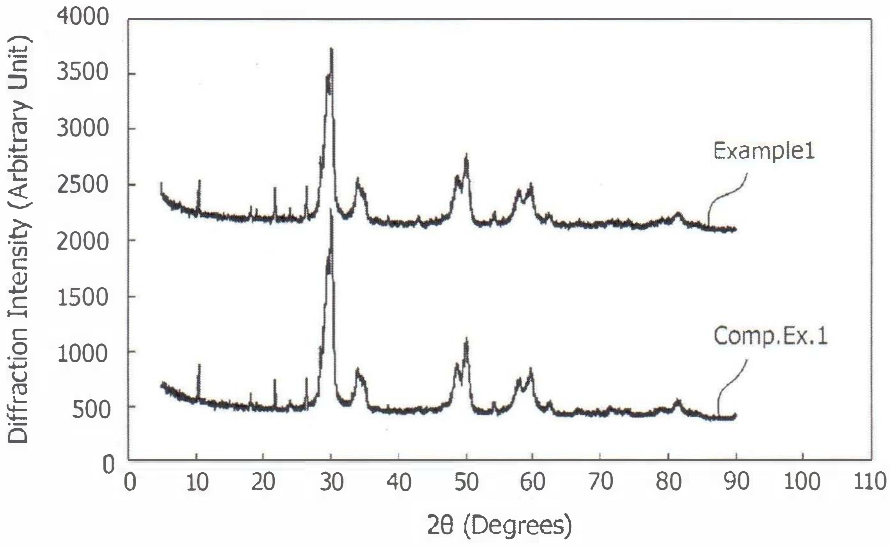

FIG. 1

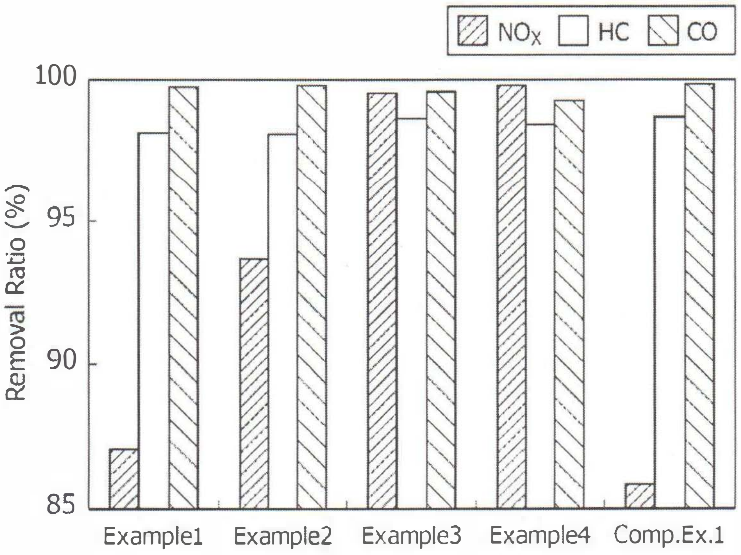

FIG. 2

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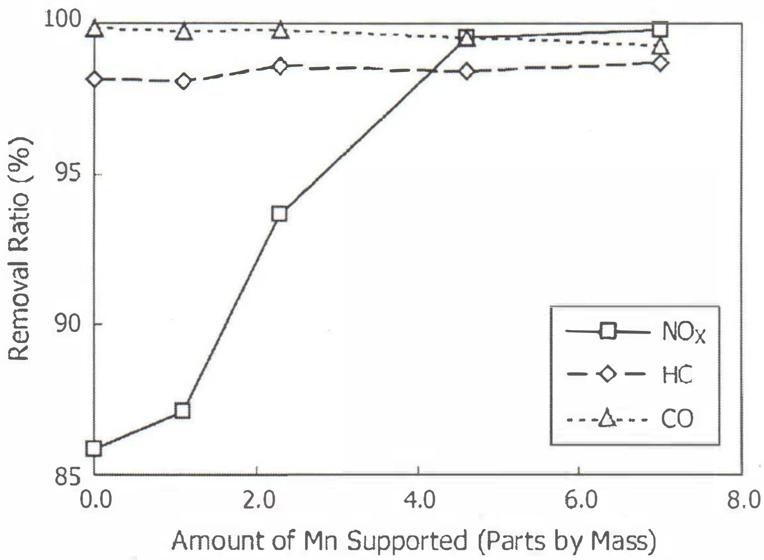

FIG. 3

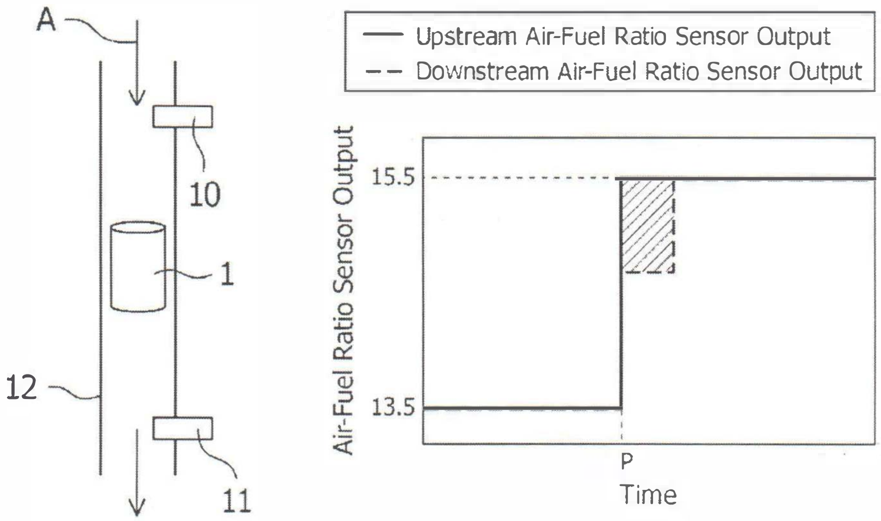

FIG. 4

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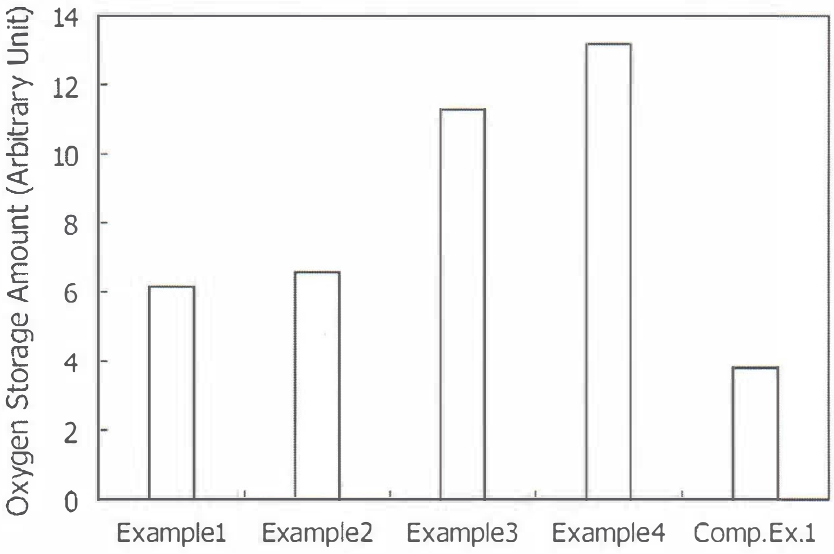

FIG. 5

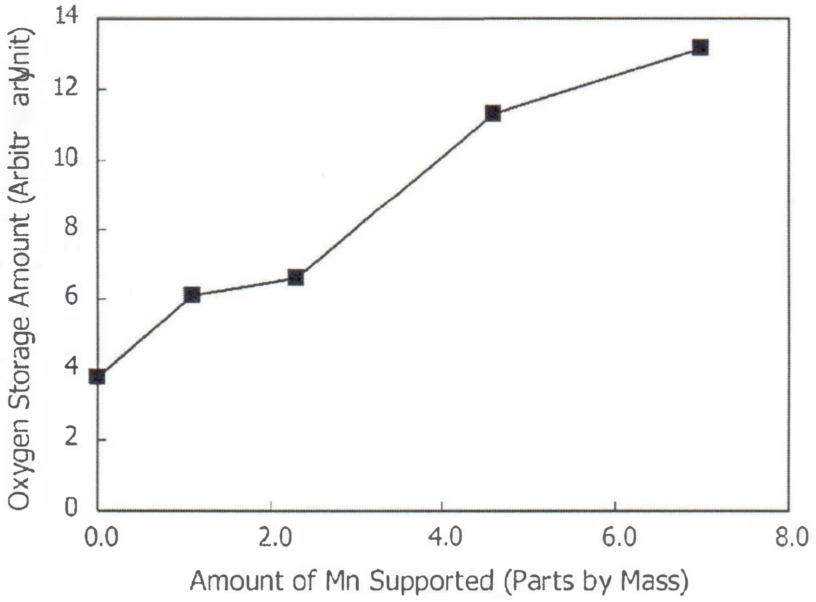

FIG. 6

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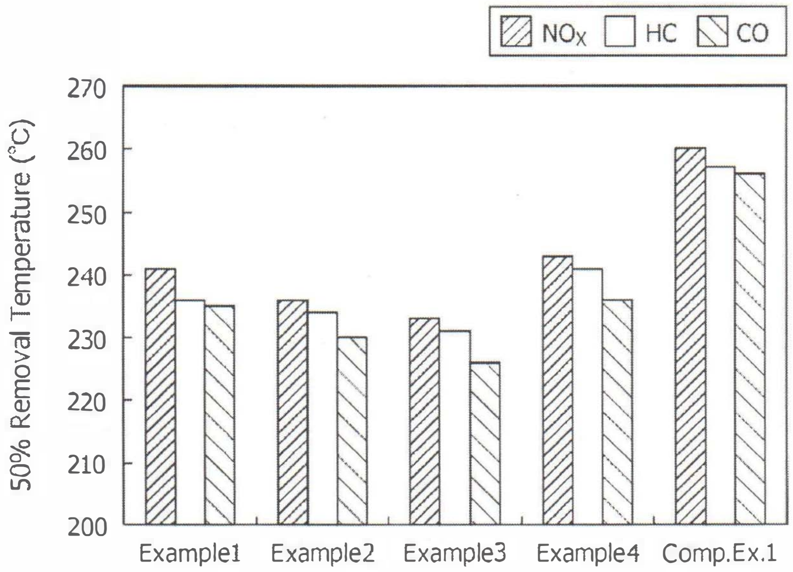

FIG. 7

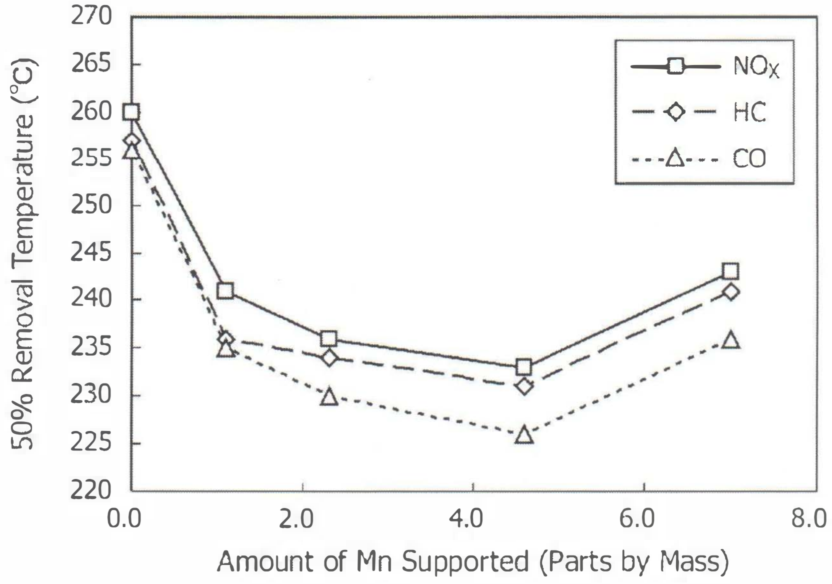

FIG. 8

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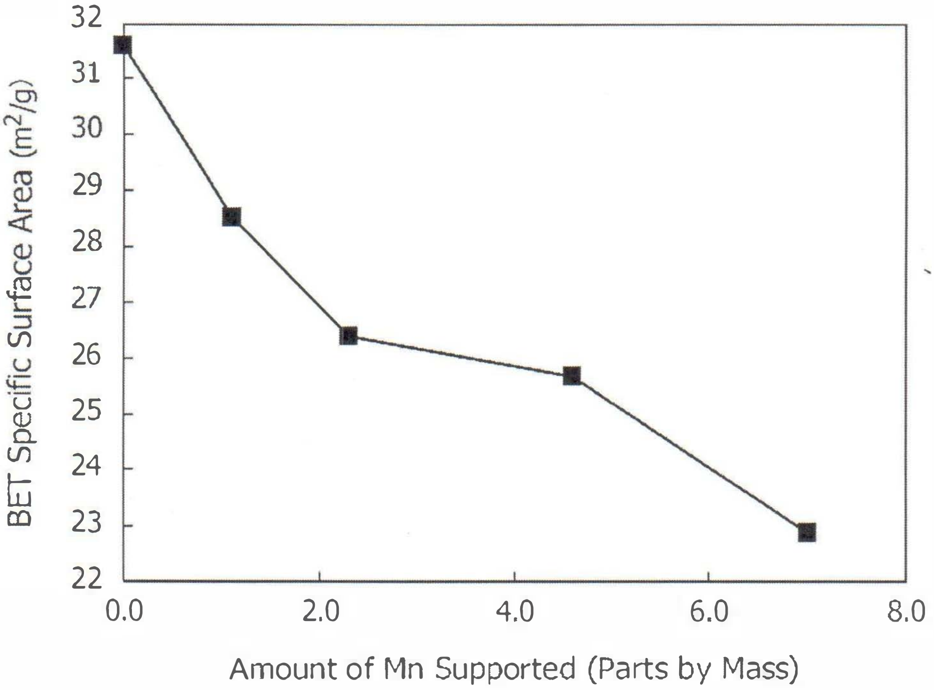

FIG. 9

November 03, 2014

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FORM 2

THE PATENTS ACT 1970

39 of 1970

&

The Patent Rules 2003

COMPLETE SPECIFICATION

(See sections 10 & rule 13)

1. TITLE OF THE INVENTION

EXHAUST GAS PURIFICATION CATALYST AND METHOD FOR PRODUCING THE SAME

2. APPLICANTS (S)

NAME	NATIONALITY	ADDRESS
SUZUKI MOTOR CORPORATION	JP	300, Takatsuka-cho, Minami-ku, Hamamatsu-shi, Shizuoka-ken, JAPAN

3. PREAMBLE TO THE DESCRIPTION

COMPLETE

The following specification particularly describes the invention and the manner in which it is to be performed.

[Name of Document] Specification

[Title of Invention]

EXHAUST GAS PURIFICATION CATALYST AND METHOD FOR PRODUCING THE SAME

[Technical Field]

[0001]

The present invention relates to an exhaust gas purification catalyst and to a method for producing the same.

[Background Art]

[0002]

Because of recent tightening of exhaust gas regulations for automobiles and CO_2 reduction issues, development of automobile fuel-efficiency improvement technologies is being advanced. For improving fuel-efficiency, it is proposed that gasoline engines should be operated with anair-fuel mixture gas being under a slightly lean condition, where the mixture gas contains air slightly in excess, (with the air-fuel ratio of the mixture gas being about 14.8), of the stoichiometry (with the air-fuel ratio of the mixture gas being 14.7, which is the theoretical air-fuel ratio). This creates the need for development of an exhaust gas purification catalyst which is adapted to such an operation.

[0003]

Conventionally, the three-way catalyst has been employed for removing harmful components such as nitrogen oxide (NOx), hydrocarbons (HC), and carbon monoxide (CO) contained in exhaust gas emitted from automobiles. The three-way catalyst is produced by using a ceramic or metal formed into a honeycomb shape as a substrate, coating a surface of the substrate with a porous inorganic material such as alumina, and further causing a trace amount of a noble metal to be supported as an active component on a surface portion of the substrate. The three-way catalyst achieves the purification by reducing NOx and oxidizing HC and CO.

[0004]

In addition, the NOx storage reduction catalyst is known as a catalyst for purification of exhaust gas emitted in an operation in the range from the stoichiometric region to a lean region with an air-fuel ratio of up to about 20. For example, Patent Document 1 describes an exhaust gas purification apparatus using a NOx storage reduction catalyst and a method for controlling the apparatus for preventing release of untreated NOx.

[Prior Art]

[Patent Document]

[0005]

[Patent Document 1] Japanese Patent Application Publication No. 2000-110616

[Summary of Invention]

[Problems to be Solved by the Invention]

[0006]

However, in an operation with a mixture gas in a lean region, a slightly lean region, or the like in whichthe air is contained in excess, it is difficult to increase the NOx removal ratio from the exhaust gas. Diesel engines, which are representative of internal combustion engines operated under conditions with lean mixture gas, have high fuel-efficiency. However, in diesel engines, it is difficult to remove NOx because of the leanness, and an exhaust gas purification apparatus for diesel engines has a very-complicated, heavy-weight, and high-cost structure in which multiple catalysts such as an oxidation catalyst and a NOx storage reduction catalyst are provided at multiple stages. For example, the exhaust gas purification apparatus described in Patent Document 1 has a two-stage structure of an upstream catalyst and a downstream catalyst in which the NOx storage reduction catalyst is disposed, and hence has a complicated structure. In addition, since the NOx storage amount of the NOx storage reduction catalyst has an upper limit, this NOx storage reduction catalyst requires an extremely complicated engine control to achieve a high NOx removal ratio, such as the rich-spike in which extra fuel is injected before the storage of NOx reaches saturation.

[0007]

The fuel-efficiency of a gasoline engine operated under a slightly lean condition is better than that of a gasoline engine operated under stoichiometric conditions, but is generally inferior to that of a diesel engine. For this reason, when an exhaust gas purification apparatus equivalent to that for a diesel engine is combined with a gasoline engine operated under a slightly lean condition, there arises such a problem that an effect on the fuel-efficiency worth the cost cannot be obtained, although the exhaust gas can be cleaner. Hence, a gasoline engine operated under a slightly lean condition requires a low-cost and simple exhaust gas purification catalyst thatcan purifyexhaust gas even though the catalyst is a single-stage catalyst, which is similar to that for a gasoline engine operated under stoichiometric conditions.

[0008]

Here, conventional three-way catalysts achieve the highest purification performance at the stoichiometric air-fuel ratio. On the other hand, in an operation under a slightly lean condition, the conventional three-way catalysts undergo remarkable deterioration in NOx removal performance, although they exhibit high removal performances of HC and CO. This is because of the following reason. Specifically, since HC and CO are removed by oxidation, the removal is rather promoted in a case in whichthe air is in excess. In contrast, since NOx is removed by reduction, it is difficult to remove NOx in a case in whichthe air is in excess. In addition, to achieve stable combustion at cold start, even a gasoline engine designed to be operated under a slightly lean condition is operated under stoichiometric conditions until the engine is warmed. In this respect, the conventional three-way catalysts have low low-temperature activity. Hence, it is necessary to develop an exhaust gas purification catalyst which has an excellent NOx removal performance even under a slightly lean condition, and which has a high low-temperature activity under stoichiometric conditions.

[0009]

The present invention has been made in view of the above-described problems, and an object of the present invention is to provide an exhaust gas purification catalyst which can achieve an extremely high NOx removal ratio during operation under a slightly lean condition, while providing HC and CO removal ratios comparable to those achieved by a conventional three-way catalyst, and which can provide a high low-temperature activity during operation under stoichiometric conditions.

[Means for Solving the Problems]

[0010]

To achieve the above-described object, the present invention provides an exhaust gas purification catalyst comprising: a support selected from a material with oxygen storage material (OSC material) and a mixture powder of an OSC material and alumina powder; at least one noble metal supported on the support, the at least one noble metal being selected from the group consisting of platinum, palladium, and rhodium; and manganese oxide further supported on the support.

[0011]

In an embodiment of the exhaust gas purification catalyst according to the present invention, an amount of the manganese oxide supported is preferably 1 to 7 parts by mass, in terms of elemental manganese, relative to 100 parts by mass of the support.

[0012]

In an embodiment of the exhaust gas purification catalyst according to the present invention, an amount of the manganese oxide supported is preferably 4 to 5 parts by mass, in terms of elemental manganese, relative to 100 parts by mass of the support.

[0013]

In an embodiment of the exhaust gas purification catalyst according to the present invention, an amount of the noble metal supported is preferably 0.1 to 5 parts by mass relative to 100 parts by mass of the support.

[0014]

In an embodiment of the exhaust gas purification catalyst according to the present invention, the OSC material preferably comprises one or more selected from the group consisting of cerium oxide, composite oxides of cerium and zirconium, and composite oxides comprising at least one rare-earth metal selected from the group consisting of lanthanum, neodymium, praseodymium, and yttrium in addition to cerium oxide or a composite oxide of cerium and zirconium.

[0015]

Another aspect of the present invention is an exhaust gas purification apparatus for a gasoline engine, the apparatus comprising the above-described exhaust gas purification catalyst.

[0016]

Still another aspect of the present invention is a method for producing an exhaust gas purification catalyst, the method comprising the steps of: causing at least one noble metal selected from the group consisting of platinum, palladium, and rhodium to be supported on a support selected from an OSC material and a mixture powder of an OSC material and alumina powder; and further causing manganese oxide to be supported on the support on which the at least one noble metal has been supported.

[Advantageous Effects of the Invention]

[0017]

The present invention makes it possible to provide an exhaust gas purification catalyst which can achieve an extremely high NOx removal ratio during operation under a slightly lean condition, while providing HC and CO removal ratios comparable to those achieved by a conventional three-way catalyst, and which can provide a high low-temperature activity during operation under stoichiometric conditions.

[Brief Description of the Drawings]

[0018]

[Fig. 1] Fig. 1 is a drawing showing XRD diffraction charts.

[Fig. 2] Fig. 2 is a graph showing removal ratios at 500°C under a slightly lean condition.

[Fig. 3] Fig. 3 is a graph showing removal ratios at 500°C under a slightly lean condition.

[Fig. 4] Fig. 4 is a diagram for illustrating the outline of measurement of oxygen storage amount.

[Fig. 5] Fig. 5 is a graph showing oxygen storage amount.

[Fig. 6] Fig. 6 is a graph showing oxygen storage amount.

[Fig. 7] Fig. 7 is a graph showing 50% removal temperatures under stoichiometric conditions.

[Fig. 8] Fig. 8 is a graph showing 50% removal temperatures under the stoichiometric conditions.

[Fig. 9] Fig. 9 is a graph showing BET specific surface area.

[Modes for Carrying Out the Invention]

[0019]

Hereinafter, an exhaust gas purification catalyst and a method for producing the exhaust gas purification catalyst according to the present invention will be described in detail. The exhaust gas purification catalyst according to the present invention comprises: a support selected from an OSC material and a mixture powder of an OSC material and alumina powder; at least one noble metal selected from the group consisting of platinum, palladium, and rhodium and supported on the support; and manganese oxide further supported on the support.

[0020]

As the support, a material having oxygen storage capacity (hereinafter referred to as OSC material) is used. The OSC material is not particularly limited, as long as the OSC material is generally used for an exhaust gas purification catalyst. The OSC material preferably comprises at least one selected from the group consisting of cerium oxide (CeO_2), composite oxides of cerium and zirconium ($Ce_xZr_{(1-x)}O_2$ (where $0.05 \leq x < 1$)), and composite oxides each comprising at least one or more rare-earth metals selected from the group consisting of lanthanum, neodymium, praseodymium, and yttrium in addition to cerium oxide or a composite oxide of cerium and zirconium. Cerium oxide has oxygen storage capacity because of the valence change represented by $Ce^{3+} \leftrightarrow Ce^{4+}$, and also has heat resistance necessary for an exhaust gas purification catalyst. A composite oxide of cerium and zirconium has higher heat resistance and higher oxygen storage/release rates. The composition ratio of the composite oxide of cerium and zirconium is represented by $Ce_xZr_{(1-x)}O_2$, where $0.05 \leq x < 1$. This is equivalent to a weight ratio of Ce of 5.6 to 81.4% by mass and a weight ratio of Zr of 0 to 68.9% by mass, relative to the composite oxide. This is because if $x < 0.05$, the ratio of Ce is so low that the OSC performance may be insufficient in some cases. The composite oxides each comprisingone or more rare-earth metals in addition tocerium oxide or a composite oxide of cerium and zirconium are also excellent in heat resistance and oxygen storage capacity. When one or more rare-earth metals selected from the group consisting of lanthanum, neodymium, praseodymium, and yttrium are combined with cerium or cerium and zirconium to form a composite oxide, the amount of each of the rare-earth metal elements added is such that the amount of each of the rare-earth metal elements in the composite oxide after calcination can be 0.1 to 10% by mass, while the amount of Ce therein can be 5.6% by mass (which is equivalent to the amount of Ce in a case in which the above-described x is 0.05) or more. This is because if the amount of the rare-earth metal added is less than 0.1% by mass, the above-described effect cannot be obtained in some cases, whereas if the amount of the rare-earth metal added exceeds 10% by mass, improvement in the effect is not observed in some cases, and only increase in costs is brought about. The use of any of these OSC materials for the support makes it possible to improve the heat resistance of the catalyst, and further improve the oxygen storage/release rates and, in turn, promote the catalytic reaction.

[0021]

The composite oxide of cerium and zirconium or the composite oxide comprising one or more rare-earth metals in addition theretocan be produced by any method. For example, the composite oxide can be obtained by adding an excess amount of an alkaline solution to an aqueous mixture solution containing nitrates of elements to constitute the composite oxide (for example, Ce nitrate, Zr nitrate, La nitrate, and the like), and calcining a coprecipitate. As the aqueous alkali solution, for example, an aqueous ammonia solution, an aqueous sodium hydroxide solution, or an aqueous potassium hydroxide solution can be used. As the aqueous alkali solution, an aqueous ammonia solution is preferably used, because the residue originated from the aqueous alkali solution is removed during the calcination. The calcination of the coprecipitate can be conducted at preferably 300 to 800°C and more preferably 500 to 800°C for 1 to 24 hours. If the calcination temperature is higher than 800°C, an adverse effect of decrease in specific surface area may occur due to sintering in some cases. Meanwhile, if the calcination temperature is lower than 300°C, formation of the composite oxide may be insufficient in some cases.

[0022]

The support may also be a mixture powder of an OSC material and alumina powder. An alumina powder is porous and excellent in gas diffusibility. Hence, the chance of contact of the catalyst with the gas increases, so that the removal ratio can be increased. Further, since alumina powder is excellent in heat resistance, the heat resistance of the catalyst can be improved by mixing alumina powder in the support. When a mixture powder of an OSC material and alumina powder is used as the support, the ratio of the alumina powder is preferably set to 10 to 90% by mass relative to the mixture powder. By setting the ratio of the alumina powder within this range, sufficient effects can be obtained on the gas diffusibility and the heat resistance.

[0023]

The noble metal supported on the support is selected from the group consisting of platinum, palladium, and rhodium. One of these noble metals can be used alone, or two or more thereof may be used in combination. The amount of the noble metal supported is preferably 0.1 to 5 parts by mass relative to 100 parts by mass of the support. This is because, if the supported amount is less than 0.1 parts by mass, a sufficient catalytic performance cannot be obtained in some cases. This is also because, if the supported amount exceeds 5 parts by mass, improvement in performance which is worth the increase in the supported amount is not observed, and the cost increases, although the catalytic performance is not impaired. Platinum, palladium, and rhodium have high heat resistance, and hence are less susceptible to degradation due to heat load, even when used for an exhaust gas purification catalyst for a gasoline engine, which is exposed to high temperatures of 900°C or above.

[0024]

The manganese oxide is further supported on the support on which the noble metal is supported. The manganese oxide is represented by the chemical formula of MnO_2. The average particle diameter of the manganese oxide supported is preferably about a size which does not exert any influence on X-ray diffraction measurement of the exhaust gas purification catalyst, for example, 100 nm or less. The present inventors have first discovered that, by supporting of manganese oxide, an exhaust gas purification catalyst can be obtained which exhibits a high NOx removal ratio and also high HC and CO removal ratios, even for a slightly lean mixture gas. Although the detailed mechanism is unclear, this is presumably achieved because of the following reasons: (a) the points of contact between the supported manganese oxide and the OSC material serve as oxygen flow paths, (b) a catalytic action owing to oxidation/reduction of the manganese oxide itself is added, (c) the supported manganese oxide serves as a diffusion barrier to suppress diffusion and coarsening of the noble metal, so that the active surface area is maintained, (d) the suppression of the diffusion and coarsening of the noble metal makes it less likely that the number of the points of contact between the OSC material and particles of the noble metal, which serve as oxygen flow paths, is reduced, and the OSC performance is consequently improved; etc.

[0025]

As described above, when the amount of the manganese oxide supported is increased, an effect of improvement in the catalytic performance can be obtained because of the improvement in OSC performance and suppression of the diffusion and coarsening of the noble metal. On the other hand, however, degradation in catalytic performance may be caused in some cases because of decrease in the specific surface area of the support. Hence, the catalytic performance is determined by the trade-off of improvement in OSC performance and suppression of diffusion and coarsening of the noble metal for decrease in specific surface area of the support. If the amount of the manganese oxide supported is too small, the effects of the improvement in OSC performance and the suppression of diffusion and coarsening of the noble metal are absent, so that the improvement in catalytic performance cannot be expected in some cases. When the amount of the manganese oxide supported is too large, the specific surface area remarkably decreases in some cases, although the improvement in OSC performance and the suppression of diffusion and coarsening of the noble metal are achieved. Hence, the amount of the manganese oxide supported is preferably 1 to 7 parts by mass and more preferably 4 to 5 parts by mass, in terms of elemental manganese, relative to 100 parts by mass of the support.

[0026]

Optionally, barium is further supported in the exhaust gas purification catalyst according to the present invention. By the further supporting of barium, NOx storage capacity can be provided to the catalyst. Hence, transient NOx can be trapped in a case in which the air-fuel ratio suddenly changes to the lean side temporarily and like cases. Consequently, an effect of improvement in robustness of the catalyst is achieved. On the other hand, barium has an extremely low electronegativity of 0.89, and strongly interacts with the noble metal, so that the noble metal in contact with the barium tends to be retained in an oxide state. Hence, barium also has an effect of inhibiting the expression of the activity of the noble metal. Considering these points, the supported amount is preferably 5 to 15 parts by mass, in terms of Ba, relative to 100 parts by mass of the support. This is because if the supported amount is less than 5 parts by mass, the NOx storage capacity may be insufficient in some cases, whereas, if the supported amount exceeds 15 parts by mass, the decrease in activity may be remarkable in some cases. The form of the barium supported is preferably barium oxide (BaO), barium carbonate ($BaCO_3$), or barium sulfate ($BaSO_4$). Barium oxide or barium carbonate is particularly preferable from the viewpoint that a large amount of NOx is adsorbed.

[0027]

The exhaust gas purification catalyst according to the present invention is provided in an exhaust gas purification apparatus for a gasoline engine, and is used for purification of exhaust gas from the gasoline engine operated under a slightly lean condition. The exhaust gas purification catalyst according to the present invention can remove not only HC and CO, but also NOx at high removal rates during operation under a slightly lean condition, even when used alone without being combined with any other catalyst. Hence, the use of the exhaust gas purification catalyst according to the present invention enables the exhaust gas purification apparatus to have a simple and light structure having a single catalyst stage alone. On the other hand, a conventional three-way catalyst undergoes remarkable deterioration in the NOx removal performance during operation under a slightly lean condition. Hence, a conventional exhaust gas purification apparatus needs to have a complicated structure in which a three-way catalyst or an oxidation catalyst for removing HC and CO is combined with a NOx storage catalyst for removing NOx, an urea injection system, or the like. Therefore, a conventional exhaust gas purification apparatus has problems of high weight and high costs. However, the exhaust gas purification catalyst according to the present invention does not require the use of a NOx storage catalyst. Hence, the exhaust gas purification catalyst according to the present invention is advantageous in that the rich-spike control for removing the stored NOx is no longer necessary, and the engine control is simplified. Moreover, the elimination of the need for extra fuel injection for rich-spike leads to further improvement in fuel-efficiency.

[0028]

Next, a method for producing the exhaust gas purification catalyst according to the present invention is described. The exhaust gas purification catalyst according to the present invention comprises the steps of: causing a noble metal to be supported on a support; and further causing manganese oxide to be supported on the support.

[0029]

In the step of causing a noble metal to be supported on a support, at least one or more noble metals selected from the group consisting of platinum, palladium, and rhodium are supported on a support selected from an OSC material and a mixture powder of an OSC material and alumina powder. In this supporting step, the support is immersed in a noble metal solution and is allowed to stand still. Thus, a precursor compound of the noble metal is attached to the support. The support is allowed to stand still in the noble metal solution for, for example, 1 to 24 hours. Subsequently, the support to which the precursor compound of the noble metal is attached is dried and calcined to immobilize the noble metal onto the support. The calcination is conducted preferably at a temperature of 150 to 800°C. If the calcination temperature is lower than 150°C, the immobilization is insufficient. As a result, when the manganese oxide is supported in the next step, the noble metal may be eluted into a manganese solution. If the calcination temperature exceeds 800°C, the catalytic performance may deteriorate because of thermal degradation in some cases. The calcination is conducted for preferably 1 to 24 hours. Noble metal particles can be fixed onto the support by the calcination.

[0030]

As a platinum solution, for example, a solution of diamminedinitro platinum, hexahydroxyplatinic acid, platinum chloride, platinum nitrate, or the like can be used. As a palladium solution, for example, a solution of palladium nitrate, palladium chloride, or the like can be used. As a rhodium solution, a solution of rhodium nitrate, rhodium chloride, rhodium acetate (dimer or monomer), or the like can be used. The concentration of each noble metal solution is preferably, for example, 0.001 to 20% by mass.

[0031]

In the step of further causing manganese oxide to be supported on the support, manganese oxide is further supported on the support on which the noble metal is supported. In this supporting step, the support on which the noble metal is supported is immersed in a manganese solution and allowed to stand still. Thus, a precursor compound of manganese oxide is attached to the support. As the manganese solution, a solution of manganese nitride, manganese chloride, manganese sulfate, any of various manganate salts, or the like can be used. The concentration of the manganese solution can be, for example, 0.01 to 20% by mass in terms of elemental manganese. The support is allowed to stand still in the manganese solution for, for example, 5 minutes to 24 hours. Subsequently, the support to which a precursor compound of manganese oxide is attached is dried and calcined to immobilize manganese oxide onto the support. The calcination is conducted at a temperature of 150 to 800°C, and preferably 300 to 800°C. This is because if the temperature is lower than 150°C, the drying speed is so low that manganese is concentrated at sites at which the solution remains, which may cause non-uniform distribution of the manganese oxide and increase in the particle diameter in some cases. The temperature is desirably higher than 300°C. Meanwhile, this is also because, if the temperature is higher than 800°C, thermal degradation such as decrease in specific surface area may occur due to sintering in some cases. The calcination is conducted for preferably 1 to 24 hours. By this step, manganese oxide having a size which does not exert any influence on X-ray diffraction measurement of the exhaust gas of the purification catalyst, for example, having an average particle diameter of 100 nm or less, can be supported with a uniform particle distribution.

[0032]

The method for producing an exhaust gas purification catalyst according to the present invention may optionally comprise a step of further causing barium to be supported. The step of further causing barium to be supported can be conducted by immersing the support on which the noble metal and manganese are supported in a barium solution, allowing the support to stand still, and then drying and calcining the support. For the barium solution, for example, barium acetate, barium nitrate, or barium oxide can be used. The concentration of the barium solution can be, for example, 0.05 to 20% by mass in terms of elemental barium.

[0033]

In the method for producing an exhaust gas purification catalyst according to the present invention, the order of the supporting of the noble metal and the manganese oxide on the support needs to be such that the noble metal is supported first, and the manganese oxide is supported later. This is because if the manganese oxide is supported before the noble metal, the noble metal is supported also on the manganese oxide, and the noble metal supported on the manganese oxide is easily coarsened. This is attributable to the fact that the electronegativity (1.61) of manganese is higher than the electronegativities of cerium and zirconium (cerium: 1.12, zirconium: 1.33), which are the main components of the OSC material, and hence the interaction acting between the manganese oxide and the noble metal is smaller than the interaction acting between the OSC material and the noble metal. In addition, the electronegativity (1.55) of alumina mixed in the support is comparable to the electronegativity of manganese. Hence, the interaction between the manganese oxide and the noble metal is comparable to the interaction between the alumina and the noble metal. However, since manganese oxide has a smaller surface area than alumina, the noble metal is easily coarsened on the manganese oxide.

[0034]

The method for producing an exhaust gas purification catalyst according to the present invention makes it possible to provide an exhaust gas purification catalyst which can achieve an extremely high NOx removal ratio during operation under a slightly lean condition, while providing HC and CO removal ratios comparable to those achieved by a conventional three-way catalyst, and which can provide a high low-temperature activity during cold start under stoichiometric conditions.

[Examples]

[0035]

Hereinafter, the present invention is described more specifically based on Examples. However, the exhaust gas purification catalyst and the method for producing the exhaust gas purification catalyst according to the present invention are not limited to the Examples below.

[0036]

[Honeycomb supports]

A slurry was prepared by mixing 400 g of an OSC material powder made of a composite oxide of cerium and zirconium at a ratio of Ce/Zr=3/7 in terms of amount of substance, 200 g of alumina powder, and 600 g of ion-exchanged water. Cylindrical honeycomb substrates (capacity: 0.025 L) having a height of 50 mm and a diameter of 25 mm were coated with this slurry, and calcined at 500°C for 1 hour. Thus, honeycomb supports were prepared. The amount of the slurry applied on each honeycomb substrate was 280 g/L.

[0037]

[Example 1]

A honeycomb support was immersed in 50 mL of a diamminedinitro platinum solution of 0.076 g/L in terms of elemental platinum and allowed to stand for 24 hours. Thus, platinum was adsorbed onto the honeycomb support. Then, excess water remaining on the support was removed. Subsequently, the honeycomb support was immersed in 50 mL of a palladium nitrate solution of 1.47 g/L in terms of elemental palladium and allowed to stand for 24 hours. Thus, palladium was adsorbed onto the honeycomb support. Then, excess water remaining on the support was removed. Subsequently, the honeycomb support was immersed in 50 mL of a rhodium nitrate solution of 0.147 g/L in terms of elemental rhodium, and allowed to stand for 24 hours. Thus, rhodium was adsorbed onto the honeycomb support. Then, excess water remaining on the support was removed, and the honeycomb support was calcined at 500°C for 1 hour. Thus, 0.15 g/L of platinum, 2.9 g/L of palladium, and 0.29 g/L of rhodium were supported. Next, the honeycomb support on which the noble metals were supported was immersed in a manganese nitride solution of 15 g/L in terms of elemental manganese, and allowed to stand for 5 minutes. Then, the excess solution remaining on the support was removed, and the honeycomb support was calcined at 500°C for 1 hour. Thus, 3.3 g/L, in terms of elemental manganese, of manganese oxide was supported. The supported amounts expressed in parts by mass relative to 100 parts by mass of the support (the mixture powder of the OSC powder and the alumina powder, excluding the honeycomb substrate; the same applies in Examples and Comparative Example below) were as follows: platinum:

0.05 parts by mass, palladium: 1.04 parts by mass, rhodium: 0.10 parts by mass, manganese oxide: 1.1 parts by mass in terms of elemental manganese.

[0038]

[Example 2]

Platinum, palladium, and rhodium were supported on a honeycomb support by the same method as in Example 1. Subsequently, the honeycomb support was immersed in a manganese nitride solution of 30 g/L in terms of elemental manganese and allowed to stand for 5 minutes. Then, the excess solution remaining on the support was removed, and the support was calcined at 500°C for 1 hour. Thus, 6.5 g/L, in terms of elemental manganese, of manganese oxide was supported. The supported amounts expressed in parts by mass relative to 100 parts by mass of the support were as follows: platinum: 0.05 parts by mass, palladium: 1.04 parts by mass, rhodium: 0.10 parts by mass, and manganese oxide: 2.3 parts by mass in terms of elemental manganese.

[0039]

[Example 3]

Platinum, palladium, and rhodium were supported on a honeycomb support by the same method as in Example 1. Subsequently, the honeycomb support was immersed in a manganese nitride solution of 60 g/L in terms of elemental manganese, and allowed to stand for 5 minutes. Then, the excess solution remaining on the support was removed, and the support was calcined at 500°C for 1 hour. Thus, 13.0 g/L, in terms of elemental manganese, of manganese oxide was supported. The supported amounts expressed in parts by mass relative to 100 parts by mass of the support were as follows: platinum: 0.05 parts by mass, palladium: 1.04 parts by mass, rhodium: 0.10 parts by mass, and manganese oxide: 4.6 parts by mass in terms of elemental manganese.

[0040]

[Example 4]

Platinum, palladium, and rhodium were supported on a honeycomb support by the same method as in Example 1. Subsequently, the honeycomb support was immersed in a manganese nitride solution of 90 g/L in terms of elemental manganese, and allowed to stand for 5 minutes. Then, the excess solution remaining on the support was removed, and the support was calcined at 500°C for 1 hour. Thus, 19.6 g/L, in terms of elemental manganese, of manganese oxide was supported. The supported amounts expressed in parts by mass relative to 100 parts by mass of the support were as follows: platinum: 0.05 parts by mass, palladium: 1.04 parts by mass, rhodium: 0.10 parts by mass, and manganese oxide: 7.0 parts by mass in terms of elemental manganese.

[0041]

[Comparative Example 1]

Platinum, palladium, and rhodium were supported on one of the above-described honeycomb supports at 0.15 g/L, 2.9 g/L, and 0.29 g/L, respectively. Then, the honeycomb support was calcined at 500°C for 1 hour. The supported amounts expressed in parts by mass relative to 100 parts by mass of the support were as follows: platinum: 0.05 parts by mass, palladium: 1.04 parts by mass, and rhodium: 0.10 parts by mass. This composition was the same as that in Example 1, except that manganese oxide is not supported, and is a composition generally employed for a three-way catalyst.

[0042]

Table 1 shows the amounts of metal catalysts supported in the exhaust gas purification catalysts of Examples 1 to 4 and Comparative Example 1.

[Table 1]

Table 1. Amounts of Metal Catalysts Supported (parts by mass)

	Amount of Mn supported (parts by mass)	Amount of Pt supported (parts by mass)	Amount of Pd supported (parts by mass)	Amount of Rh supported (parts by mass)
Example 1	1.1	0.05	1.04	0.10
Example 2	2.3	0.05	1.04	0.10
Example 3	4.6	0.05	1.04	0.10
Example 4	7.0	0.05	1.04	0.10
Comp. Ex. 1	0.0	0.05	1.04	0.10

[0043]

X-ray diffraction measurement (Cu-Kα radiation) was conducted regarding Example 1 and Comparative Example 1. Fig. 1 shows the diffraction charts. The diffraction charts of Example 1 and Comparative Example 1 were identical, although they were different in the presence or absence of the supporting of manganese oxide. This indicates that the manganese oxide did not contribute to the diffraction, i.e., the form of the manganese oxide was an ultrafine-particulate form. The particle diameter of the manganese oxide was plausibly about 100 nm or less.

[0044]

[Measurement of Removal Ratios]

The catalysts of Examples 1 to 4 and Comparative Example 1 were subjected to endurance testing by being held in air at 900°C for 20 hours, and were then evaluated for catalytic performance under a slightly lean condition. A model gas having an air-fuel ratio of 14.8, which was a model of a slightly lean exhaust gas, and which was made up of nitrogen monoxide (NO), propylene (C_3H_6), propane (C_3H_8), carbon monoxide (CO), oxygen (O_2), carbon dioxide (CO_2), water (H_2O), and nitrogen (N_2), was passed through each catalyst at a space velocity of 90000/h. The removal ratio was calculated according to the following formula from the ratio of the concentrations of each component in the model gas measured before and after the model gas passed through the catalyst. Figs. 2 and 3 show the results. The temperature of the model gas was 500°C. Table 2 shows the specific composition of the model gas. Note that the air-fuel ratio of the model gas was shown on the assumption that a model gas composition with an equivalent ratio of 1 was equivalent to an air-fuel ratio of 14.7.

(Removal Ratio) = 100 × {1 - (post-catalyst concentration)/(pre-catalyst concentration)}

[0045]

[Table 2]

Table 2. Composition of Slightly Lean Model Gas (air-fuel ratio: equivalent to

14.8)

Air-fuel ratio		Equivalent to 14.8
Base Gas	N_2 (ppm)	the balance
	CO_2 (%)	14.2
	O_2 (%)	0
	NO (ppm)	3600
	NO_2 (ppm)	0
	CO (ppm)	2196
	C_3H_6 (ppm)	363
	C_3H_8 (ppm)	182
	H_2O (%)	10
Perturbation	O_2 (%)	1.78
	CO (ppm)	19162
	C_3H_6 (ppm)	272
	C_3H_8 (ppm)	136

[0046]

As shown in Fig. 2, the exhaust gas purification catalysts of Examples 1 to 4 in which manganese oxide was supported achieved improved nitrogen oxide (NOx) removal ratios under the slightly lean condition. On the other hand, it was shown that the catalyst of Comparative Example 1, which was equivalent to a conventional three-way catalyst, was insufficient in nitrogen oxide (NOx) removal ratio. Moreover, as shown in the graph of Fig. 3, it was found that when the amount of the manganese oxide supported was 1 part by mass or more in terms of elemental manganese, the nitrogen oxide (NOx) removal ratio under the slightly lean condition increased, and that the removal ratio reached approximately 100% at 4 parts by mass or more. Moreover, irrespective of the amount of manganese supported, the removal ratios of hydrocarbons (HC) and carbon monoxide (CO) had high values and were comparable to those achieved by the catalyst of Comparative Example 1, which was equivalent to a conventional three-way catalyst.

[0047]

[Measurement of Oxygen Storage Amount]

The oxygen storage amounts of catalysts subjected to endurance test by being held in air at 900°C for 20 hours were investigated. Fig. 4 shows the outline of the oxygen storage amount measurement. Regarding a catalyst 1, model gases, which were models of exhaust gases with air-fuel ratios being equivalent to 13.5 and 15.5, respectively, and which were made up of nitrogen monoxide (NO), propylene (C_3H_6), propane (C_3H_8), carbon monoxide (CO), oxygen (O_2), carbon dioxide (CO_2), water (H_2O), and nitrogen (N_2), were alternately passed in a gas flow path 12 with a switching cycle of 45 seconds at a space velocity 45000/h. The oxygen storage amount of the catalyst was determined from the area of a region (the hatched portion in Fig. 4) defined by the delay time of a downstream air-fuel ratio sensor output 11 arranged after the catalyst from an upstream air-fuel ratio sensor output 10 arranged before the catalyst and by the difference in output between the two sensors. The temperature of the model gas was 500°C. Table 3 shows the specific compositions of the model gases. From the results shown in Fig. 5, it was found that the exhaust gas purification catalysts of Examples 1 to 4 in which manganese oxide was supported had higher oxygen storage amounts than the exhaust gas purification catalyst of Comparative Example 1 in which manganese oxide was not supported. Moreover, as shown in Fig. 6, it was found that, as the amount of the manganese oxide supported increased, the oxygen storage amount increased, i.e., the OSC performance was improved. The oxygen storage occurs through the points of contact between the OSC material and the noble metal particles. Hence, the large oxygen storage amount means that the number of the points of contact between the noble metal particles and the OSC material was large, and, in other words, that the noble metal particles were fine. Although the details were unclear, it is conceivable that the supported manganese oxide served as a diffusion barrier of the noble metals, and suppressed the diffusion and coarsening of the noble metals. In addition to this, plausible reasons for the improvement in OSC performance were as follows: the points of contact between the manganese oxide and the OSC material also served as flow paths of oxygen; manganese oxide itself was oxidized/reduced; etc.

[0048]

[Table 3]

Table 3. Compositions of Model Gases with Air-Fuel Ratios being Equivalent to 13.5 and 15.5, respectively

Air-fuel ratio		Equivalent to 13.5	Equivalent to 15.5
Base Gas	N2 (ppm)	the balance	the balance
	CO_2 (%)	14	14
	O_2 (%)	1.39	0
	NO (ppm)	4417	4417
	NO_2 (ppm)	0	0
	CO (ppm)	1968	11532
	C_3H_6 (ppm)	259	555
	C_3H_8 (ppm)	130	278
	H_2O (%)	10	10

[0049]

[Measurement of Low-Temperature Activity]

The low-temperature activity of the catalysts subjected to endurance testing (after being held in air at 900°C for 20 hours) in a stoichiometric exhaust gas was investigated. A model gas, which was a model of a stoichiometric exhaust gas with an air-fuel ratio being equivalent to 14.7, and which was made up of nitrogen monoxide (NO), propylene (C_3H_6), propane (C_3H_8), carbon monoxide (CO), oxygen (O_2), carbon dioxide (CO_2), water (H_2O), and nitrogen (N_2), was passed through each catalyst, while the temperature was raised from 200°C to 500°C at a rate of 30°C/minute. The removal ratio was calculated from the ratio of concentrations of each component in the model gas measured before and after the model gas passed through the catalyst. Figs. 7 and 8 show the 50% removal temperatures (the temperature at which each removal ratio reached 50%), which are indicative of the low-temperature activity. Table 4 shows the specific composition of the model gas. As shown in Fig. 7, it was found that the exhaust gas purification catalysts of Examples 1 to 4 had lower 50% removal temperatures under the stoichiometric condition than the exhaust gas purification catalyst of Comparative Example 1, and were excellent in low-temperature activity. Moreover, as shown in Fig. 8, when the amount of the manganese oxide supported was about 5 parts by mass or less, it was observed that the low-temperature activity was improved with the increase in the amount of manganese supported. However, when the amount of the manganese oxide supported exceeded about 5 parts by mass in terms of elemental manganese, the low-temperature activity turned to decrease. Hence, it has been shown that the amount of the manganese oxide supported is preferably 7 parts by mass or less in terms of elemental manganese. Note that, here, the amounts of the manganese oxide supported are shown in terms of elemental manganese, and do not include the mass of the oxygen constituting the manganese oxide with the elemental manganese.

[0050]

[Table 4]

Table 4. Composition of Stoichiometric Model Gas (air-fuel ratio: equivalent to 14.7)

Air-fuel ratio		14.7
Base Gas	N_2 (ppm)	the balance
	CO_2 (%)	14.2

	O_2 (%)	0
	NO (ppm)	3483
	NO_2 (ppm)	0
	CO (ppm)	2503
	C_3H_6 (ppm)	378
	C_3H_8 (ppm)	189
	H_2O (%)	10
Perturbation	O_2 (%)	1.62
	CO (ppm)	20534
	C_3H_6 (ppm)	272
	C_3H_8 (ppm)	136

[0051]

[Measurement of BET Specific Surface Area]

Catalysts subjected to endurance testing (after being held in air at 900°C for 20 hours) were subjected to BET specific surface area measurement by using nitrogen (N_2) as the adsorption gas. Fig. 9 shows the measurement results. From the results shown in Fig. 9, it was found that the specific surface area decreased with the increase in the amount of the manganese oxide supported. Since decrease in specific surface area leads to deterioration in gas diffusibility, it has been shown that the supporting of manganese oxide also causes deterioration in catalytic performance.

[0052]

From the above-described experimental results, it was shown that, by the supporting of manganese oxide, the exhaust gas purification catalysts of Examples 1 to 4 achieved increased oxygen storage amounts and improved nitrogen oxide (NOx) removal ratios under a slightly lean condition. Moreover, it was shown that the exhaust gas purification catalysts of Examples 1 to 4 achieved enhanced low-temperature activity under a stoichiometric condition.

In addition, it has been found that the supporting of manganese oxide has two effects, namely, a catalytic performance improvement effect owing to the improvement in OSC performance and suppression of diffusion and coarsening of the noble metal, and a catalytic performance deterioration effect due to the decrease in specific surface area, and that the catalytic performance is determined by trade-off there between. Therefore, it has been found that the amount of the manganese oxide supported is preferably 1 part by mass to 7 parts by mass and more preferably 4 parts by mass to 5 parts by mass, in terms of elemental manganese.

[Reference Signs List]

[0053]

1	catalyst
10	upstream air-fuel ratio sensor
11	downstream air-fuel ratio sensor
12	gas flow path
A	gas flow

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[Name of Document] **Claims**

We Claim:

[Claim 1] An exhaust gas purification catalyst comprising:

a support selected from a material with oxygen storage capacity (OSC material) and a mixture powder of an OSC material and alumina powder;

at least one noble metal supported on the support, the at least one noble metal selected from the group consisting of platinum, palladium, and rhodium; and

manganese oxide further supported on the support.

[Claim 2] The exhaust gas purification catalyst according to claim 1, wherein

an amount of the manganese oxide supported is 1 to 7 parts by mass, in terms of elemental manganese, relative to 100 parts by mass of the support.

[Claim 3] The exhaust gas purification catalyst according to claim 1 or 2, wherein

an amount of the manganese oxide supported is 4 to 5 parts by mass, in terms of elemental manganese, relative to 100 parts by mass of the support.

[Claim 4] The exhaust gas purification catalyst according to any one of claims 1 to 3, wherein

an amount of the noble metal supported is 0.1 to 5 parts by mass relative to 100 parts by mass of the support.

[Claim 5] The exhaust gas purification catalyst according to any one of claims 1 to 4, wherein the OSC material comprises one or more selected from the group consisting of cerium oxide, composite oxides of cerium and zirconium, and composite oxides comprising at least one rare-earth metal selected from the group consisting of lanthanum, neodymium, praseodymium, and yttrium in addition to cerium oxide or a composite oxide of cerium and zirconium.

[Claim 6] An exhaust gas purification apparatus for a gasoline engine, comprising the exhaust gas purification catalyst according to any one of claims 1 to 5.

[Claim 7] A method for producing an exhaust gas purification catalyst, comprising the steps of:

causing at least one noble metal selected from the group consisting of platinum, palladium, and rhodium to be supported on a support selected from an OSC material and a mixture powder of an OSC material and alumina powder; and

further causing manganese oxide to be supported on the support on which the at least one noble metal has been supported.

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[Name of Document] **Abstract**

[Abstract]

[Problem to be Solved] To provide an exhaust gas purification catalyst which can achieve an extremely high NOx removal ratio during operation under a slightly lean condition, while providing HC and CO removal ratios comparable to those achieved by a conventional three-way catalyst, and which can provide a high low-temperature activity during operation under a stoichiometric condition.

[Solution] Provided is an exhaust gas purification catalyst comprising: a support selected from an OSC material and a mixture powder of an OSC material and alumina powder; at least one noble metal supported on the support, the at least one noble metal being selected from the group consisting of platinum, palladium, and rhodium; and manganese oxide further supported on the support.

[Selected Drawing] None

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