integrated value of the NOX sensor.

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