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(54) HYDROGEN-CONTAINING GAS PRODUCING SYSTEM AND EXHAUST GAS PURIFYING SYSTEM USING SAME

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(57) **ABSTRACT**

A hydrogen-containing gas producing system of an onboard type, for producing hydrogen-containing gas to be used for purification of exhaust gas of an internal combustion engine. The hydrogen-containing system comprises a fuel supply source for supplying fuel as a raw material of the hydrogen-containing gas. A carrier gas supply source is provided for supplying a carrier gas for carrying the fuel. A device is provided for vaporizing the fuel so as to form a vaporized fuel serving as a reaction gas. The fuel vaporizing device is connected to the fuel supply source and the carrier gas supply source. Additionally, a reforming section is connected to the fuel vaporizing device, for reforming the reaction gas so as to produce the hydrogen-containing gas.

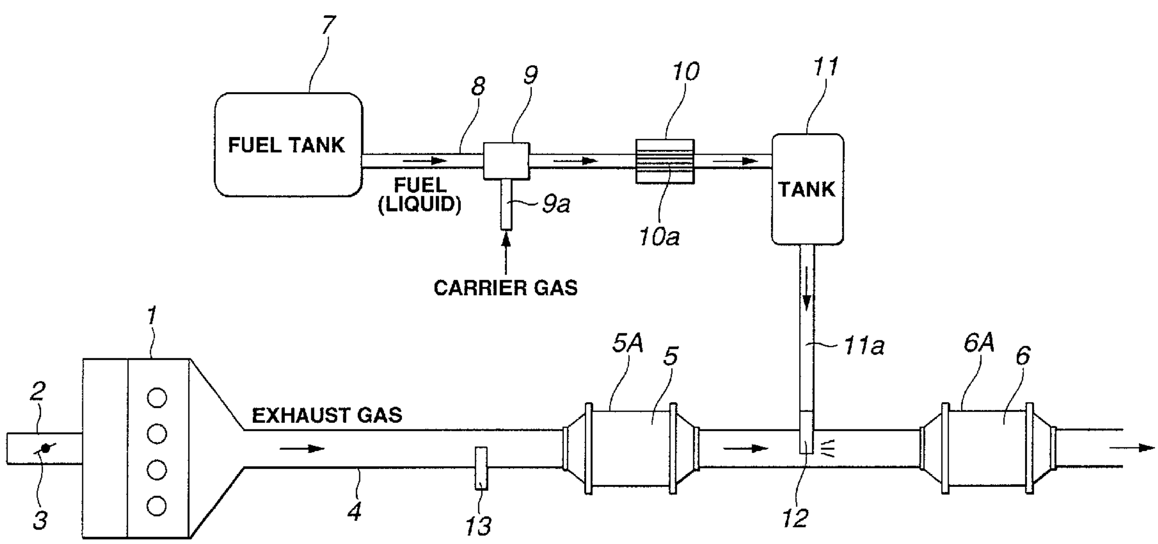
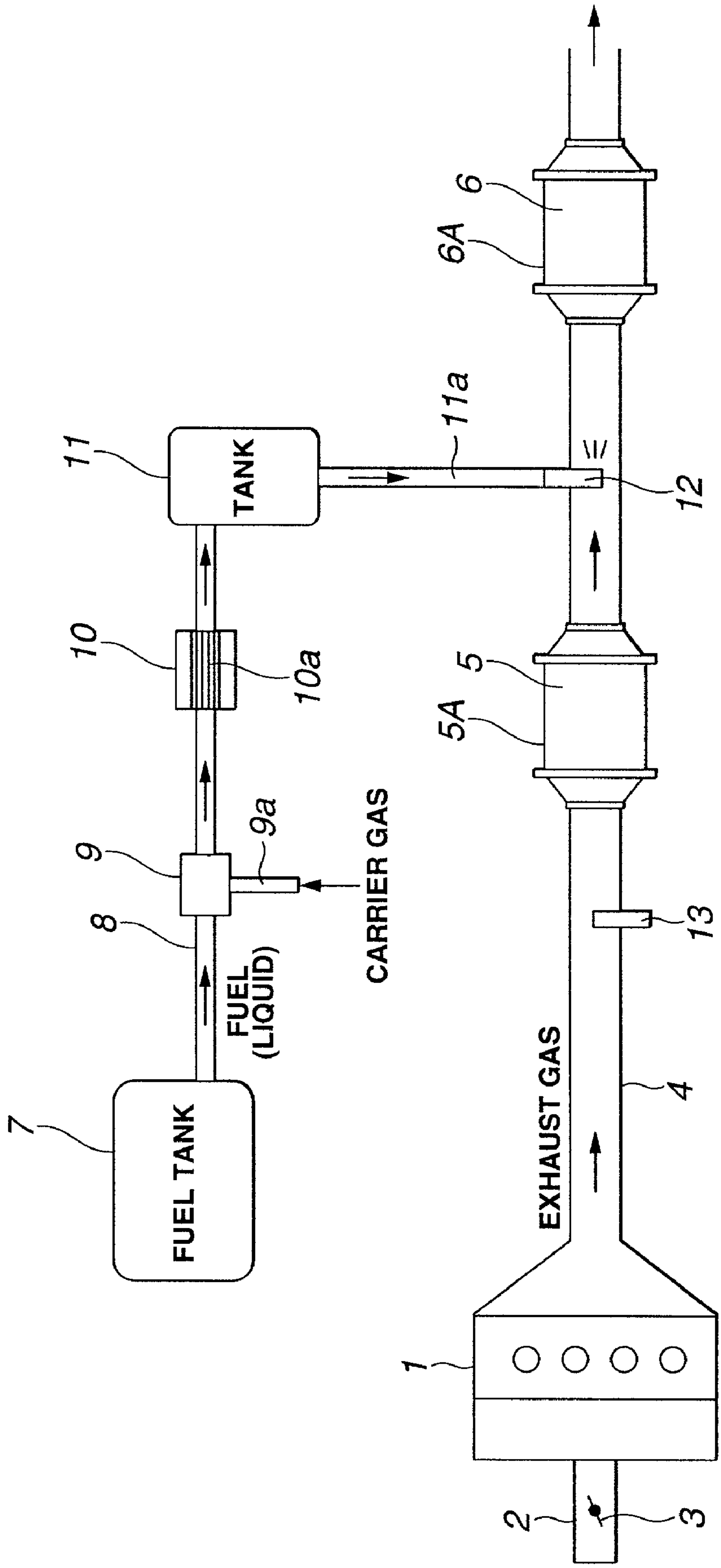


FIG.1



FUEL TANK
7
FUEL
(LIQUID)
8
9
9a
CARRIER GAS
10
10a
11
TANK
11a
12
EXHAUST GAS
4
13
5
5A
6
6A
1
2
3

FIG.2A

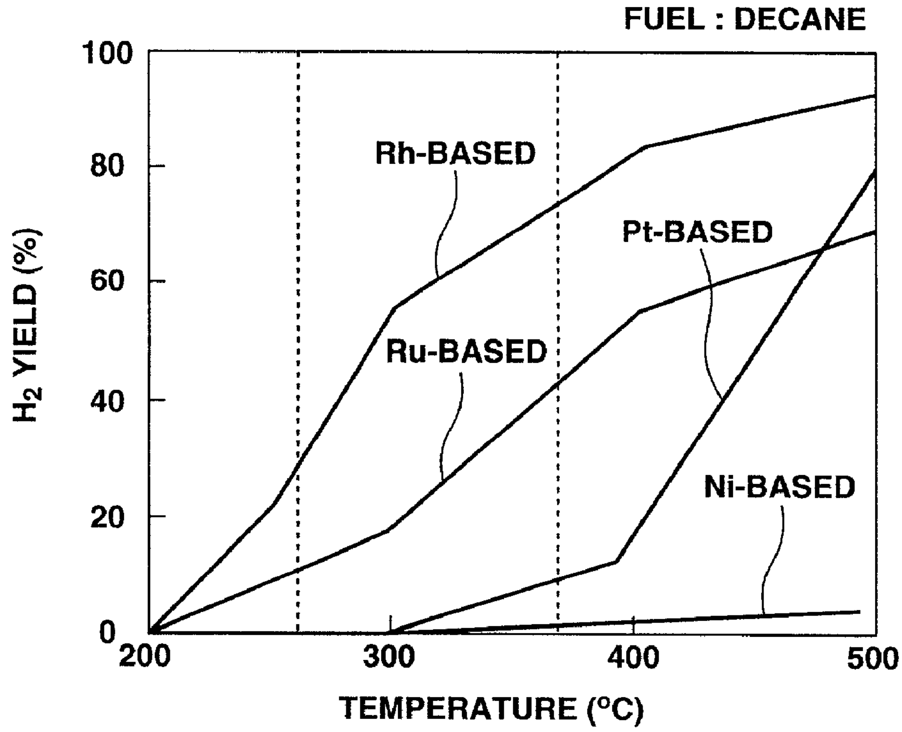

FUEL : DECANE
100
80
60
40
20
0
H2 YIELD (%)
Rh-BASED
Pt-BASED
Ru-BASED
Ni-BASED
200
300
400
500
TEMPERATURE (°C)

FIG.2B

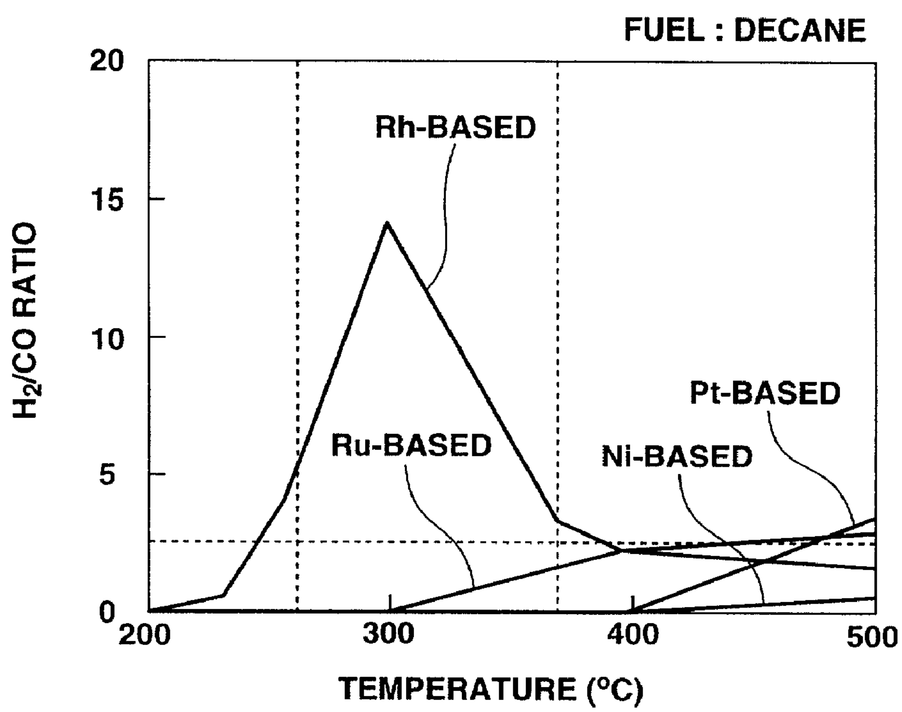

FUEL : DECANE
20
15
10
5
0
H2/CO RATIO
Rh-BASED
Pt-BASED
Ru-BASED
Ni-BASED
200
300
400
500
TEMPERATURE (°C)

FIG.3A

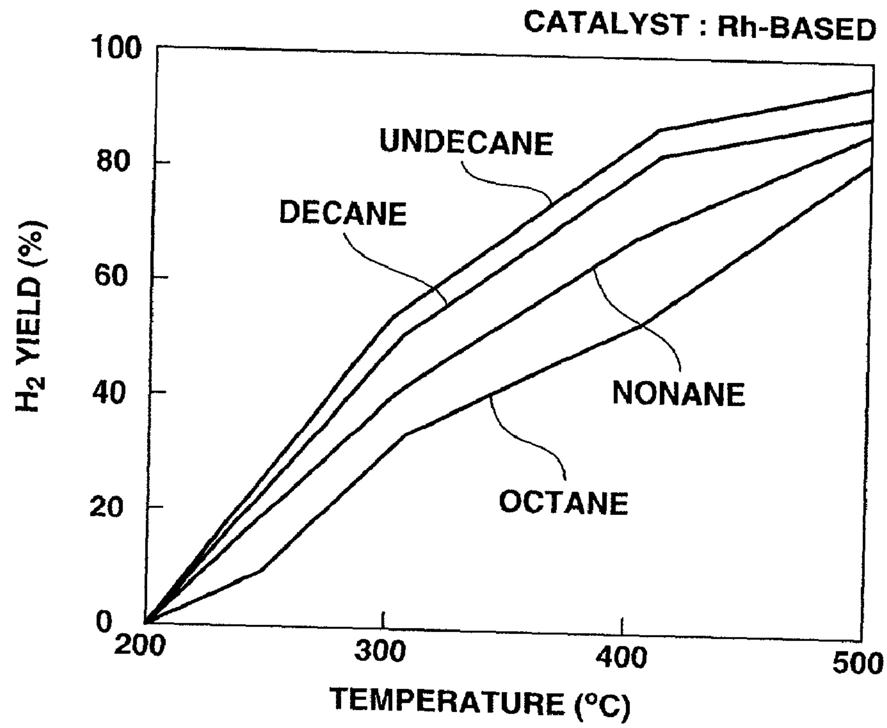

CATALYST : Rh-BASED
100
80
60
40
20
0
H_2 YIELD (%)
UNDECANE
DECANE
NONANE
OCTANE
200
300
400
500
TEMPERATURE (°C)

FIG.3B

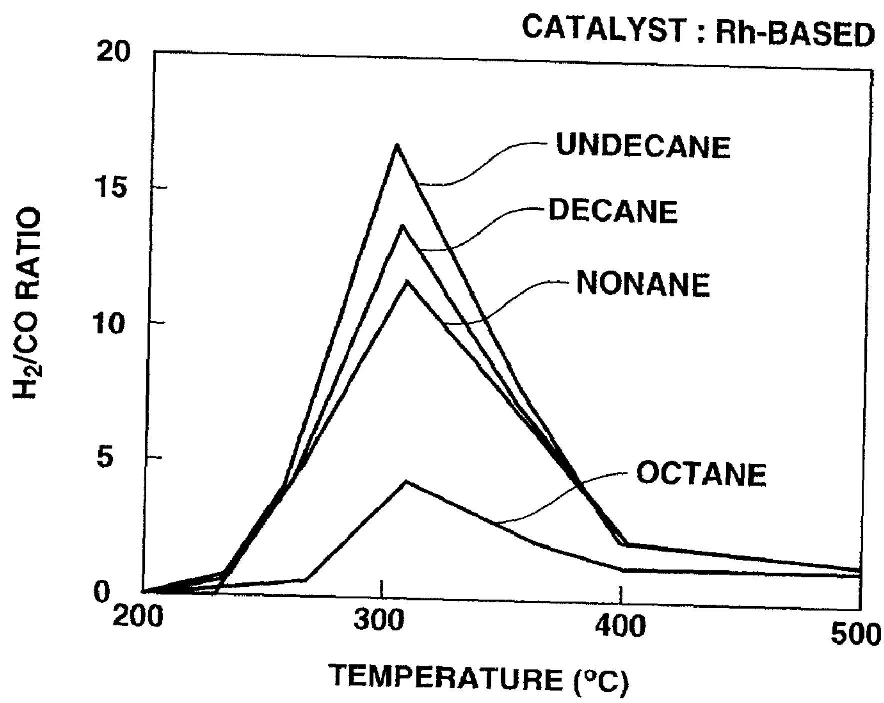
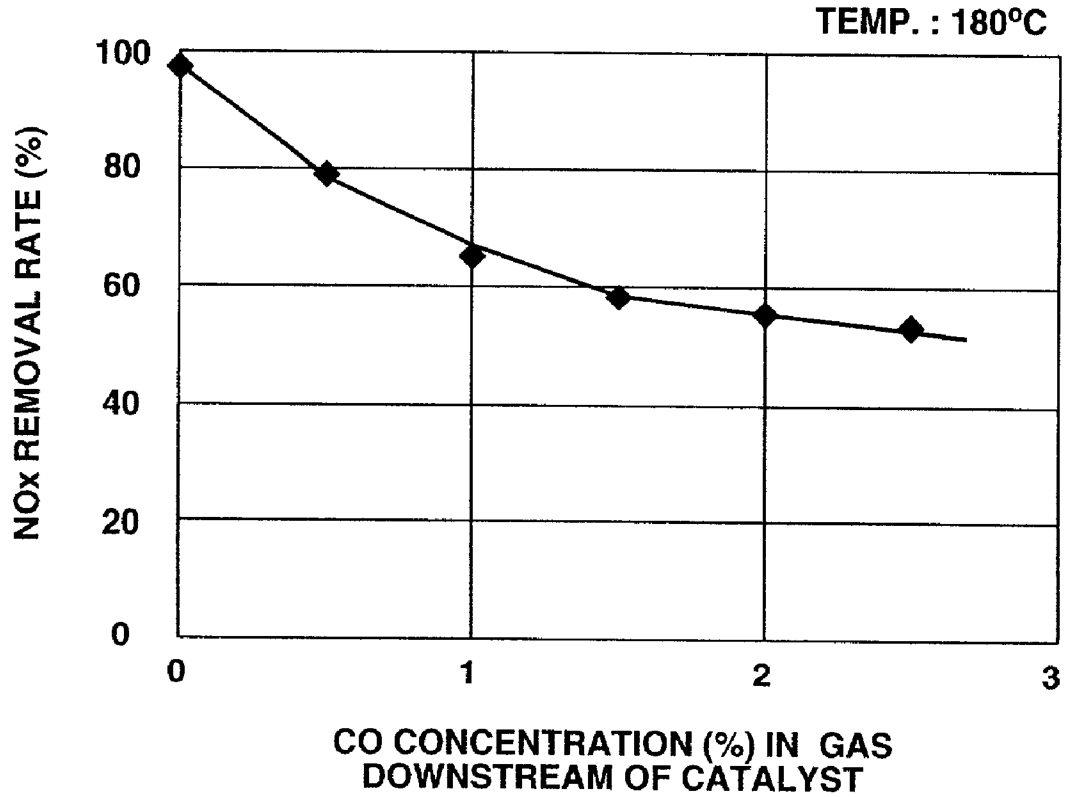

CATALYST : Rh-BASED
20
15
10
5
0
H_2/CO RATIO
UNDECANE
DECANE
NONANE
OCTANE
200
300
400
500
TEMPERATURE (°C)

FIG.4


TEMP. : 180°C
100
80
60
40
20
0
NOx REMOVAL RATE (%)
0
1
2
3
CO CONCENTRATION (%) IN GAS
DOWNSTREAM OF CATALYST

HYDROGEN-CONTAINING GAS PRODUCING SYSTEM AND EXHAUST GAS PURIFYING SYSTEM USING SAME

BACKGROUND OF THE INVENTION

[0001] This invention relates to improvements in a hydrogen-containing gas producing system and an exhaust gas purifying system using the hydrogen-containing gas producing system, and more particularly to the exhaust gas purifying system for reducing or removing nitrogen oxides (NOx) in exhaust gas having its lean condition by using a catalyst.

[0002] Hitherto, so-called lean-burn engines operated at an air/fuel ratio higher or leaner than a stoichiometric level have been come into wide use from the view points of improving fuel economy (fuel consumption) and reducing emission of carbon dioxide. Attention has been particularly paid on diesel engines as the lean-burn engines in view of the fact that the diesel engines are high in combustion efficiency and good in fuel economy.

[0003] However, the lean-burn engines discharge so-called lean exhaust gas high in oxygen content as compared with that of exhaust gas discharged from an engine which is operated around a stoichiometric air-fuel ratio. Therefore, drawbacks have been encountered in the lean-burn engines, in which reduction or removal of NOx is difficult in case of using a conventional three-way catalyst. Additionally, the lean-burns are low in combustion efficiency and therefore is low in exhaust gas temperature as compared with conventional engines. There is a tendency that exhaust gas temperature further lowers upon further improvements in combustion of the engines. As a result, the frequency at which the temperature of exhaust gas is 200° C. or lower becomes high. In this regard, it has been desired to effectively purify exhaust gas in such a low exhaust gas temperature condition.

[0004] In order to solve the above problems, a variety of countermeasures have been studied. For example, it has been proposed to secondarily supply hydrocarbons, alcohols and the like serving as a reducing agent to a gas inlet section of a catalyst layer. In connection with this, for example, a method of mounting onboard a tank for storing the reducing agent and a method of directly using fuel for a vehicle as the reducing agent have been proposed. However, the former method has the problems of obtaining a place for the tank, increasing the weight of the vehicle and supplying the reducing agent. The latter method has the problems of unavoidably sacrificing the fuel economy or fuel consumption for an engine, of low in NOx reducing efficiency in a low exhaust gas temperature condition, and the like.

[0005] Additionally, a system for reducing NOx in a lean exhaust gas at a high efficiency is disclosed in Japanese Patent No. 2600492. The system includes a NOx adsorbing or trapping agent which functions to adsorb or trap NOx when the air/fuel ratio of exhaust gas flowing thereinto is lean or large (as compared with a stoichiometric value) and to release NOx by lowering an oxygen concentration in exhaust gas flowing thereinto. In this system, a three-way catalyst is used to release and reduce the adsorbed NOx, so that it is required to put the air/fuel ratio of exhaust gas of the engine around the stoichiometric value or rich (small) as compared with the stoichiometric value, or to supply hydrocarbons as the reducing agent to an exhaust gas passageway. This raises the problem of sacrificing the fuel economy or fuel consumption of the vehicle. Further, this raises the problems of mounting a tank for storing the reducing agent and of increasing the weight of the vehicle thereby sacrificing the fuel economy of the engine. Furthermore, even this system has been desired to be improved in NOx adsorption or trap performance of the NOx adsorbing agent and in NOx reducing performance of the three-way catalyst in a low exhaust gas temperature condition of 200° C. or lower.

SUMMARY OF THE INVENTION

[0006] It is, therefore, an object of the present invention to provide an improved hydrogen-containing gas producing system and an improved exhaust gas purifying system using the hydrogen-containing gas producing system, which can overcome drawbacks encountered in conventional exhaust gas purifying systems.

[0007] Another object of the present invention is to provide improved hydrogen-containing gas producing system and exhaust gas purifying system using the hydrogen-containing gas producing system, which can remove or reduce NOx at a high efficiency in a low exhaust gas temperature-condition of 200° C. or lower, preventing the fuel economy or fuel consumption of a vehicle from degrading owing to mounting a tank for storing a NOx reducing agent and the like on a vehicle.

[0008] An aspect of the present invention resides in a hydrogen-containing gas producing system of an onboard type, for producing hydrogen-containing gas to be used for purification of exhaust gas of an internal combustion engine. The hydrogen-containing system comprises a fuel supply source for supplying fuel as a raw material of the hydrogen-containing gas. A carrier gas supply source is provided for supplying a carrier gas for carrying the fuel. A device is provided for vaporizing the fuel so as to form a vaporized fuel serving as a reaction gas. The fuel vaporizing device is connected to the fuel supply source and the carrier gas supply source. Additionally, a reforming section is connected to the fuel vaporizing device, for reforming the reaction gas so as to produce the hydrogen-containing gas.

[0009] Another aspect of the present invention resides in an exhaust gas purifying system for an internal combustion engine. The exhaust gas purifying system comprises a hydrogen-containing gas producing system of an onboard type, for producing hydrogen-containing gas to be used for purification of exhaust gas of an internal combustion engine, the hydrogen-containing system including a fuel supply source for supplying fuel as a raw material of the hydrogen-containing gas, a carrier gas supply source for supplying a carrier gas for carrying the fuel, a device for vaporizing the fuel so as to form a vaporized fuel as a reaction gas, the fuel vaporizing device being connected to the fuel supply source and the carrier gas supply source, and a reforming section connected to the fuel vaporizing device, for reforming the reaction gas so as to produce the hydrogen-containing gas. The reforming section is connected to a part of an exhaust gas passageway of the internal combustion engine so as to introduce the hydrogen-containing gas into exhaust gas. Additionally, a NOx adsorbing and reducing catalyst is disposed in the exhaust gas passageway downstream of the part. The NOx adsorbing and reducing catalyst is adapted to adsorb nitrogen oxides in exhaust gas in a condition that exhaust gas is in a lean region, and to reduce nitrogen oxides in exhaust gas in a condition that exhaust gas is within a range including a stochiometric region and a rich region. In the above exhaust gas purifying system, the hydrogen-containing gas from the reforming section of the hydrogen-containing gas is supplied into the exhaust gas passageway at the part which is upstream of the NOx adsorbing and reducing catalyst, at a low temperature range in which a temperature of exhaust gas at a position immediately upstream of the NOx adsorbing and reducing catalyst is not higher than 250° C., and in the condition that exhaust gas is within the range including the stoichiometric region and the rich region.

[**0010**] A further aspect of the present invention resides in a hydrogen-containing gas producing system of an onboard type, for producing hydrogen-containing gas to be used for purification of exhaust gas of an internal combustion engine. The hydrogen-containing system comprises a fuel supply source for supplying fuel as a raw material of the hydrogen-containing gas. A carrier gas supply source is provided for supplying a carrier gas for carrying the fuel. A fuel vaporizing means is provided for vaporizing the fuel so as to form a vaporized fuel serving as a reaction gas, the fuel vaporizing means receiving the fuel from the fuel supply source and the carrier gas from the carrier gas supply source. Additionally, a reforming section is connected to the fuel vaporizing device, for reforming the reaction gas so as to produce the hydrogen-containing gas.

[**0011**] A still further aspect of the present invention resides in an exhaust gas purifying system for an internal combustion engine mounted on an automotive vehicle. The exhaust gas purifying system comprises a catalyst for reducing nitrogen oxides in exhaust gas of the engine, disposed in an exhaust gas passageway of the engine and mounted on the vehicle, the catalyst containing at least one of platinum and palladium. Additionally, a hydrogen-containing gas producing system is provided for producing hydrogen-containing gas, mounted on the vehicle. The hydrogen-containing system includes a fuel supply source for supplying fuel as a raw material of the hydrogen-containing gas, a carrier gas supply source for supplying a carrier gas for carrying the fuel, a device for vaporizing the fuel so as to form a vaporized fuel as a reaction gas, the fuel vaporizing device being connected to the fuel supply source and the carrier gas supply source, and a reforming section connected to the fuel vaporizing device, for reforming the reaction gas so as to produce the hydrogen-containing gas. The reforming section is connected to a part of the exhaust gas passageway upstream of the catalyst so that the hydrogen-containing gas is supplied to the catalyst.

BRIEF DESCRIPTION OF THE DRAWINGS

[**0012**] **FIG. 1** is a schematic illustration of an embodiment of an exhaust gas purifying system including a hydrogen-containing gas producing system, according to the present invention, incorporated in an exhaust system of an automotive internal combustion engine;

[**0013**] **FIG. 2A** is a graph showing difference in hydrogen yield in tests for producing a hydrogen-containing gas, depending on the kinds of catalysts used in the hydrogen-containing gas producing system of **FIG. 1**;

[**0014**] **FIG. 2B** is a graph showing difference in H_2/CO ratio in the hydrogen-containing gas in the tests for producing the hydrogen-containing gas, depending on the kinds of the catalysts used in the hydrogen-containing gas producing system of **FIG. 1**;

[**0015**] **FIG. 3A** is a graph showing difference in hydrogen yield in the tests for producing a hydrogen-containing gas, depending on the kinds of fuels or raw materials (different in the number of carbon atoms) used in the hydrogen-containing gas producing system of **FIG. 1**;

[**0016**] **FIG. 3B** is a graph showing difference in H_2/CO ratio in the hydrogen-containing gas in the tests for producing the hydrogen-containing gas, depending on the kinds of the fuels or raw materials (different in the number of carbon atoms) used in the hydrogen-containing gas producing system of **FIG. 1**; and

[**0017**] **FIG. 4** is a graph showing the NOx removal rate of a NOx adsorbing and reducing catalyst upon supply of the hydrogen-containing gas from the hydrogen-containing gas producing system of **FIG. 1** in terms of the CO concentration in a laboratory model gas flowing through the catalyst, in tests for evaluation of the hydrogen-containing gas on NOx reduction characteristics for the catalyst.

DETAILED DESCRIPTION OF THE INVENTION

[**0018**] According to the present invention, a hydrogen-containing gas producing system of an onboard type is for producing hydrogen-containing gas to be used for purification of exhaust gas of an internal combustion engine. The hydrogen-containing system comprises a fuel supply source for supplying fuel as a raw material of the hydrogen-containing gas. A carrier gas supply source is provided for supplying a carrier gas for carrying the fuel. A device is provided for vaporizing the fuel so as to form a vaporized fuel serving as a reaction gas. The fuel vaporizing device is connected to the fuel supply source and the carrier gas supply source. Additionally, a reforming section is connected to the fuel vaporizing device, for reforming the reaction gas so as to produce the hydrogen-containing gas. The hydrogen-containing gas producing system is mounted on a vehicle such as an automotive vehicle.

[**0019**] The hydrogen-containing gas producing system is used as a part of an exhaust gas purifying system for an internal combustion engine. The exhaust gas purifying comprises a NOx adsorbing and reducing catalyst is disposed in the exhaust gas passageway downstream of the part. The NOx adsorbing and reducing catalyst is adapted to adsorb nitrogen oxides in exhaust gas in a condition that exhaust gas is in a lean region, and to reduce nitrogen oxides in exhaust gas in a condition that exhaust gas is within a range including a stochiometric region and a rich region. The reforming section of the hydrogen-containing gas producing system is connected to the exhaust gas passageway upstream of said NOx adsorbing and reducing catalyst. In the above exhaust gas purifying system, the hydrogen-containing gas from the reforming section of the hydrogen-containing gas is supplied into the exhaust gas passageway at the part which is upstream of the NOx adsorbing and reducing catalyst, at a low temperature range in which a temperature of exhaust gas at a position immediately upstream of the NOx adsorbing and reducing catalyst is not higher than 250° C., and in the condition that exhaust gas is within the range including the stoichiometric region and the rich region.

[0020] The principle of the present invention is founded on the present inventors' findings that NOx in exhaust gas can be very effectively reduced when a noble metal-based catalyst containing Pt and/or Pd (palladium) is used as an exhaust gas purifying catalyst, and hydrogen (H_2) is supplied as a NOx reducing agent to the noble metal-based catalyst, even under a low exhaust temperature condition in which the temperature of exhaust gas immediately upstream of the noble metal-based catalyst is around 250° C. This is assumed to be based on the fact that the reactivity of H_2 with NOx is considerably high.

[0021] In this connection, there are phenomena that CO impedes the reduction reaction of NOx in a relatively low temperature condition of not higher than 250° C. Additionally, when an air/fuel (A/F) ratio is made small or rich (in fuel) to, for example, about 11, a CO concentration in exhaust gas is remarkably increased to several % (by volume). Under a circumstance having such a high CO concentration and a low exhaust gas temperature condition of not higher than 250° C., a sufficient reducing ability for NOx cannot be obtained even if H_2 high in reactivity with NOx is used as the reducing agent.

[0022] In the exhaust gas purifying system using the hydrogen-containing gas, according to the present invention, the NOx reduction impeding phenomena of CO can be avoided while H_2 having the high NOx reducing ability even in the low exhaust gas temperature condition can be used without raising the CO concentration by positively making the air/fuel ratio small. This synergistic effect depends on the present inventors' knowledge can realize a high NOx reducing characteristics suppressing degradation of fuel consumption (or fuel economy). In other words, according to the present invention, NOx can be reduced or removed at -a high efficiency even under a low exhaust gas temperature condition while making it unnecessary to conduct a control for positively making the air/fuel ratio small so that a sufficient NOx reduction effect can be obtained even at the air/fuel ratio of about 13. Additionally, it is very important that the hydrogen-containing gas which is low in CO content or concentration (% by volume or ppm) can be produced in an onboard manner, i.e., in a hydrogen-containing gas producing system mounted on the vehicle (automotive vehicle).

[0023] The hydrogen-containing gas producing system according to the present invention depends also on the following inventors' findings: The hydrogen-containing gas can be produced suitably in the onboard manner upon the fact that the hydrogen-containing gas producing system includes a reforming section using a Rh-based fuel reforming catalyst, a reaction temperature and an oxygen concentration in a reaction gas to be supplied to the reforming catalyst are regulated respectively within certain ranges. Additionally, the hydrogen-containing gas which hardly contains CO can be obtained by using as the fuel (hydrocarbons) or raw material whose carbon number (the number of carbon atoms in a hydrocarbon) is not smaller than 9 (C_9).

[0024] Thus, the present invention is basically different from conventional techniques in a point of realizing production and supply of the hydrogen-containing gas which takes account of impeding a NOx reduction reaction by CO. Additionally, the hydrogen-containing gas having a relatively low CO concentration can be obtained at a low temperature without inviting a weight-increase of the vehicle and a degradation of fuel economy, or the like problem encountered in the conventional techniques in which a tank for storing hydrocarbons and alcohols as a NOx reducing agent is mounted on the vehicle or fuel (for engine) is used as the reducing agent. Hence, the present invention can provide less disadvantages against cost and fuel economy of the vehicle.

[0025] Hereinafter, the hydrogen-containing gas producing system will be discussed.

[0026] The hydrogen-containing gas producing system produces hydrogen-containing gas having a gas composition suitable for purification of exhaust gas of the engine in the onboard manner or on the vehicle. The hydrogen-containing gas is supplied to an exhaust gas purifying catalyst thereby reducing or removing NOx in exhaust gas at a high efficiency even in a low exhaust gas temperature condition in which the temperature of exhaust gas at a position immediately upstream of the exhaust gas purifying catalyst is not higher than 250° C.

[0027] The hydrogen-containing gas producing system includes a fuel supply source for supplying fuel as a raw material of the hydrogen-containing gas; a carrier gas supply source for supplying a carrier gas for carrying the fuel; a fuel vaporizing means or device for vaporizing the fuel so as to form a vaporized fuel as a reaction gas, the fuel vaporizing device being connected to the fuel supply source and the carrier gas supply source; and a reforming section connected to the fuel vaporizing device, for reforming the reaction gas so as to produce the hydrogen-containing gas.

[0028] An example of the fuel vaporizing means is a device or process in which the carrier gas from the carrier gas supply source is blown to a liquid fuel from the fuel supply source in a gas mixer so as to atomize the liquid fuel thereby obtaining vaporized fuel. However, the fuel vaporizing means is not limited particularly to this example. A gas discharged from the gas mixer contains the vaporized fuel and the carrier gas which are in a mixed state, and is sent as a reaction gas to the reforming section. When the gas from the gas mixture is passed through the reforming section, a reforming reaction occurs to produce the hydrogen-containing gas.

[0029] The carrier gas is not limited to a particular gas as far as it is suitable for producing the hydrogen-containing gas, so that the carrier gas may be air. It is practical that the carrier gas is a part of exhaust gas discharged from the internal combustion engine mounted on the vehicle, the part of the exhaust gas being introduced into the gas mixer so as to be used as the carrier gas. The carrier gas functions not only to atomize the liquid fuel but also to carry the vaporized fuel to the reforming section.

[0030] The fuel supply source may be a fuel tank containing fuel used to producing the hydrogen-containing gas; however, it is preferable in the present invention that a fuel tank for fuel to be supplied to the internal combustion engine is commonly used also as the fuel tank for the fuel to be used for production of the hydrogen-containing gas, from the viewpoint of suppressing fuel consumption and the like of the engine under size-reduction and weight-lightening of the hydrogen-containing gas producing system.

[0031] The reforming section for reforming the above-mentioned reaction gas from the gas mixer includes the fuel reforming catalyst containing rhodium (Rh). Preferably, the fuel reforming catalyst contains Rh carried on alumina. By using this fuel reforming catalyst containing Rh carried on alumina, the hydrogen-containing gas containing a low CO concentration can be produced in the onboard manner by controlling a reaction temperature (at which the reforming reaction occurs) of the reaction gas at 260 to 340° C. and by controlling an oxygen concentration (% by volume or ppm) in the reaction gas, at a value represented by the following formula (1):

An oxygen concentration in the reaction gas≦an average carbon number of hydrocarbons in the liquid fuel×a concentration (% by volume or ppm) of the liquid fuel in the reaction gas×½ (1)

[0032] The above formula (1) may be converted as follows, in case that the concentration of the liquid fuel is calculated as that of a hydrocarbon having one carbon atom: An oxygen concentration in the reaction gas<a concentration of the liquid fuel (calculated as a hydrocarbon having one carbon atom) in the reaction gas×½. In this connection, for example, in case that the concentration of C_8H_{18} is 100 ppm, the concentration calculated as a hydrocarbon having one carbon atom is 800 ppm.

[0033] Although controlling the reaction temperature may be made under heating by a heater, it is practical to controlling the reaction temperature under heating by using heat of exhaust gas discharged from the internal combustion engine.

[0034] The hydrogen-containing gas producing system may be provided with a hydrogen-containing gas storing means or device for storing the hydrogen-containing gas produced by the hydrogen-containing gas producing system. It will be understood that the hydrogen-containing gas stored in the hydrogen-containing gas storing means can be supplied to the exhaust gas purifying catalyst at a suitable timing. A practical example of the hydrogen-containing gas storing means is a tank; however, the hydrogen-containing gas storing means is not limited to the tank as far as it is suitable for storing and supplying the hydrogen-containing gas.

[0035] The liquid fuel to be used for production of the hydrogen-containing gas is preferably light oil or diesel fuel. It is to be noted that the CO concentration of the hydrogen-containing gas to be produced can be suppressed to a low level by using light oil as the liquid fuel to be used for production of the hydrogen-containing gas. Additionally, the CO concentration in the hydrogen-containing gas can be suppressed to a low level also by using fuel whose hydrocarbons have the carbon number of not smaller than 9. In this regard, it is also effective to prepare hydrocarbons as the raw material for the hydrogen-containing gas by separating and extracting the hydrocarbons having the carbon number of not smaller than 9, from the liquid fuel.

[0036] The hydrogen-containing gas contains much hydrogen (H_2) and is useful as the NOx reducing agent. The hydrogen-containing gas also contains, for example, carbon dioxide (CO_2), and unreacted HC (hydrocarbons) remaining after production of CO and the hydrogen-containing gas, in which it is preferable that the CO content or concentration in the hydrogen-containing gas is low. The CO content is preferably not higher than 100 ppm. When the hydrogen-containing gas is produced under conditions including the above-mentioned catalyst having Rh carried on alumina, reaction temperature and oxygen concentration, the hydrogen-containing gas having the CO content of not higher than 100 ppm can be obtained.

[0037] Next, the exhaust gas purifying system using the hydrogen-containing gas, according to the present invention will be discussed.

[0038] The exhaust gas purifying system includes the hydrogen-containing gas producing system and a NOx adsorbing (trapping) and reducing catalyst disposed in an exhaust gas passageway of the internal combustion engine. The NOx adsorbing and reducing catalyst functions to adsorb (trap) NOx when exhaust gas is in a lean region and to reduce NOx when exhaust gas is in a stoichiometric region or in a rich region. In the lean region, exhaust gas has an air/fuel ratio larger or leaner (in fuel) than a stoichiometric level, and therefore corresponds to so-called lean exhaust gas. In the stoichiometric region, exhaust gas has an air/fuel ratio around the stoichiometric level. In the rich region, exhaust gas has an air/fuel ratio smaller or richer (in fuel) than the stoichiometric level, and therefore corresponds to so-called rich exhaust gas. The NOx adsorbing and reducing catalyst is a noble metal-based catalyst including a carrier formed of refractory inorganic compound such as alumina, carrying or containing noble metal(s) such as Pt and/or Pd. It is preferable for increasing the amount of NOx to be adsorbed in the NOx adsorbing and reducing catalyst in the lean region of exhaust gas, that the NOx adsorbing and reducing catalyst contains alkali metal(s), alkaline-earth metal(s) and/or rare earth element(s) such as barium (Ba), cesium (Cs), magnesium (Mg), potassium (K), sodium (Na), lanthanum (La), cerium (Ce) and/or the like.

[0039] The hydrogen-containing gas produced by the hydrogen-containing gas producing system is supplied to the exhaust gas passageway upstream of the NOx adsorbing and reducing catalyst so as to be used for exhaust gas purification or reduction of NOx. Supply of the hydrogen-containing gas is regulated in relation to an oxygen concentration in exhaust gas discharged from the internal combustion engine. More specifically, the hydrogen-containing gas is supplied to the NOx adsorbing and reducing catalyst when exhaust gas is in the stoichiometric region or the rich region and the temperature of exhaust gas at the position immediately upstream of the NOx adsorbing and reducing catalyst is not higher than 250° C. At this time, H_2 is supplied in a concentration (% by volume) of preferably not less than 1%, more preferably not less than 1.5% in exhaust gas flowing through the exhaust gas passageway immediately upstream of the NOx adsorbing and reducing catalyst. In order to supply the hydrogen-containing gas under the above-mentioned conditions, it is preferable, for example, to once store the produced hydrogen-containing gas in the tank for hydrogen-containing gas, and then to supply the stored hydrogen-containing gas under pressure into exhaust gas in relation to the oxygen concentration in exhaust gas. The oxygen concentration in exhaust gas can be detected by an oxygen (O_2) sensor or the like, disposed at a suitable position in the exhaust gas passageway which position is upstream of a hydrogen-containing gas supply inlet at which the hydrogen-containing gas is supplied into exhaust gas flowing through the exhaust gas passageway.

[0040] The exhaust gas purifying system according to the present invention may be provided with a three-way catalyst, in which the three-way catalyst, the hydrogen-containing gas supply inlet and the NOx adsorbing and reducing catalyst are arranged or disposed in the exhaust gas passageway in the order mentioned in a direction of flow of exhaust gas. With this arrangement, first, gas components such as NOx, HC, CO and the like are removed, and then NOx remaining not-reduced by the upstream-side three-way catalyst is reduced at a high efficiency by the downstream-side NOx adsorbing and reducing catalyst. This is effective particularly in the low exhaust gas temperature condition where NOx cannot be sufficiently reduced by the three-way catalyst.

[0041] According to the above exhaust gas purifying system, NOx can be reduced or removed at a very high efficiency even in a condition where exhaust gas temperature is low. This can realize a clean exhaust gas in internal combustion engines such as diesel engines, thus making it possible to offer automotive vehicles which are excellent in environmental protection and in fuel economy (fuel consumption), taking warming-up phenomena of the earth into consideration.

EXAMPLES

[0042] The present invention will be more readily understood with reference to the following Examples in comparison with Comparative Examples; however, these Examples are intended to illustrate the invention and are not to be construed to limit the scope of the invention.

[0043] An embodiment of the exhaust gas purifying system including the hydrogen-containing gas producing system, according to the present invention will be discussed hereinafter with reference to **FIG. 1**.

[0044] The exhaust gas purifying system was incorporated with an exhaust system (not identified) of engine **1** which is of the cylinder direct injection type wherein fuel is directly injected into each engine cylinder, and has four engine cylinders and a displacement of 2.5 liters. Engine **1** was equipped with a common rail type fuel injection system (not shown). Throttle valve **3** was disposed in intake pipe or intake air passageway **2** of the engine so as to control an amount of air to be supplied to the engine cylinders. The engine cylinders of the engine were in communication with a catalytic converter **5A** including three-way catalyst **5**, through exhaust gas passageway **4**. Catalytic converter **5A** was in communication with another catalytic converter **6A** including NOx adsorbing and reducing catalyst **6**, through exhaust gas passageway **4**. The NOx adsorbing and reducing catalyst is honeycomb-type and monolithic, and has a volume of 1.7 liters.

[0045] The hydrogen-containing gas producing system included fuel tank **7** for storing fuel as a raw material for production of the hydrogen-containing gas. The fuel in the fuel tank is fed through pipe **8** to gas mixer **9**. A part of exhaust gas (as the carrier gas) of the engine and/or air are blown to the fuel within the gas mixer, so that the fuel is vaporized. In the gas mixer, the vaporized fuel is in a state of being mixed with the part of exhaust gas and/or air thereby forming a reaction gas. This reaction gas was introduced into catalytic reactor **10** which had been heated at 260 to 340° C. The catalytic reactor included a reforming catalyst **10***a* by which a reforming reaction of the fuel. In the catalytic reactor, hydrogen was produced to form the hydrogen-containing gas. The hydrogen-containing gas was stored in reserve tank **11**. The stored hydrogen-containing gas was to be injected through hydrogen-containing gas ejection nozzle **12** in accordance with a variation or change of the air/fuel ratio of exhaust gas flowing through exhaust gas passageway **4**, so that the hydrogen-containing gas was supplied into the exhaust gas passageway upstream of the NOx adsorbing and reducing catalyst and downstream of the three-way catalyst. The air/fuel ratio of exhaust gas was controlled by regulating the throttle valve, the common rail type fuel injection system and/or a so-called post fuel injection (accomplishing combustion control in the engine cylinders) under a feedback control using oxygen (O_2) sensor **13** disposed in the exhaust gas passageway. The post fuel injection means an auxiliary fuel injection made subsequent to a main fuel injection in each engine cylinder.

[0046] The reforming catalyst of catalytic reactor **10** includes a honeycomb type substrate having about 400 cells per square inch and having a volume of 150 cc. The substrate had been coated with Rh/alumina catalyst component in an amount of 120 g per one liter of the substrate. The Rh/alumina catalyst component had been prepared by causing alumina to carry about 2% by weight of Rh. The walls (defining each cell) had been covered with a coat layer of the Rh/alumina catalytic component, so that each cell serves as a gas passage through which exhaust gas flows.

[0047] In order to maintain the temperature within catalytic reactor **10** at 260 to 340° C., it is practical to use heat of exhaust gas of the engine though heating by a heater may be proposed. To heat the catalytic reactor by using heat of exhaust gas, catalytic reactor **10** may be connected to exhaust gas passageway or pipe **4** to constitute a heat exchanger.

<Tests for Producing Hydrogen-containing Gas>

Example 1

[0048] Tests for producing the hydrogen-containing gas was conducted by operating the hydrogen-containing gas producing system including the catalytic reactor **10**, under a condition simulating that of a so-called micro-reactor (the catalytic reactor) which is small-sized and suitable for an onboard use, thereby producing the hydrogen-containing gas which was discharged from the catalytic reactor. The tests included four tests which were the same with each other with the exception that the four tests respectively used undecane (C_{11}), decane (C_{10}), nonane (C_9) and octane (C_8) as the fuel (hydrocarbons) contained in the fuel tank **7**. The reaction temperature of a catalytic layer of the reforming catalyst of the catalytic reactor **10** was set within a range of 200 to 500° C.

[0049] In these tests, the reforming catalyst of the catalytic reactor **10** had been prepared by coating the honeycomb type substrate with a coat layer of a Rh/alumina catalyst component which had been prepared by causing γ-alumina having a specific surface area of about 230 m^2/g to carry about 2% by weight of Rh.

[0050] In each test, the yield of H_2 in the hydrogen-containing gas was continuously measured upon variation of the reaction temperature, and a H_2/CO ratio (volume or ppm) in the hydrogen-containing gas was continuously measured upon variation of the reaction temperature. The results of these measurements are shown in **FIGS. 3A and 3B** in which the four tests using undecane, decane, nonane and octane are indicated respectively by "undecane", "decane", "nonane" and "octane". The results of the measurements in the test using decane are shown as "Rh-based" also in **FIGS. 2A and 2B**.

Comparative Example 1

[**0051**] The procedure in Example 1 was repeated with the exception that a coat layer of a Ru/alumina catalyst component prepared similarly to that of Example 1 was used in place of the coat layer of the Rh/alumina catalyst component, and that only one test using decane (C_{10}) as the fuel was conducted in place of the four tests of Example 1. In this test, the yield of H_2 in the hydrogen-containing gas was continuously measured upon variation of the reaction temperature, and a H_2/CO ratio (volume) was continuously measured upon variation of the reaction temperature. The results of these measurements are shown as "Ru-based" in **FIGS. 2A and 2B**.

Comparative Example 2

[**0052**] The procedure in Example 1 were repeated with the exception that a coat layer of a Pt/alumina catalyst component prepared similarly to that of Example 1 was used in place of the coat layer of the Rh/alumina catalyst component, and that only one test using decane (C_{10}) as the fuel was conducted in place of the four tests of Example 1. In this test, the yield of H_2 in the hydrogen-containing gas was continuously measured upon variation of the reaction temperature, and a H_2/CO ratio (volume) was continuously measured upon variation of the reaction temperature. The results of these measurements are shown as "Pt-based" in **FIGS. 2A and 2B**.

Comparative Example 3

[**0053**] The procedure in Example 1 were repeated with the exception that a coat layer of a Ni/alumina catalyst component prepared similarly to that of Example 1 was used in place of the coat layer of the Rh/alumina catalyst component, and that only one test using decane (C_{10}) as the fuel was conducted in place of the four tests of Example 1. In this test, the yield of H_2 in the hydrogen-containing gas was continuously measured upon variation of the reaction temperature, and a H_2/CO ratio (volume) was continuously measured upon variation of the reaction temperature. The results of these measurements are shown as "Ni-based" in **FIGS. 2A and 2B**.

[**0054**] The test results in **FIGS. 2A** to **3**B depict the followings: In case that nonane, decane or undecane is used as the fuel (raw material), the amount of CO (by-product) produced is peculiarly very small within a reaction temperature range of from 260 to 340° C., thereby proving that the preferable conditions for production of the hydrogen-containing gas are very effective. Additionally, in case that octane is used as the fuel (raw material), it is recognized that a considerable amount of CO (by-product) produced is produced within the above reaction temperature range. In contrast, in case of nonane, decane or undecane is used as the fuel (raw material), it is apparent that the amount of CO (by-product) produced is sharply reduced, in which the CO concentration becomes not higher than 100 ppm.

[**0055**] <Tests for Evaluation of Hydrogen-containing Gas on NOx Reduction Characteristics for NOx Adsorbing and Reducing Catalyst>

[**0056**] A NOx adsorbing and reducing catalyst as shown in **FIG. 1** was prepared to contain Pt/Rh-based catalyst component and carry Ba component upon impregnation of Ba. The NOx adsorbing and reducing catalyst was subjected to six tests. In each test, two laboratory model gases (lean gas and rich gas) simulating actual lean exhaust gas and rich exhaust gas from an automotive internal combustion engine were flown alternately through the NOx adsorbing and reducing catalyst, in which the lean gas was flown for 40 seconds whereas the rich gas was flown for 2 seconds; and the temperature of the lean or rich gas immediately upstream of the NOx adsorbing and reducing catalyst was set at 180° C. In this test, the hydrogen-containing gas obtained in Example 1 was introduced into the model gas upstream of the NOx adsorbing and reducing catalyst. In the six tests, the CO concentration in the rich gas were respectively 0, 0.5, 1.0, 1.5, 2.0 and 2.5% by volume. The compositions of the lean gas and the rich gas were as follows:

[**0057**] The lean gas:

[**0058**] HC (C_3H_6)=1500 ppm

[**0059**] NO=200 ppm

[**0060**] CO=1000 ppm

[**0061**] H_2O=10 vol %

[**0062**] O_2=5 vol %

[**0063**] N_2=balance

[**0064**] The rich gas:

[**0065**] HC (C_3H_6)=3500 ppm

[**0066**] NO=200 ppm

[**0067**] CO=0.5, 1.0, 1.5, 2.0 and 2.5 vol %

[**0068**] H_2=1.0 vol %

[**0069**] O_2=1000 ppm

[**0070**] H_2O=10 vol %

[**0071**] N_2=balance

[**0072**] During each test, a NOx removal rate was determined in the following manner: The concentration (volume or ppm) A of NOx in the model gas upstream of the NOx adsorbing and reducing catalyst was measured while the concentration B of NOx in the model gas downstream of the NOx adsorbing and reducing catalyst was measured. The NOx removal rate (% by volume) was calculated by [(1−the concentration B/the concentration A)×100]. The results of the tests are shown in **FIG. 4**.

[**0073**] The results of **FIG. 4** depicts that, in case using hydrogen (or the hydrogen-containing gas) as a reducing agent for NOx, an extremely high NOx removal rate was obtained even in a low gas temperature condition of 180° C. under a condition where the concentration of co-existing CO is low, thus proving the effectiveness of the hydrogen-containing gas to exhaust gas purification.

[0074] As appreciated from the above, according to the present invention, the hydrogen-containing gas containing much hydrogen and low in CO content is used as the reducing agent for NOx contained in exhaust gas. This hydrogen-containing gas is produced in the onboard manner by the hydrogen-containing gas producing system which is incorporated in the exhaust gas purifying system. Accordingly, NOx can be removed or reduced at a high efficiency even in a low exhaust gas temperature condition of 200° C. or lower, without degrading the fuel economy by avoiding mounting onboard a tank or the like for storing the NOx reducing agent.

[0075] The entire contents of Japanese Patent Application P2000-302065 (filed Oct. 2, 2000) are incorporated herein by reference.

[0076] Although the invention has been described above by reference to certain embodiments and examples of the invention, the invention is not limited to the embodiments and examples described above. Modifications and variations of the embodiments and examples described above will occur to those skilled in the art, in light of the above teachings. The scope of the invention is defined with reference to the following claims.

What is claimed is:

1. A hydrogen-containing gas producing system of an onboard type, for producing hydrogen-containing gas to be used for purification of exhaust gas of an internal combustion engine, said hydrogen-containing system comprising:

a fuel supply source for supplying fuel as a raw material of the hydrogen-containing gas;

a carrier gas supply source for supplying a carrier gas for carrying the fuel;

a device for vaporizing the fuel so as to form a vaporized fuel serving as a reaction gas, -said fuel vaporizing device being connected to said fuel supply source and said carrier gas supply source; and

a reforming section connected to said fuel vaporizing device, for reforming the reaction gas so as to produce the hydrogen-containing gas.

2. A hydrogen-containing gas producing system as claimed in claim 1, wherein the hydrogen-containing gas contains carbon monoxide in an amount of not more than 100 ppm.

3. A hydrogen-containing gas producing system as claimed in claim 1, wherein said fuel supply source is adapted to supply liquid fuel serving as the raw material of the hydrogen-containing gas, said fuel vaporizing device is a gas mixer which is arranged to vaporize the liquid fuel under action of the carrier gas so as to form the vaporized fuel serving as the reaction gas.

4. A hydrogen-containing gas producing system as claimed in claim 1, wherein said reforming section includes a fuel reforming catalyst containing rhodium.

5. A hydrogen-containing gas producing system as claimed in claim 1, further comprising a hydrogen-containing gas storing device for storing the hydrogen-containing gas from said reforming section.

6. A hydrogen-containing gas producing system as claimed in claim 1, wherein said fuel supply source also serves as a fuel supply source for supplying fuel to the internal combustion engine.

7. A hydrogen-containing gas producing system as claimed in claim 3, wherein said reforming section is adapted to produce the hydrogen-containing gas at a reaction temperature of the reaction gas, ranging from 260 to 340° C. and under a condition represented by the following formula:

an oxygen concentration in the reaction gas≦an average carbon number of hydrocarbons in the liquid fuel×a concentration of the liquid fuel in the reaction gas×½.

8. A hydrogen-containing gas producing system as claimed in claim 3, wherein the liquid fuel is light oil.

9. A hydrogen-containing gas producing system as claimed in claim 3, wherein the liquid fuel has hydrocarbons whose number of carbon atoms is not smaller than 9.

10. A hydrogen-containing gas producing system as claimed in claim 1, wherein the fuel has hydrocarbons which are separated and extracted from a liquid fuel, each of the hydrocarbons has a number of carbon atoms, not smaller than 9.

11. An exhaust gas purifying system for an internal combustion engine, comprising:

a hydrogen-containing gas producing system of an onboard type, for producing hydrogen-containing gas to be used for purification of exhaust gas of an internal combustion engine, said hydrogen-containing system including a fuel supply source for supplying fuel as a raw material of the hydrogen-containing gas, a carrier gas supply source for supplying a carrier gas for carrying the fuel, a device for vaporizing the fuel so as to form a vaporized fuel as a reaction gas, said fuel vaporizing device being connected to said fuel supply source and said carrier gas supply source, and a reforming section connected to said fuel vaporizing device, for reforming the reaction gas so as to produce the hydrogen-containing gas, said reforming section being connected to a part of an exhaust gas passageway of the internal combustion engine so as to introduce the hydrogen-containing gas into exhaust gas; and

a NOx adsorbing and reducing catalyst disposed in the exhaust gas passageway downstream of said part, said NOx adsorbing and reducing catalyst being adapted to adsorb nitrogen oxides in exhaust gas in a condition that exhaust gas is in a lean region, and to reduce nitrogen oxides in exhaust gas in a condition that exhaust gas is within a range including a stochiometric region and a rich region, wherein the hydrogen-containing gas from said reforming section of said hydrogen-containing gas is supplied into the exhaust gas passageway at said part which is upstream of said NOx adsorbing and reducing catalyst, at a low temperature range in which a temperature of exhaust gas at a position immediately upstream of said NOx adsorbing and reducing catalyst is not higher than 250° C., and in the condition that exhaust gas is within the range including the stoichiometric region and the rich region.

12. An exhaust gas purifying system as claimed in claim 11, further comprising a three-way catalyst disposed in the exhaust gas passageway upstream of said part to which a supply inlet for the hydrogen-containing gas is located.

13. A hydrogen-containing gas producing system of an onboard type, for producing hydrogen-containing gas to be used for purification of exhaust gas of an internal combustion engine, said hydrogen-containing system comprising:

a fuel supply source for supplying fuel as a raw material of the hydrogen-containing gas;

a carrier gas supply source for supplying a carrier gas for carrying the fuel;

means for vaporizing the fuel so as to form a vaporized fuel serving as a reaction gas, said fuel vaporizing means receiving the fuel from said fuel supply source and the carrier gas from said carrier gas supply source; and

a reforming section connected to said fuel vaporizing device, for reforming the reaction gas so as to produce the hydrogen-containing gas.

14. An exhaust gas purifying system for an internal combustion engine mounted on an automotive vehicle, comprising:

a catalyst for reducing nitrogen oxides in exhaust gas of the engine, disposed in an exhaust gas passageway of the engine and mounted on the vehicle, said catalyst containing at least one of platinum and palladium; and

a hydrogen-containing gas producing system for producing hydrogen-containing gas, mounted on the vehicle, said hydrogen-containing system including a fuel supply source for supplying fuel as a raw material of the hydrogen-containing gas, a carrier gas supply source for supplying a carrier gas for carrying the fuel, a device for vaporizing the fuel so as to form a vaporized fuel as a reaction gas, said fuel vaporizing device being connected to said fuel supply source and said carrier gas supply source, and a reforming section connected to said fuel vaporizing device, for reforming the reaction gas so as to produce the hydrogen-containing gas, said reforming section being connected to a part of the exhaust gas passageway upstream of said catalyst so that the hydrogen-containing gas is supplied to said catalyst.

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