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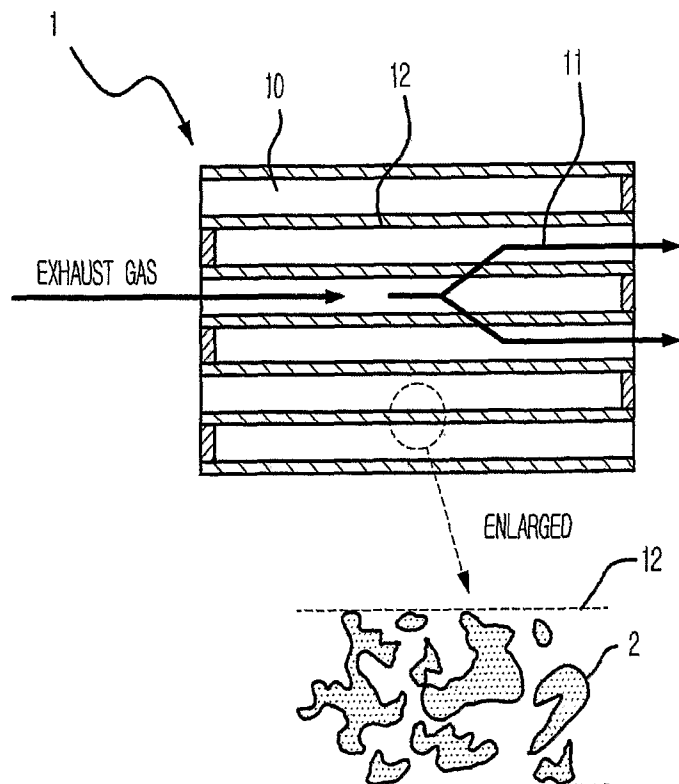
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[Continued on next page]

(54) Title: EXHAUST GAS-PURIFYING CATALYST



(57) **Abstract:** An exhaust gas-purifying catalyst is disclosed. The catalyst includes a filter substrate having a wall flow structure and a catalyst bed formed on cell partition walls of the filter substrate. The catalyst bed contain a porous oxide, a noble metal supported on the porous oxide, and an alkali metal supported on the porous oxide in an amount of 0.6 mole or more per 1L of the filter substrate. Since a large amount of alkali metal is supported, the alkali metal is likely to contact particulate material(PM) mainly containing carbon. Accordingly, the oxidation temperature of the PM can be lowered. Thus, it is possible to oxidize PM even at a low temperature of 300 °C or below.



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## DESCRIPTION

## EXHAUST GAS-PURIFYING CATALYST

## BACKGROUND OF THE INVENTION

## 1. Field of the Invention

[0001] The present invention relates to an exhaust gas-purifying catalyst capable of purifying particulate material (hereinafter, referred to as "PM"), which is contained in a diesel exhaust gas or the like and mainly contains carbon, from a low-temperature range. The exhaust gas-purifying catalyst according to the present invention is particularly useful as a catalyst for purifying exhaust gas for diesel engines because it can purify not only PM, but also HC, CO, or NO<sub>x</sub>.

## 2. Description of the Related Art

[0002] As to gasoline engines, amounts of noxious ingredients contained in an exhaust gas have been remarkably reduced by virtue of the strict regulations for exhaust gases and the advance of technologies coping with such regulations. On the other hand, as to diesel engines, it is difficult to purify exhaust gases, as compared to gasoline engines, due to an unusual circumstance of diesel engines that noxious ingredients are emitted in the form of PM (carbon particulates, sulfur-based particulates such as sulfate particulates, high-molecular hydrocarbon particulates (soluble organic fraction (SOF)), or the like).

[0003] Known exhaust gas purifiers for diesel engines, which have

been developed up to date, are mainly classified into a trap type (wall flow structure) and an open type (straight flow structure). For the trap type exhaust gas purifier, a clogged honeycomb structure (a diesel PM filter (hereinafter, referred to as a "DPF")) made of ceramic is known. For example, a DPF is known which includes a ceramic honeycomb structure with cells clogged at opposite ends of openings thereof in the form of a checkered pattern alternately. The DPF includes inlet cells each clogged at an exhaust gas downstream side thereof, outlet cells each arranged adjacent to the inlet cells and clogged at an exhaust gas upstream side thereof, and cell partition walls partitioning the inlet cells and the outlet cells from each other. In this DPF, exhaust gas is filtered by pores of the cell partition walls, which capture PM, so that emission of PM is suppressed.

[0004] In the above-mentioned DPF, however, an increase in pressure loss occurs due to accumulation of PM. As a result, it is necessary to regenerate the DPF by periodically removing the accumulated PM using a certain means. In accordance with a conventional technology, when an increase in pressure loss as mentioned above occurs, it is possible to regenerate DPF by burning the accumulated PM using a flow of hot exhaust gas. In this case, however, an increased amount of the accumulated PM may cause an increase in temperature during the burning process. For this reason, the DPF may be melted and damaged, or may be broken due to thermal stress.

[0005] Therefore, filter catalysts have recently been developed. For example, Japanese Patent Publication No. 7-106290 discloses a filter catalyst, the filter catalyst comprises a coating layer

made of alumina, etc. and formed on surfaces of cell partition walls of a DPF, and a catalytic metal such as platinum (Pt) supported on the coating layer. With this filter catalyst, captured PM is oxidized and burnt in accordance with a catalytic reaction of the catalytic metal. As the PM is burnt simultaneously with or successively to the capture thereof, the filter catalyst can be continuously regenerated. The catalytic reaction is carried out at a relatively low temperature. Also, the burning is carried out for a small amount of captured PM. As a result, the thermal stress applied to the filter catalyst is low. Thus, there is an advantage in that breakage of the filter catalyst is prevented.

[0006] Japanese Patent Application Publication No. 9-094434 also discloses a filter catalyst wherein a coating layer supporting a catalytic metal is formed not only on cell partition walls, but also on pores of the cell partition walls. Since the catalytic metal is also supported in the pores of the cell partition walls, the catalytic metal is likely to contact the PM. The PM captured by the pores can also be oxidized and burnt.

[0007] Supporting alkali metal or alkaline earth metal on a coating layer of a filter catalyst, together with noble metal, is also disclosed in Japanese Patent Application Publication No. 2003-049627 or Japanese Patent Application Publication No. 2003-049631. The alkali metal or alkaline earth metal forms a nitrate or sulfate in an exhaust gas. When the nitrate or sulfate is decomposed, active oxygen is emitted. With the active oxygen, it is possible to oxidize the PM. Thus, it is possible to effectively oxidize the PM, and thus, to effectively purify the

exhaust gas.

[0008] However, the filter catalyst including the coating layer supporting alkali metal or alkaline earth metal, together with noble metal, also has a problem in that a sufficient PM oxidation performance cannot be exhibited in a general operation range of about 400°C or below.

#### SUMMARY OF THE INVENTION

[0009] The present invention has been made in view of the above-mentioned problems, and it is an aspect of the invention to provide an exhaust gas-purifying catalyst which is capable of oxidizing PM even in a low-temperature range of 300°C or below and enhancing PM oxidation performance.

[0010] In one aspect, the present invention provides an exhaust gas-purifying catalyst comprising: a filter substrate having a wall flow structure, the filter substrate including inlet cells each clogged at an exhaust gas downstream side of the inlet cell, outlet cells each arranged adjacent to the inlet cells and clogged at an exhaust gas upstream side of the outlet cell, and porous cell partition walls partitioning the inlet cells and the outlet cells from each other and having a plurality of pores; and a catalyst bed formed on the cell partition walls, wherein the catalyst bed contains a porous oxide, a noble metal supported on the porous oxide, and an alkali metal supported on the porous oxide in an amount of 0.6 mole or more per 1L of the filter substrate, and oxidizes particulate material (PM), which mainly contains carbon, and is captured by the filter substrate, from a low-temperature range of 300°C or below.

[0011] The catalyst may further comprise a protection layer formed between the filter substrate and the catalyst bed, and made of an oxide reactable with the alkali metal.

#### BRIEF DESCRIPTION OF THE DRAWINGS

[0012] The above and other objects, and features of the present invention will become apparent from the following description of preferred embodiment, given in conjunction with the accompanying drawings, in which:

FIG. 1 is an explanation view illustrating a structure of an exhaust gas-purifying catalyst according to an exemplary embodiment of the present invention;

FIG. 2 is a graph depicting a PM oxidation initiation temperature and a PM oxidation peak temperature;

FIG. 3 is a graph depicting a relation between temperature and differential pressure;

FIG. 4 is a graph depicting a relation between potassium supporting amount and PM oxidation initiation temperature; and

FIG. 5 is an explanation view illustrating a structure of an exhaust gas-purifying catalyst according to another exemplary embodiment of the present invention.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0013] Various embodiments of the present invention will now be described in detail with reference to the accompanying drawings.

[0014] The present invention provides an exhaust gas-purifying catalyst including a filter substrate and a catalyst bed formed on cell partition walls of the filter substrate. The filter

substrate has a wall flow structure similar to a conventional DPF including inlet cells each clogged at an exhaust gas downstream side thereof, outlet cells each arranged adjacent to the inlet cells and clogged at an exhaust gas upstream side thereof, and porous cell partition walls partitioning the inlet cells and the outlet cells from each other and having a plurality of pores.

[0015] The filter substrate may be formed of a metal foam or a heat-resistant non-woven fabric. The filter substrate may also be made of heat-resistant ceramics such as cordierite or silicon carbide. For example, where the filter substrate is made of heat-resistant ceramics, a clayey slurry containing cordierite powder as a major component thereof is prepared. The prepared slurry is shaped by extrusion, and is then calcined. In place of the cordierite powder, a mixture of alumina powder, magnesia powder and silica powder having the same composition as the cordierite may be prepared. Openings of the cells at one end of the filter substrate are clogged in the form of a checkered pattern by clayey slurries having a shape similar to that of the cell openings, respectively. Also, openings of the cells each arranged adjacent to one of the clogged cells are clogged at the other end of the filter substrate. Thereafter, the clogging material is fixed using calcining or the like. Thus, a filter substrate having a honeycomb structure can be fabricated. The cross-sectional shapes of the inlet cells and outlet cells may be triangular, square, hexagonal, circular, etc. Of course, they are not limited to such shapes.

[0016] The cell partition walls have a porous structure allowing an exhaust gas to pass therethrough. In order to form pores in

the cell partition walls, combustible powder such as carbon powder, wood powder, starch, or resin powder is mixed with the slurry. As the combustible powder is burnt during the calcining process, pores are formed in the cell partition walls. It is possible to control the diameter and volume of the pores by adjusting the size and content of the combustible powder. The inlet cells and outlet cells are communicated with each other by the pores. Accordingly, although PM is captured in the pores, gas can flow from the inlet cells to the outlet cells via the pores.

[0017] Preferably, the cell partition walls have a porosity of 40% to 70%. Also, the pores preferably have an average diameter of 10  $\mu\text{m}$  to 40 $\mu\text{m}$ . Where the cell partition walls have the porosity and average pore diameter ranging as described above, it is possible to suppress an increase in pressure loss even when the catalyst bed is formed to range from 100g/L to 200g/L. It is also possible to suppress a decrease in strength. Thus, capture of PM can be more effectively achieved.

[0018] In the exhaust gas-purifying catalyst according to the present invention, the catalyst bed is provided at the cell partition walls of the filter substrate. Although the catalyst bed may be formed only on the surfaces of the cell partition walls, it is preferred that the catalyst bed be also formed on the surfaces of the pores in the cell partition walls. The catalyst bed contains a porous oxide, noble metal supported on the porous oxide, and alkali metal supported on the porous oxide.

[0019] The porous oxide may include alumina, zirconia, titania, silica, or ceria conventionally used as a catalyst support, or a composite oxide or mixture of at least two of the catalyst

supports. Among these materials,  $\gamma$ -alumina having a large specific surface area is preferable.

[0020] The noble metal supported on the porous oxide may be selected from Pt, Pd, Rh, Ir, Ru, etc. Among these elements, it is preferable to select Pt, which exhibits a high oxidation activity to PM. Preferably, the supported amount of the noble metal ranges from 0.1g to 5g per 1L of the filter substrate. When the supported amount of the noble metal is less than the above range, it is impractical due to an excessively low activity. On the other hand, when the supported amount of the noble metal is more than the above range, saturated activity is exhibited, and the costs are increased. The supporting of the noble metal may be achieved by an adsorption supporting method, a impregnating supporting method, or the like using a solution containing a nitrate of the noble metal dissolved therein.

[0021] For the alkali metal supported on the porous oxide, Na, K, Li, Cs, etc. may be used. Among these elements, K is preferable which exhibits a particularly-high oxidation activity to PM. Preferably, the supported amount of the alkali metal is 0.6 mole or more per 1L of the filter substrate. When the supported amount of the alkali metal is less than the above range, it is difficult to initiate oxidation of PM at a temperature of 300°C or below. Although there is no particular upper limit of the supported amount of the alkali metal, it is preferred that the supported amount of the alkali metal have an upper limit of about 2 moles per 1L of the filter substrate, for purification of exhaust gases of vehicles. When the supported amount of the alkali metal exceeds the upper limit, a degradation in the activity of the noble

metal occurs, thereby degrading the performance capable of purifying HC, CO, NO<sub>x</sub>, etc.

[0022] In addition to the noble metal and alkali metal, transition metals, typical metals, alkaline earth metals, rare earth elements, etc. may be supported in catalyst bed within a range giving no adverse effect on the purification performance.

[0023] The catalyst bed is formed by preparing a slurry of the porous oxide powder with a binder ingredient such as an alumina sol and water, applying the slurry to the cell partition walls, and calcining the applied slurry, thereby forming a coating layer. In this case, it is preferable to support the noble metal and alkali metal on the coating layer. Alternatively, a slurry may be prepared using catalyst powder prepared by previously supporting the noble metal on the porous oxide powder. In this case, the supporting of the alkali metal may be performed after the formation of the catalyst bed using the prepared slurry. The application of the slurry to the cell partition walls may be achieved using a general dipping method. However, it is preferable to remove a surplus of the slurry filled in the pores, while forcibly filling the slurry in the pores of the cell partition walls by air blow or air suction.

[0024] In this case, the formation amount of the coating layer or catalyst bed preferably ranges from 30g to 200g per 1L of the filter substrate. When the formation amount of the coating layer or catalyst bed is less than 30g/L, it is impossible to prevent a degradation in the durability of the noble metal. On the other hand, the formation amount of the coating layer or catalyst bed exceeding 200g/L is impractical due to an excessively high

pressure loss.

[0025] Preferably, a protection layer made of an oxide reactable with the alkali metal is formed between the filter substrate and the catalyst bed. The protection layer functions to suppress the alkali metal supported in the catalyst bed from migrating to the filter substrate in a high-temperature atmosphere, and thus, to suppress a degradation in the strength of the filter substrate. It is also possible to suppress a degradation in the concentration of the alkali metal in the catalyst bed caused by the migration of the alkali metal to the filter substrate. Accordingly, a degradation in PM oxidation activity can be suppressed.

[0026] Examples of the oxide reactable with the alkali metal may be  $\text{TiO}_2$ ,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{B}_2\text{O}_3$ ,  $\text{P}_2\text{O}_5$ , etc. Preferably, the formation amount of the protection layer corresponds to a thickness of 0.001 $\mu\text{m}$  to 5 $\mu\text{m}$  or ranges from 1g to 50g per 1L of the filter substrate. When the formation amount of the protection layer is less than the above range, it is difficult to suppress the migration of the alkali metal to the filter substrate. On the other hand, the formation amount of the protection layer exceeding the above range is impractical due to an excessive increase in pressure loss.

[0027] That is, in the exhaust gas-purifying catalyst according to the present invention, alkali metal is supported in an amount of 0.6 mole or more per 1L of the filter substrate. As a large amount of alkali metal is supported as described above, it is possible to achieve an increase in the possibility that the alkali metal comes into contact with PM. Also, the temperature, at which PM can be oxidized, is lowered, so that PM can be oxidized at a

low temperature of 300°C or below.

[0028] Accordingly, the exhaust gas-purifying catalyst according to the present invention can purify PM by oxidation from a low-temperature range lower than 300°C, so that the PM oxidation performance can be considerably enhanced. As a result, accumulation of PM is suppressed, thereby suppressing an increase in pressure loss. Thus, continuous regeneration of the catalyst for PM purification can be stably achieved, so that it is possible to prevent defects such as cracks caused by forced regeneration.

[0029] Where a protection layer made of an oxide reactable with the alkali metal is formed between the filter substrate and the catalyst bed, as described above, it is possible to suppress the alkali metal from migrating to the filter substrate by the protection layer. Accordingly, it is possible to suppress a degradation in the strength of the filter substrate in accordance with a reaction of the alkali metal with cordierite. It is also possible to suppress a degradation in PM oxidation performance because consumption of the alkali metal is suppressed in accordance with the reaction.

#### EXAMPLES

(Example 1)

[0030] FIG. 1 illustrates an exhaust gas-purifying catalyst according to this example. This catalyst includes: a filter substrate 1 including inlet cells 10 each clogged at an exhaust gas downstream side thereof, outlet cells 11 each arranged adjacent to the inlet cells, and clogged at an exhaust gas upstream side thereof, and porous cell partition walls 12 partitioning the

inlet cells 10 and the outlet cells 11 from each other; and a catalyst bed 2 formed on the surfaces of the cell partition walls 12 and on the surfaces of pores formed in the cell partition walls 12.

[0031] For the filter substrate 1, a commercially-available DPF made of cordierite is used. This DPF has a test piece size (35cc, 30mm (diameter) x 50mm (length)), and a porosity of 60% to 67%, a pore volume of 0.58cc/g to 0.65cc/g, and an average pore diameter of 25 $\mu$ m to 35 $\mu$ m at the cell partition walls 12. A detailed description of the structure of the catalyst bed 2 will be given through a description of a method for manufacturing the catalyst bed 2.

[0032] A slurry is prepared by mixing catalyst powder previously supporting Pt with  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> powder (specific surface area of 220m<sup>2</sup>/g), together with an alumina sol and ion-exchanged water, such that the mixture has a viscosity of 100cps or less. The prepared slurry is milled such that solid grains thereof have an average diameter of 1 $\mu$ m or less. Thereafter, the filter substrate 1 is dipped in the slurry, to allow the slurry to be introduced into the cells. The slurry is then sucked from the end of the filter substrate 1 opposite to the dipped end in a state in which the filter substrate 1 has been upwardly taken out of the slurry, to remove a surplus of the slurry from the filter substrate 1. After being dried by ventilation, the filter substrate 1 is calcined at 500°C for 3 hours. This procedure is performed two times, in order to adjust the formation of the coating layer such that the coating layer is formed on the inlet cells 10 and outlet cells 11 in substantially same amounts, respectively. The

formation amount of the coating layer is 150g per 1L of the filter substrate 1. The coating layer is formed on the surfaces of the inlet cells 10 and outlet cells 11 and on the surfaces of the pores. The Pt supporting amount of the coating layer is 3g/L.

[0033] In order to support Li in the coating layer in an amount of 0.6 mole/L, a certain amount of a lithium acetate aqueous solution having a certain concentration is then impregnated into the coating layer. After being dried, the coating layer is calcined at 300°C for 3 hours. Thus, the coating layer 2 supporting Pt and Li is completely formed.

(Comparative Example 1)

[0034] An exhaust gas-purifying catalyst according to Comparative Example 1 is prepared in the same manner as Example 1, except that the supported amount of Li is 0.3 mole/L.

(Example 2)

[0035] An exhaust gas-purifying catalyst according to Example 2 is prepared in the same manner as Example 1, except that a potassium acetate aqueous solution is used in place of the lithium acetate aqueous solution, and K is supported in the coating layer in an amount of 0.6 mole/L.

(Example 3)

[0036] An exhaust gas-purifying catalyst according to Example 3 is prepared in the same manner as Example 1, except that a potassium acetate aqueous solution is used in place of the lithium acetate aqueous solution, and K is supported in the coating layer in an amount of 1.5 mole/L.

(Comparative Example 2)

[0037] An exhaust gas-purifying catalyst according to

Comparative Example 2 is prepared in the same manner as Example 1, except that a potassium acetate aqueous solution is used in place of the lithium acetate aqueous solution, and K is supported in the coating layer in an amount of 0.3 mole/L.

(Comparative Example 3)

[0038] An exhaust gas-purifying catalyst according to Comparative Example 3 is prepared in the same manner as Example 1, except that the alkali metal is not supported.

(Comparative Example 4)

[0039] An exhaust gas-purifying catalyst according to Comparative Example 4 is prepared in the same manner as Example 1, except that a barium acetate aqueous solution is used in place of the lithium acetate aqueous solution, and Ba is supported in the coating layer in an amount of 0.3 mole/L.

<Experimental Example 1>

[0040] Each of the above-described catalysts was mounted to an exhaust system of an engine bench, to which a diesel engine (displacement volume: 2,000 cc) was mounted. For attachment of PM to each catalyst, the diesel engine was operated for 2 hours under the conditions of an engine RPM of 2,000 rpm, a torque of 3.0 kg, and an exhaust gas temperature of 250°C.

[0041] Each PM-attached catalyst was loaded in an evaluation apparatus, and was then subjected to an increase in temperature from room temperature to a temperature of 600°C at a rate of 10°C/min under the condition in which a model gas consisting of 10% of O<sub>2</sub>, 500 ppm of NO, and the balance of N<sub>2</sub> flowed through the catalyst at a flow rate of 0.03m<sup>3</sup>/min.

[0042] The concentration of CO<sub>2</sub> in a gas emitted from each

catalyst during the temperature increase was continuously measured. Based on the results of the measurement, the temperature, at which emission of CO<sub>2</sub> was begun, was recorded as a PM oxidation initiation temperature, and the temperature, at which the measured CO<sub>2</sub> concentration had a peak value, was recorded as a PM oxidation peak temperature. FIG. 2 depicts the recorded results.

<Experimental Example 2>

[0043] For each of the catalysts according to Example 2 and 3 and Comparative Example 2, the pressure difference between the gas introduced into the catalyst and the gas emitted from the catalyst during the temperature increase was continuously measured. FIG. 3 depicts the measured results.

<Evaluation>

[0044] Referring to FIG. 2, it can be seen that the catalysts of the examples, wherein Li or K is supported in an amount of 0.6 mole/L, exhibit a low PM oxidation initiation temperature and a low PM oxidation peak temperature, as compared to the catalysts of Comparative Examples 1 and 2. That is, it can be clearly seen that the catalysts of the examples can oxidize PM from a low-temperature range, and exhibit a high PM oxidation activity in the low-temperature range.

[0045] It can also be seen that the supported amount of K is preferable to be 1.5g/L, as compared to 0.6g/L, because the catalyst of Example 3 exhibits a lower temperatures than that of Example 2. Also, it can be seen that K is more preferable than Li because the catalyst of Example 2 exhibits a lower temperatures than that of Example 1. On the other hand, it can be seen that

Ba representing the alkaline earth metal of Comparative Example 4 has no effect obtained in a supported state.

[0046] As shown in FIG. 3, in the catalyst of Example 2, the differential pressure thereof, which has increased, slightly decreases around 300°C, again increases, and then greatly decreases around 400°C. In the catalyst of Example 3, the differential pressure thereof, which has increased, greatly decreases around 280°C. In the catalyst of Comparative Example 2, however, the differential pressure thereof still exhibits an increase around 300°C, and initially exhibits a decrease around 400°C.

[0047] That is, the decrease in differential pressure in the catalyst of Example 2 near 300°C for the moment is due to the presence of K in a high concentration of 0.6 mole/L. In the catalyst of Example 3, wherein K is supported in a high concentration of 1.5 mole/L, this decrease is predominantly exhibited. As shown in FIG. 2, effect differences among Example 2, Example 3, and Comparative Example 2 correspond to differences of the above-described action, respectively. Accordingly, it can be seen that it is necessary to support K in an amount of 0.6 mole/L.

#### <Experimental Example 3 · Evaluation>

[0048] A plurality of catalysts were prepared in the same manner as that of Example 2, except that they had different K supporting amounts within a range of 0 mole/L to 1.5 mole/L, respectively. For each of the prepared catalysts, a PM oxidation initiation temperature was measured in accordance with the above-described method. FIG. 4 depicts the measured results.

[0049] Referring to the curve of FIG. 4, it can be seen that there is an inflection point around a K supporting amount of 0.5 mole/L, and a PM oxidation initiation temperature of 300°C or below is exhibited when the K supporting amount is 0.6 mole/L or more. (Example 4)

[0050] FIG. 5 illustrates an exhaust gas-purifying catalyst according to this example. The catalyst according to this example includes: a filter substrate 1 including inlet cells 10 each clogged at an exhaust gas downstream side thereof, outlet cells 11 each arranged adjacent to the inlet cells and clogged at an exhaust gas upstream side thereof, and cell partition walls 12 partitioning the inlet cells 10 and the outlet cells 11 from each other; a protection layer 3 formed on the surfaces of the cell partition walls 12 and on the surfaces of pores formed in the cell partition walls 12; and a catalyst bed 2 formed on the surface of the protection layer 3. This catalyst is identical to that of Example 2, except that the catalyst includes the protection layer 3. Accordingly, a detailed description of the structure of the catalyst bed 2 will be given through a description of a method for manufacturing the catalyst bed 2.

[0051] The filter substrate 1 is dipped in a slurry, in which a silica sol is distributed, to allow the slurry to be introduced into the cells. The slurry is then sucked from the end of the filter substrate 1 opposite to the dipped end in a state in which the filter substrate 1 has been upwardly taken out of the slurry, to remove a surplus of the slurry from the filter substrate 1. After being dried by ventilation, the filter substrate 1 is calcined at 500°C for 3 hours. This procedure is performed two

times, in order to adjust the formation of the protection layer such that the protection layer is formed on the inlet cells 10 and outlet cells 11 in substantially same amounts, respectively. The formation amount of the protection layer is 20g per 1L of the filter substrate 1 (substantially a thickness of 1 $\mu$ m). Thereafter, the catalyst bed 2 is formed in the same manner as that of Example 2.

(Example 5)

[0052] The protection layer 3 which is made of TiO<sub>2</sub> is formed in the same manner as that of Example 4, except that a titania sol is used in place of the silica sol. Thereafter, the catalyst bed 2 is formed in the same manner as that of Example 2.

(Example 6)

[0053] The protection layer 3 which is made of Al<sub>2</sub>O<sub>3</sub> is formed in the same manner as that of Example 4, except that an alumina sol is used in place of the silica sol. Thereafter, the catalyst bed 2 is formed in the same manner as that of Example 2.

<Experimental Example 4 · Evaluation>

[0054] For each of the catalysts according to Embodiments 2, 4, 5, and 6, and Comparative Example 3, a high-temperature durability test was carried out by maintaining the catalyst in a heated state in an electric furnace at 700°C for 10 hours. Thereafter, the above-described test was carried out to measure a PM oxidation initiation temperature. For each catalyst subjected to the high-temperature durability test, the strength of the filter substrate 1 was measured by Autograph. Based on the measured results, the catalysts were evaluated to be "○" when exhibiting a compressive strength of more than 2 MPa, "△" when exhibiting

a compressive strength ranging from 1.5 MPa to 2 MPa, or "x" when exhibiting a compressive strength of less than 1.5 MPa. Table 1 shows the evaluated results.

[0055] [Table 1]

|               | K<br>Supporting<br>Amount | Protection<br>Layer            | PM Oxidation<br>Initiation Temp. | Substrate<br>Strength |
|---------------|---------------------------|--------------------------------|----------------------------------|-----------------------|
| Example 2     | 0.6 mole/L                | -                              | 360°C                            | x                     |
| Example 4     | 0.6 mole/L                | SiO <sub>2</sub>               | 316°C                            | ○                     |
| Example 5     | 0.6 mole/L                | TiO <sub>2</sub>               | 319°C                            | ○                     |
| Example 6     | 0.6 mole/L                | Al <sub>2</sub> O <sub>3</sub> | 341°C                            | △                     |
| Comp. Exam. 3 | -                         | -                              | 434°C                            | ○                     |

[0056] Referring to Table 1, it can be seen that the catalyst of Example 2 exhibits a degradation in substrate strength after the high-temperature durability test. However, such a degradation in substrate strength can be suppressed by forming a protection layer, as in Examples 4 to 6. When a protection layer made of SiO<sub>2</sub> or TiO<sub>2</sub> is formed, results similar to those of Comparative Example 3 supporting no K are obtained. In this case, accordingly, it is possible to greatly suppress a degradation in substrate strength.

[0057] While the invention has been shown and described with respect to the preferred embodiments, it will be understood by those skilled in the art that various changes and modifications may be made without departing from the spirit and scope of the invention as defined in the following claims.

## CLAIMS

1. An exhaust gas-purifying catalyst comprising:  
a filter substrate having a wall flow structure, the filter substrate including inlet cells each clogged at an exhaust gas downstream side of the inlet cell, outlet cells each arranged adjacent to the inlet cells and clogged at an exhaust gas upstream side of the outlet cell, and porous cell partition walls partitioning the inlet cells and the outlet cells from each other and having a plurality of pores; and  
a catalyst bed formed on the cell partition walls,  
wherein the catalyst bed contains a porous oxide, a noble metal supported on the porous oxide, and an alkali metal supported on the porous oxide in an amount of 0.6 mole or more per 1L of the filter substrate,  
wherein the catalyst bed oxidizes particulate material, which mainly contains carbon and is captured by the filter substrate, from a low-temperature range of 300°C or below.
2. The exhaust gas-purifying catalyst according to claim 1, wherein the supported amount of the alkali metal is 2 mole or less per 1L of the filter substrate.
3. The exhaust gas-purifying catalyst according to claim 1, wherein the alkali metal is potassium.
4. The exhaust gas-purifying catalyst according to claim 1, further comprising a protection layer formed between the filter

substrate and the catalyst bed, and made of an oxide reactable with the alkali metal.

5. The exhaust gas-purifying catalyst according to claim 4, wherein the protection layer has a thickness of 0.001 $\mu$ m to 5 $\mu$ m.

FIG. 1

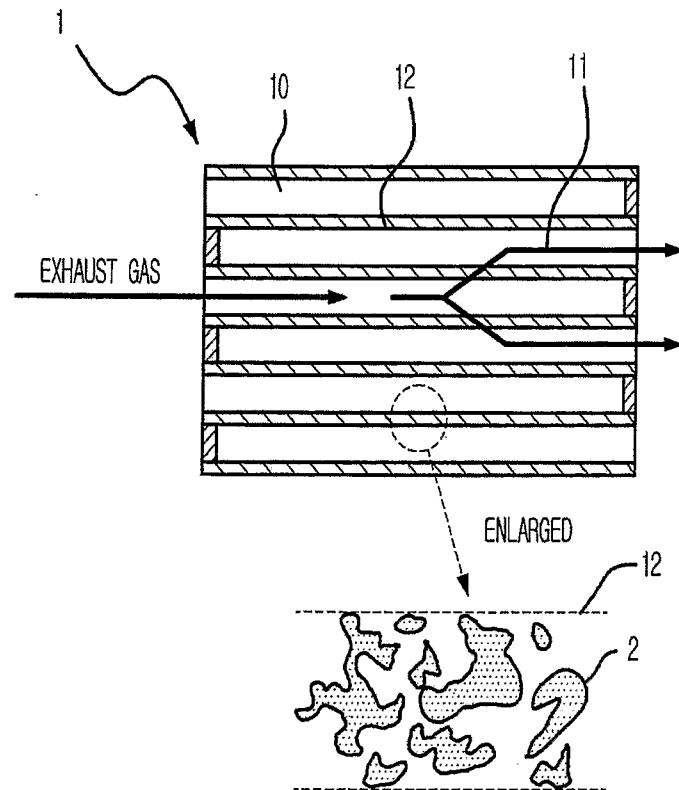


FIG. 2

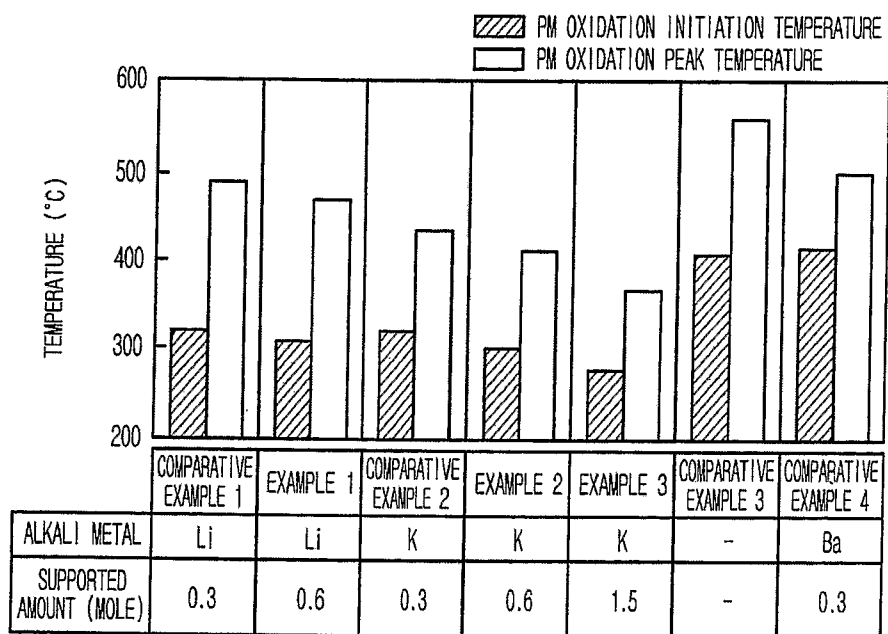


FIG. 3

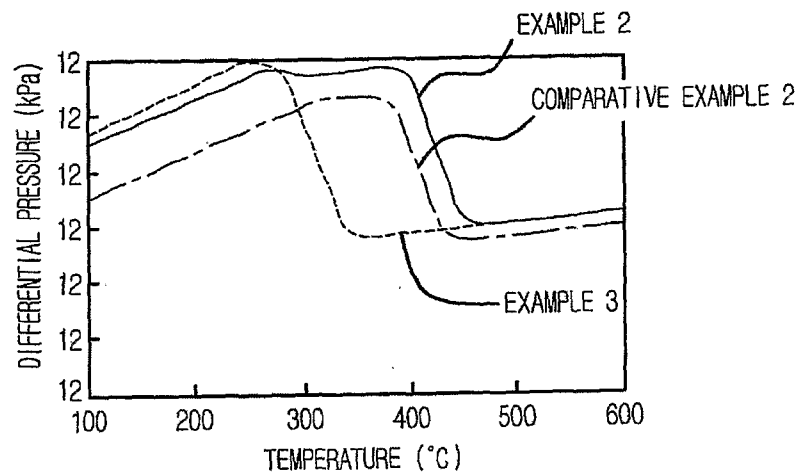


FIG. 4

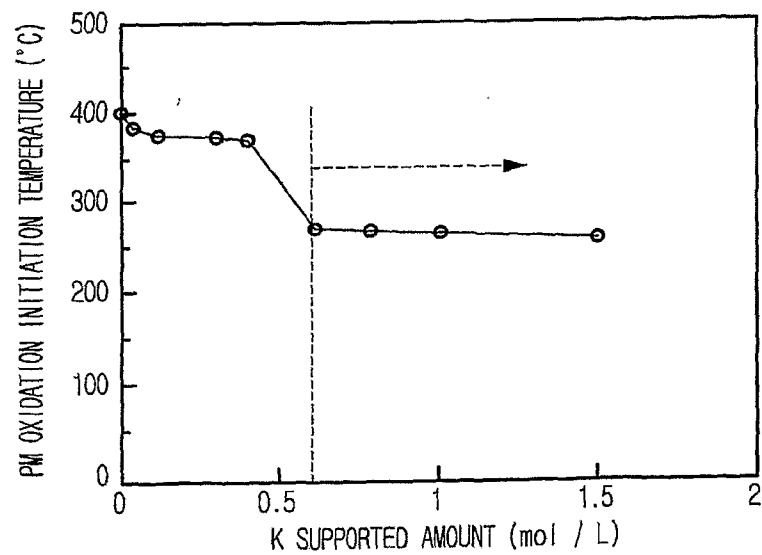
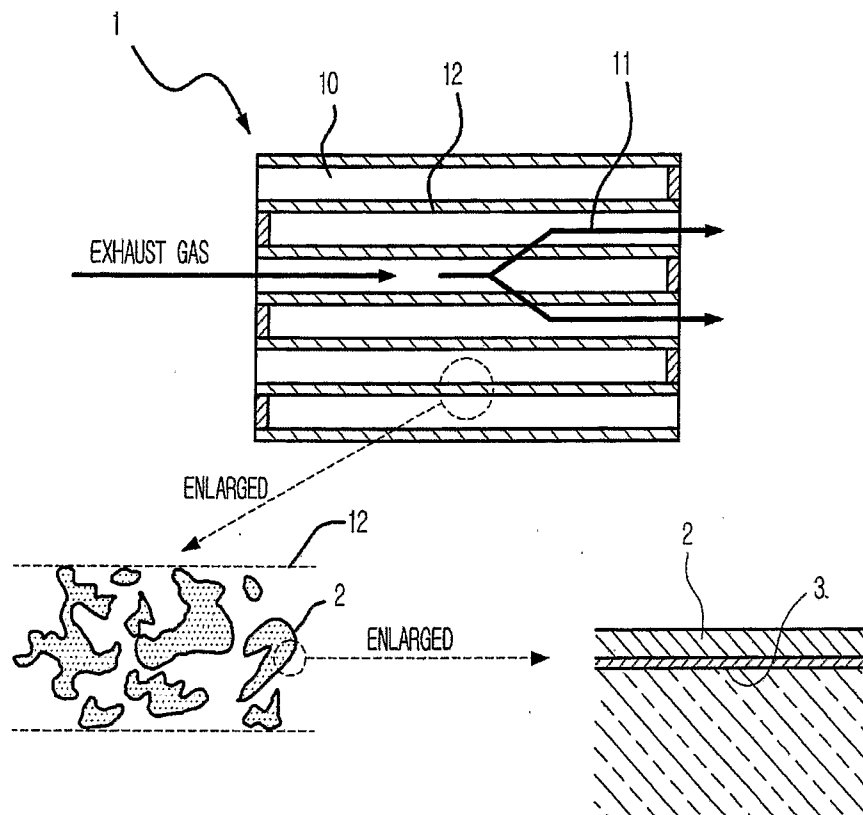


FIG. 5



# INTERNATIONAL SEARCH REPORT

International application No  
PCT/JP2007/050857

## A. CLASSIFICATION OF SUBJECT MATTER

INV. B01D46/24 B01D53/94 B01J23/58 B01D33/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B01D B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                       | Relevant to claim No. |
|-----------|--------------------------------------------------------------------------------------------------------------------------|-----------------------|
| X         | US 2003/083197 A1 (NODA NAOMI [JP] ET AL)<br>1 May 2003 (2003-05-01)<br>claims 1-7; examples 1-6<br>-----                | 1-5                   |
| X         | EP 1 319 436 A1 (NGK INSULATORS LTD [JP])<br>18 June 2003 (2003-06-18)<br>paragraphs [0022], [0031]; claims 1-4<br>----- | 1-5                   |
| A         | EP 1 350 554 A (TOYOTA MOTOR CO LTD [JP])<br>8 October 2003 (2003-10-08)<br>the whole document<br>-----                  | 1-5                   |



Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

18 May 2007

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/JP2007/050857

| Patent document<br>cited in search report | Publication<br>date | Patent family<br>member(s)                                        | Publication<br>date                                  |
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| EP 1350554 A                              | 08-10-2003          | CN 1445015 A<br>JP 2003340291 A<br>US 2004038812 A1               | 01-10-2003<br>02-12-2003<br>26-02-2004               |