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<p>(21) 国際出願番号 PCT/JP99/06951</p> <p>(22) 国際出願日 1999年12月10日(10.12.99)</p> <p>(30) 優先権データ 特願平10/352272 1998年12月11日(11.12.98) JP</p> <p>(71) 出願人 (米国を除くすべての指定国について) 株式会社 日立製作所(HITACHI, LTD.)(JP/JP) 〒101-8010 東京都千代田区神田駿河台四丁目6番地 Tokyo, (JP)</p> <p>(72) 発明者 ; および (75) 発明者 / 出願人 (米国についてのみ) 金枝雅人(KANEEDA, Masato)(JP/JP) 奥出幸二郎(OKUDE, Kojiro)(JP/JP) 飯塚秀宏(IIZUKA, Hidehiro)(JP/JP) 小川敏雄(OGAWA, Toshio)(JP/JP) 永山更成(NAGAYAMA, Kosei)(JP/JP) 山下寿生(YAMASHITA, Hisao)(JP/JP) 藤谷守男(FUJITANI, Morio)(JP/JP) 〒319-1292 茨城県日立市大みか町七丁目1番1号 株式会社日立製作所 日立研究所内 Ibaraki, (JP)</p>	<p>北原雄一(KITAHARA, Yuichi)(JP/JP) 黒田 修(KURODA, Osamu)(JP/JP) 平塚俊史(HIRATSUKA, Toshifumi)(JP/JP) 〒312-0062 茨城県ひたちなか市高場2520番地 株式会社 日立製作所 自動車機器グループ内 Ibaraki, (JP)</p> <p>(74) 代理人 弁理士 作田康夫(SAKUTA, Yasuo) 〒100-8220 東京都千代田区丸の内一丁目5番1号 株式会社 日立製作所内 Tokyo, (JP)</p> <p>(81) 指定国 AU, CA, KR, US, 欧州特許 (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE)</p> <p>添付公開書類 国際調査報告書</p>	
<p>(54)Title: EXHAUST EMISSION CONTROL SYSTEM FOR INTERNAL COMBUSTION ENGINES, EXHAUST EMISSION CONTROL METHOD AND EXHAUST EMISSION CONTROL CATALYST</p>		
<p>(54)発明の名称 内燃機関の排ガス浄化装置、排ガス浄化方法及び排ガス浄化触媒</p>		
<p>(57) Abstract Nitrogen oxides contained in exhaust gas from lean-burn engines-mounted internal combustion engines are effectively controlled. An exhaust emission control system and method therefor for controlling nitrogen oxides contained in combustion exhaust gas from internal combustion engines in the presence of a catalyst using reducing gases such as carbon monoxide and hydrogen carbide contained in the exhaust gas, wherein the catalyst used consists of a porous carrier, all of Rh, Pt and Pd, at least selected one of alkali metal and alkali earth metal and Mn or its compound, all formed on the porous carrier.</p>		

ABSTRACT

Nitrogen oxides contained in an exhaust gas emitted from a lean-burn engine-mounted internal combustion engines are eliminated with a high efficiency.

5 In an exhaust gas purification apparatus and process for eliminating nitrogen oxides contained in a combustion exhaust gas emitted from an internal combustion engine with a reducing gas such as carbon monoxide, hydrocarbons, etc. contained in the exhaust gas in the
10 presence of a catalyst, a catalyst comprising all of Rh, Pt and Pd, at least one member selected from alkali metals and alkaline earth metals, and Mn or its compound, supported on a porous carrier is used.



DESCRIPTION

INTERNAL COMBUSTION ENGINE EXHAUST GAS PURIFICATION
5 APPARATUS, EXHAUST GAS PURIFICATION PROCESS AND EXHAUST
GAS PURIFICATION CATALYST

Technical Field

The present invention relates to an exhausts gas
10 purification apparatus, an exhaust gas purification
process and an exhaust gas purification catalyst with high
elimination efficiency of NO_x from NO_x-containing exhaust
gases such as combustion exhaust gases from internal
combustion engines such as automobile engines, etc.

15

Background Art

Lean-burn engines capable of bringing an
air/fuel ratio into a fuel-lean stage have been nowadays
regarded as promising automobile internal combustion
20 engines from the viewpoint of reduced fuel consumption.
However, the exhaust gases from such engines are in such
an oxidizing atmosphere that the O₂ concentration of the
exhaust gases is more than a stoichiometric amount
necessary for complete combustion of reducing components
25 contained in the exhaust gases (said atmosphere will be
hereinafter referred as "oxidizing atmosphere"). The
conventional ternary catalysts are directed to efficient
purification of NO_x, HC and CO in such a reducing



atmosphere that the O₂ concentration of the exhaust gases is not more than a stoichiometric amount necessary for complete combustion of reducing components contained in the exhaust gases (said atmosphere will be hereinafter referred to as "reducing atmosphere"), failing to show a satisfactory NO_x elimination activity in the oxidizing atmosphere. Thus, it has been keenly desired to develop catalysts capable of effectively eliminating NO_x, HC and CO, particularly NO_x, in the oxidizing atmosphere.

For exhaust gas purification directed to the lean-burn engines, W093/07363 and W093/08383 propose to provide an NO_x absorbent in the exhaust gas passage. The NO_x absorbent can absorb NO_x from the exhaust gases during the fuel-lean combustion and discharge the absorbed NO_x when the O₂ concentration of the exhaust gases is lowered.

JP-A-8-299793 also proposes to provide a catalyst which comprises an NO_x-absorbing component capable of absorbing NO_x from the exhaust gases during the fuel-lean combustion and an NO_x-reducing component capable of reducing the absorbed NO_x in the exhaust gas passage.

With more and more intensified atmospheric regulation of the automobile exhaust gases, much higher NO_x elimination activity and durability are required for the NO_x elimination catalysts directed to the lean-burn engines. The present invention provides an exhaust gas purification catalyst with distinguished NO_x elimination activity and durability, particularly distinguished head resistance and SO_x resistance, an exhaust gas purification



apparatus and an exhaust gas purification process using said catalyst.

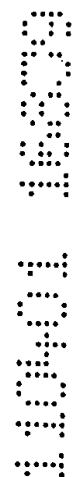
Disclosure of the Invention

According to one aspect of the present invention there is provided an internal combustion engine exhaust gas purification apparatus, which comprises an exhaust gas purification catalyst provided in an internal combustion engine exhaust gas passage through which an air/fuel ratio-lean exhaust gas and an air/fuel ratio-rich or stoichiometric exhaust gas flows, wherein the exhaust gas purification catalyst comprises a porous carrier and an active component supported on the porous carrier, the active component comprising Rh, Pt and Pd, at least one member selected from alkali metals, and Mn.

10 According to another aspect of the present invention there is provided an internal combustion engine exhaust gas purification process, which comprises contacting an exhaust gas emitted from a lean-burn operated internal combustion engine with an exhaust gas purification catalyst, thereby purifying the exhaust gas, wherein the exhaust gas is contacted with a catalyst containing an active component comprising Rh, Pt and Pd, at
 15 least one member selected from alkali metals, and Mn, supported on a porous carrier.

According to a further aspect of the present invention there is provided a lean NOx elimination catalyst, which comprises a porous carrier and an active component supported on the porous carrier, wherein the active component comprises Rh, Pt and Pd, at least one member selected from alkali metals, and Mn, amounts of supported active metals being
 20 0.0003 to 0.01 part by mole of Rh, 0.002 to 0.05 parts by mole of Pt and 0.001 to 0.2 parts by mole of Pd, 0.05 to 3 parts by mole of each of the alkali metals and 0.05 to 2 parts by mole of Mn in terms of metal elements on the basis of 1.5 parts by mole of the porous carrier.

One member selected from the alkali metals can serve the desired purpose, but two or more members from alkali metals and alkaline earth metals can further improve the activity. It seems that new active sites are formed on the catalyst owing to two or more members of these metals supported on the carrier. An amount of supported alkali metals and preferably additional alkaline earth metals is preferably in a range of 0.05 to 3 parts by mole each of the supported metals in terms of metal elements on the basis of 1.5 parts by mole of the porous carrier, where "parts by mole" means a proportion of one component to another in terms of moles; for example, "3 parts by mole of supported component B to 1.5 parts by mole of component A" means that component B is supported in a ratio of component B to component A being 3:1.5 terms of moles, irrespective of the absolute amount of component A. In case the amount of supported alkali metals is less than 0.05



parts by mole each, the improvement of NOx elimination activity is less effective, whereas in case of more than 3 parts by mole the specific surface area of the alkali metals becomes undesirably smaller.

5

The porous carrier may be supported on a substrate, where 0.3 to 4 moles of the porous carrier can be supported on 1 l of the substrate preferably from the viewpoint of NOx elimination activity. In case the amount of supported porous carrier is less than 0.3 moles, the dispersibility of active components becomes poor, whereas in case of more than 4 moles the specific surface area of the porous carrier itself becomes undesirably smaller.

Mn is present in the form of metal or an oxide or a composite oxide with Al, etc. and seems to serve to capture NOx in the oxidizing atmosphere and further serve to improve the high temperature durability of the catalyst. By inclusion of both of at least one member of the alkali metals and alkaline earth metals and Mn the NOx-capturing effect can be further improved.

An amount of supported Mn is preferably in a range of 0.05 to 2 parts by mole in terms of metal element on the basis of 1.5 parts by mole of the porous carrier. In case the amount of supported Mn is less than 0.05 parts by mole, the effect is not remarkable, whereas in case of more than 2 parts by mole the specific surface area of the catalyst becomes undesirably smaller.

Rh, Pt and Pd can enhance the elimination



activity and high temperature durability. For the improvement of the activity and durability, the active component contains all of these noble metals.

Amounts of supported noble metals are preferably
5 in ranges of 0.002 to 0.05 parts by mole of Pt, 0.0003 to 0.01 part by mole of Rh and 0.001 to 0.2 parts by mole of Pd, all in terms of metal elements, on the basis of 1.5 parts by mole of the porous carrier. In case the amount of supported noble metals are less than their lower limits
10 the effect is not remarkable, whereas in case of more than the upper limits the specific surface areas of the noble metals per se become smaller without remarkable effect.

When at least one of rare earth metals is supported thereon in addition to the foregoing components,
15 the NO_x elimination activity and high temperature durability can be further improved, where it is preferable to contain 0.02 to 0.5 parts by mole of each in terms of metal elements on the basis of 1.5 parts by mole of the porous carrier. In case of less than 0.02 parts by mole,
20 the effect is not remarkable, whereas in case of more than 0.5 parts by mole the specific surface area of the catalyst becomes undesirably smaller. Preferable rare earth metals are La, Nd and Ce.

By further adding at least one of Ti and Si
25 thereto, the NO_x elimination efficiency and also the SO_x resistance can be further improved. It seems that the effect of Ti and Si on the SO_x resistance improvement is due to Ti and Si being formed into composite metals



together with Mn, alkali metals and alkaline earth metals. By further adding at least one of Co, Ni and Cu thereto, the NOx elimination activity and the heat resistance can be further improved. Amounts of supported Ti, Co, Si, Ni
5 and Cu are preferably in a range of 0.01 to 2 parts by mole of each in terms of metal elements on the basis of 1.5 parts by mole of the porous carrier.

The present catalyst can further contain at least one of B and P.

10 B and P are present in the form of simple substances or oxides or composite oxides with at least one member selected from alkali metals and Al, and seem to serve to capture NOx in the oxidizing atmosphere, play a role of attracting CO, hydrocarbons, etc. as reducing
15 agents onto the catalyst surface and serve to further improve the heat resistance and the SOx resistance of the catalyst. By controlling mixing sequence of B or P or firing temperature, etc. during the catalyst preparation, they can be brought into the oxide form or the composite
20 oxide form.

An amount of supported B or P is preferably in a range of 0.01 to 2 parts by mole of each in terms of elements on the basis of 1.5 parts by mole of the porous carrier. In case of less than 0.01 part by mole of
25 supported B or P the effect is not remarkable, whereas in case of more than 2 parts by mole the specific surface area of the catalyst becomes undesirably smaller.

The catalyst can be prepared by any procedure



utilizing physical means or chemical reactions such as impregnation, kneading, coprecipitation, sol-gel formation, ion exchange, vapor deposition, etc.

Starting materials for use in the catalyst preparation include various compounds such as nitrate compounds, acetate compounds, complex compounds, hydroxides, carbonate compounds, organic compounds etc., metals and metal oxides.

For the porous carrier, metal oxides, composite oxides, etc. such as alumina, titania, silica, silica-alumina, zirconia, magnesia, etc. can be used, among which alumina is most preferable. The present catalyst can be used upon coating onto a substrate. Cordierite is a most suitable substrate, but even a metal such as stainless steel can be used as well.

The NOx elimination catalyst can be used in any form, for example, honeycomb form, pellet form, plate form, granule form, powder form, etc., among which the honeycomb form is most preferable.

The present catalyst has an effect of eliminating NOx contained in the exhaust gases emitted from internal combustion engines during the lean-burn operation with high elimination efficiency. The NOx elimination effect of the present catalyst seems due to an action of capturing NOx contained in the lean-burn exhaust gas on the catalyst surface, thereby eliminating NOx from the exhaust gas and an action of reducing the captured NOx, thereby eliminating it. Capturing of NOx seems to be



effected by absorption, chemisorption, etc.

The exhaust gas during the lean-burn operation contain oxygen at a higher concentration than the stoichiometric amount necessary for complete combustion of
5 reducing components (HC and CO) in the exhaust gas and thus is in an oxidizing atmosphere. The exhaust gas in an oxidizing atmosphere will be hereinafter referred to as "lean exhaust gas " or "air/fuel ratio-lean exhaust gas". An exhaust gas emitted from internal combustion engines
10 upon combustion in a theoretical air/fuel ratio will be hereinafter referred to as "stoichiometric exhaust gas" or "air/fuel ratio-stoichiometric exhaust gas". An exhaust gas emitted from internal combustion engines operated in fuel excess over the theoretical air/fuel ratio contains
15 oxygen at a lower concentration than the stoichiometric amount necessary for complete combustion of the reducing components contained in the exhaust gas and thus is in a reducing atmosphere. The exhaust gas in a reducing atmosphere will be hereinafter referred to as "rich
20 exhaust gas" or "air/fuel ratio-rich exhaust gas".

One embodiment of the present invention provides an exhaust gas purification apparatus provided with said catalyst in the exhaust gas passage from internal combustion engines in lean-burn operation.

25 Another embodiment of the present invention provides an exhaust gas purification process for purifying an exhaust gas emitted by lean-burn operation upon contacting the exhaust gas with said catalyst.



When the present catalyst is kept in continuous contact with an air/fuel ratio-lean exhaust gas, the NOx elimination efficiency will be gradually lowered, because the amount of captured NOx on the catalyst surface

5 gradually increases, thereby weakening the capturing action. When the NOx elimination efficiency is so lowered, it is desirable to temporarily shift the lean-burn operation to a theoretical air/fuel ratio operation or a fuel excess operation, thereby bringing the air/fuel ratio

10 of the exhaust gas into a stoichiometric or fuel-rich exhaust gas, the NOx elimination action can proceed so actively that the NOx captured on the catalyst surface can be rapidly eliminated to regenerate the catalyst. Thus, when the operation is shifted again to the lean-burn

15 operation once again, high NOx elimination efficiency can be obtained. The duration of the theoretical air/fuel ratio or fuel excess operation is only a few seconds to a few minutes.

The present catalyst can be used in combination

20 with a combustion catalyst capable of combusting HC and CO. For the combustion catalyst capable of combusting HC and CO, it is desirable to use a catalyst comprising Pt and Rh supported on an alumina carrier or a catalyst comprising Ag and Mn supported on an alumina carrier. The combustion

25 catalyst can be provided at a position upstream or downstream of the present catalyst or at both upstream and downstream positions.



Brief Description of Drawings

Fig. 1 is a schematic view of an exhaust gas purification apparatus according to one embodiment of the present invention.

5 Fig. 2 is a view showing an NOx elimination catalyst and a combustion catalyst provided in an exhaust gas passage from an automobile engine.

Best Modes for Carrying Out the Invention

10 Fig. 1 shows one embodiment of the present exhaust gas purification apparatus.

In Fig. 1 are shown a lean-burn engine 99, a suction system comprising an air cleaner 1, an air flow sensor 2 and a throttle valve 3, an exhaust gas
15 purification system comprising an oxygen concentration sensor 7, an exhaust gas temperature sensor 8, a catalyst outlet gas temperature sensor 9, an exhaust gas purification catalyst 10, etc., an engine control unit (ECU) 11, etc. ECU 11 comprises an I/O as an input/output
20 interface, an LSI, a microprocessing unit (MPU), memory units RAM and ROM memorizing a large number of control programs, a timer/counter, etc.

Suction air to the engine is filtered through the air cleaner, then metered by the air flow sensor 2,
25 passed through the throttle valve 3, subjected to fuel injection from an injector 5, and fed to the engine 99 as a mixed gas. Air flow sensor signals and other sensor signals are input into the ECU (Engine Control Unit) 11.



ECU evaluates the operating state of the internal combustion engine and the state of the exhaust gas purification catalyst and judges an operating air/fuel ratio, thereby controlling the injection time of the injector 5, etc. to set the fuel concentration of the mixed gas to a desired value. The mixed gas introduced into the cylinder is ignited by an ignition plug 6 controlled by a signal from ECU 11 and combusted. The combustion exhaust gas is led to the exhaust gas purification system. The exhaust gas purification system is provided by the exhaust gas purification catalyst 10, which eliminates NO_x, HC and CO in the exhaust gas by its ternary catalyst function during the stoichiometric operation, and eliminates NO_x by the NO_x capturing function and also eliminates HC and CO by the combustion function at the same time during the lean operation. The NO_x elimination activity of the exhaust gas purification catalyst is always determined during the lean operation by the judgement of ECU and control signals to shift the air/fuel ratio, etc. to the fuel-rich state during the combustion, when the NO_x elimination activity is lowered, thereby regaining the NO_x capturing action of the catalyst. By the foregoing operations, the exhaust gas can be effectively purified under all the engine combustion conditions of lean operation and stoichiometric operation (including the fuel-rich operation). An A/F sensor can be used in place of the oxygen concentration sensor 7.

Fig. 2 shows the case of providing a hydrocarbon



and CO combustion catalyst downstream of the exhaust gas purification catalyst 10. In Fig. 2, the remaining hydrocarbon and CO as not eliminated by the exhaust gas purification catalyst are eliminated by the combustion catalyst 20.

The present invention will be described in detail below, referring to Examples, which are not limitative of the present invention.

10 [Example 1]

A cordierite honeycomb (400 cells/inc²) was coated with a slurry prepared from alumina powder and alumina precursor and made acidic by nitric acid, dried and fired to obtain an alumina coat honeycomb as coated with 1.5 moles of alumina per 1 l of the apparent honeycomb volume. The alumina coat honeycomb was impregnated with a mixed solution of dinitrodiamine Pt nitric acid solution and Rh nitrate solution, dried at 200°C and then fired at 600°C. Then, the supported Pt and Rh-contained honeycomb was impregnated with a mixed solution of Na nitrate solution, Mn nitrate solution and Pd nitrate solution, dried at 200°C and then fired at 600°C. Thus, Example catalyst 1 containing 0.0022 parts by mole of Rh, 0.014 parts by mole of Pt, 0.8 parts by mole of Na, 0.2 parts by mole of Mn and 0.014 parts by mole of Pd in terms of metal elements on the basis of 1.5 parts by mole of alumina was prepared. The catalyst will be hereinafter expressed as 0.8 NaMnPd-RhPt/Al₂O₃. Likewise, Example Catalysts 2 to 9,



which contained 0.8 parts by mole each of Li, K, Rb, Cs, Mg, Ca, Sr and Ba, respectively, as supported in place of Na, while changing the amounts of supported Mn, Pd, Rh and Pt, and Example Catalysts 10 to 41 containing at least two members of alkali metals and alkaline earth metals without changing the amounts of supported Mn, Pd, Rh and Pt were prepared. In the same manner as for Example Catalyst 1, Comparative Example Catalysts 1 to 9 containing 0.0022 parts by mole of Rh, 0.014 parts by mole of Pt, 0.014 parts by mole of Pd and 0.8 parts by mole of each of Na, Li, K, Rb, Cs, Mg, Ca, Sr and Ba in terms of metal elements respectively, as supported on the basis of 1.5 parts by mole of alumina, without containing Mn, and likewise Comparative Example Catalysts 10 to 14 containing at least two members of alkali metals and alkaline earth metals without containing Mn and without changing the amounts of supported Pd, Rh and Pt, were prepared as Comparative Example Catalysts.

20 [Test Example 1]
(Test Procedure)

The foregoing catalysts were subjected to an NO_x elimination test under the following conditions.

25 6 cc of the honeycomb catalyst was set into a quartz glass reactor tube. The reactor tube was inserted into an electric furnace and heat controlled so that the gas introduced into the reactor tube could be set to temperatures of 300°C, 400°C and 500°C. The following gases



were introduced into the reactor tube: a model gas, i.e. an assumed exhaust gas as would be emitted from an automobile engine operated in the theoretical air/fuel ratio (which will be hereinafter referred to as "stoichiometric model gas") and a model gas, i.e. an assumed exhaust gas as would be emitted from a lean-burn operated automobile engine (which will be hereinafter referred to as "lean model gas"), where these two model gases were introduced into the reactor tube upon switching from one to another at every 3 minutes. The stoichiometric model gas had such a composition as NOx: 1,000 ppm, C₃H₆: 600 ppm, CO: 0.6%, CO₂: 12%, O₂: 0.5%, H₂: 0.3%, H₂O: 10%, and N₂: the balance. The lean model gas had such a composition as NOx: 600 ppm, C₃H₆: 500 ppm, CO: 0.1%, CO₂: 10%, O₂: 5%, H₂O: 10% and N₂: the balance. NOx concentration was measured at the inlet to and the outlet from the catalyst, and NOx elimination efficiency one minute after switching to the lean model gas was calculated according to the following equation:

$$\text{NOx elimination efficiency (\%)} = (\text{NOx concentration of inlet gas} - \text{NOx concentration of outlet gas}) \div \text{NOx concentration of inlet gas} \times 100$$

Test for determining the NOx elimination efficiency as mentioned above will be referred to as Test Example 1.

(Test Results)

Test results of Example Catalysts 1 to 41 and



Comparative Catalysts 1 to 14 according to Test Example 1 are shown in Table 1. In the fuel-rich burn operation, all the catalysts constantly had an NO_x elimination efficiency of 90% or more at 300°C and 100% at 400°C, showing the

5 satisfactory ternary catalyst activity. In case of the present catalysts, the NO_x elimination efficiency was not changed during both of the lean-burn operation and the stoichiometric burn operation even after a plurality of switched operations. The HC and CO elimination efficiency

10 during the lean-burn operation was 90% or more. Example Catalyst containing at least one member of alkali metals and alkaline earth metals, and all of Mn and Rh, Pt and Pd had evidently higher NO_x elimination efficiencies than those of Comparative Example Catalysts.



Table 1

Catalyst		NOx elimination efficiency (%)		
		300°C	400°C	500°C
Example Catalyst 1	0.8NaMnPd-RhPt/Al ₂ O ₃	88	92	87
Example Catalyst 2	0.8LiMnPd-RhPt/Al ₂ O ₃	86	88	71
Example Catalyst 3	0.8KMnPd-RhPt/Al ₂ O ₃	82	96	91
Example Catalyst 4	0.8RbMnPd-RhPt/Al ₂ O ₃	87	97	94
Example Catalyst 5	0.8CsMnPd-RhPt/Al ₂ O ₃	83	99	95
Example Catalyst 6	0.8MgMnPd-RhPt/Al ₂ O ₃	71	85	63
Example Catalyst 7	0.8CaMnPd-RhPt/Al ₂ O ₃	82	93	75
Example Catalyst 8	0.8SrMnPd-RhPt/Al ₂ O ₃	82	92	80
Example Catalyst 9	0.8BaMnPd-RhPt/Al ₂ O ₃	73	71	54
Example Catalyst 10	0.2Li0.6NaMnPd-RhPt/Al ₂ O ₃	82	91	73
Example Catalyst 11	0.4Li0.4KMnPd-RhPt/Al ₂ O ₃	85	94	92
Example Catalyst 12	0.4Li0.4RbMnPd-RhPt/Al ₂ O ₃	75	77	69
Example Catalyst 13	0.4Li0.4CsMnPd-RhPt/Al ₂ O ₃	85	93	91
Example Catalyst 14	0.6Li0.1MgMnPd-RhPt/Al ₂ O ₃	72	61	50
Example Catalyst 15	0.4Li0.4CaMnPd-RhPt/Al ₂ O ₃	75	91	77
Example Catalyst 16	0.4Li0.4SrMnPd-RhPt/Al ₂ O ₃	84	90	75
Example Catalyst 17	0.4Li0.4BaMnPd-RhPt/Al ₂ O ₃	72	70	55
Example Catalyst 18	0.8Na0.6KMnPd-RhPt/Al ₂ O ₃	91	90	93
Example Catalyst 19	0.8Na0.4RbMnPd-RhPt/Al ₂ O ₃	85	80	81
Example Catalyst 20	0.8Na0.4CsMnPd-RhPt/Al ₂ O ₃	86	90	85
Example Catalyst 21	0.8Na0.75MgMnPd-RhPt/Al ₂ O ₃	92	99	94
Example Catalyst 22	0.8Na0.4CaMnPd-RhPt/Al ₂ O ₃	80	90	71
Example Catalyst 23	0.4Na0.2SrMnPd-RhPt/Al ₂ O ₃	89	87	81
Example Catalyst 24	0.4K0.2CsMnPd-RhPt/Al ₂ O ₃	95	98	85
Example Catalyst 25	0.4K0.4RbMnPd-RhPt/Al ₂ O ₃	81	85	73
Example Catalyst 26	0.4K0.4CaMnPd-RhPt/Al ₂ O ₃	80	80	63
Example Catalyst 27	0.6K0.4SrMnPd-RhPt/Al ₂ O ₃	82	86	75



Catalyst		NOx elimination efficiency (%)		
		300°C	400°C	500°C
Example Catalyst 28	0.6K0.4BaMnPd-RhPt/Al ₂ O ₃	80	76	77
Example Catalyst 29	0.3Cs0.1MgMnPd-RhPt/Al ₂ O ₃	85	90	85
Example Catalyst 30	0.3Cs0.2CaMnPd-RhPt/Al ₂ O ₃	82	85	80
Example Catalyst 31	0.3Cs0.4SrMnPd-RhPt/Al ₂ O ₃	86	88	75
Example Catalyst 32	0.3Cs0.4BaMnPd-RhPt/Al ₂ O ₃	73	85	80
Example Catalyst 33	0.4Sr0.1MgMnPd-RhPt/Al ₂ O ₃	88	90	82
Example Catalyst 34	0.4Sr0.4CaMnPd-RhPt/Al ₂ O ₃	81	85	78
Example Catalyst 35	0.4Sr0.4BaMnPd-RhPt/Al ₂ O ₃	71	82	77
Example Catalyst 36	0.4Li1.2Na0.6KMnPd-RhPt/Al ₂ O ₃	98	99	91
Example Catalyst 37	0.8Na0.2Ca0.1MgMnPd-RhPt/Al ₂ O ₃	80	87	75
Example Catalyst 38	0.4Na0.15Sr0.1MgMnPd-RhPt/Al ₂ O ₃	83	88	78
Example Catalyst 39	0.4Na0.15Sr0.2CaMnPd-RhPt/Al ₂ O ₃	76	80	70
Example Catalyst 40	0.4Li0.4K0.2SrMnPd-RhPt/Al ₂ O ₃	88	93	90
Example Catalyst 41	0.4Li0.4Na0.4K0.2CsMnPd-RhPt/Al ₂ O ₃	95	98	95
Comp. Ex. Catalyst 1	0.8NaPd-RhPt/Al ₂ O ₃	67	63	35
Comp. Ex. Catalyst 2	0.8LiPd-RhPt/Al ₂ O ₃	68	51	35
Comp. Ex. Catalyst 3	0.8KPd-RhPt/Al ₂ O ₃	58	57	42
Comp. Ex. Catalyst 4	0.8RbPd-RhPt/Al ₂ O ₃	40	59	47
Comp. Ex. Catalyst 5	0.8CsPd-RhPt/Al ₂ O ₃	35	61	50
Comp. Ex. Catalyst 6	0.8MgPd-RhPt/Al ₂ O ₃	50	38	23
Comp. Ex. Catalyst 7	0.8CaPd-RhPt/Al ₂ O ₃	58	52	28
Comp. Ex. Catalyst 8	0.8SrPd-RhPt/Al ₂ O ₃	51	57	36
Comp. Ex. Catalyst 9	0.8BaPd-RhPt/Al ₂ O ₃	57	51	32
Comp. Ex. Catalyst 10	0.8Na0.1MgPd-RhPt/Al ₂ O ₃	52	60	40
Comp. Ex. Catalyst 11	0.4Sr0.4BaPd-RhPt/Al ₂ O ₃	49	61	29
Comp. Ex. Catalyst 12	0.6K0.4BaPd-RhPt/Al ₂ O ₃	55	53	30
Comp. Ex. Catalyst 13	0.8Na0.2Ca0.1MgPd-RhPt/Al ₂ O ₃	51	55	40
Comp. Ex. Catalyst 14	0.4Na0.15Sr0.2CaPd-RhPt/Al ₂ O ₃	54	49	36



[Test Example 2]

(Test procedure)

Example Catalyst 1, 3, 8, 11, 18, 21, 33, 36, 38 and 40, and Comparative Example Catalyst 1 to 5, 11 and 13 were fired at 800°C for 5 hours, and then subjected to the test in the same test procedure as Test Example 1.

(Test Results)

Test results are shown in Table 2. The present catalysts had evidently higher NO_x elimination efficiencies than those of Comparative Example Catalysts and had distinguished high temperature durabilities.

Table 2

Catalyst		NO _x elimination efficiency (%)		
		300°C	400°C	500°C
Example Catalyst 1	0.8NaMnPd-RhPt/Al ₂ O ₃	73	85	73
Example Catalyst 3	0.8KMnPd-RhPt/Al ₂ O ₃	75	80	70
Example Catalyst 8	0.8SrMnPd-RhPt/Al ₂ O ₃	78	80	69
Example Catalyst 11	0.4Li0.4KMnPd-RhPt/Al ₂ O ₃	80	85	84
Example Catalyst 18	0.8Na0.6KMnPd-RhPt/Al ₂ O ₃	79	82	87
Example Catalyst 21	0.8Na0.075MgMnPd-RhPt/Al ₂ O ₃	88	91	89
Example Catalyst 33	0.4Sr0.1MgMnPd-RhPt/Al ₂ O ₃	72	79	69
Example Catalyst 36	0.4Li1.2Na0.6KMnPd-RhPt/Al ₂ O ₃	83	93	88
Example Catalyst 38	0.4Na0.15Sr0.1MgMnPd-RhPt/Al ₂ O ₃	75	81	72
Example Catalyst 40	0.4Li0.4K0.2SrMnPd-RhPt/Al ₂ O ₃	80	76	69
Comp. Ex. Catalyst 1	0.8NaPd-RhPt/Al ₂ O ₃	41	40	15
Comp. Ex. Catalyst 2	0.8LiPd-RhPt/Al ₂ O ₃	35	39	21
Comp. Ex. Catalyst 3	0.8KPd-RhPt/Al ₂ O ₃	45	48	35



Catalyst		NOx elimination efficiency (%)		
		300°C	400°C	500°C
Comp. Ex. Catalyst 4	0.8RbPd-RhPt/Al ₂ O ₃	33	49	34
Comp. Ex. Catalyst 5	0.8CsPd-RhPt/Al ₂ O ₃	35	33	21
Comp. Ex. Catalyst 11	0.4Sr0.4BaPd-RhPt/Al ₂ O ₃	24	40	22
Comp. Ex. Catalyst 13	0.8Na0.2Ca0.1MgPd-RhPt/Al ₂ O ₃	38	40	31

[Example 2]

In the same manner as in Example 1, Example Catalysts 42 to 47 were prepared by adding Cu, Co or Ni to Example Catalysts 21 and 36, respectively, and evaluated according to Test Example 1. Amounts of supported Cu, Co and Ni were 0.1 part by mole each in terms of metal elements on the basis of 1.5 parts by mole of alumina.

10 (Test Results)

Test results are shown in Table 3. Example Catalysts containing Co, Ni or Cu had higher activities than those of Comparative Example Catalysts 1 to 14 shown in Table 1.

15

Table 3

Catalyst		NOx elimination efficiency (%)		
		300°C	400°C	500°C
Example Catalyst 42	NaMgMnPd-RhPt0.1Cu/Al ₂ O ₃	93	99	96
Example Catalyst 43	NaMgMnPd-RhPt0.1Co/Al ₂ O ₃	94	99	95
Example Catalyst 44	NaMgMnPd-RhPt0.1Ni/Al ₂ O ₃	95	99	97
Example Catalyst 45	LiNaKMnPd-RhPt0.1Cu/Al ₂ O ₃	87	95	93
Example Catalyst 46	LiNaKMnPd-RhPt0.1Co/Al ₂ O ₃	86	96	94
Example Catalyst 47	LiNaKMnPd-RhPt0.1Ni/Al ₂ O ₃	84	99	93



[Example 3]

In the same manner as in Example 1, Example Catalysts 48 to 51 were prepared by adding Ti or Si to Example Catalysts 21 and 36, respectively. Amounts of supported Ti and Si were 0.1 parts by mole each in terms of metal elements on the basis of 1.5 parts by mole of alumina.

[Test Example 3]

10 (Test Procedure)

In Test Example 1, only an SO₂-added lean gas was passed through the reaction tube. An amount of SO₂ added to the lean gas was 0.01%. Then, an NO_x elimination efficiency was determined according to the procedure of Test Example 1. Test temperature was 400°C.

(Test Results)

Test results of Example Catalysts 48 to 51 and Comparative Example Catalysts 1 and 3 according to Test Example 3 are shown in Table 4. Example Catalysts 48 to 51 had higher NO_x elimination efficiencies than those of Comparative Example Catalysts 1 and 3 and also had a good SO_x durability.



Table 4

Catalyst		NOx elimination efficiency (%)		
		300°C	400°C	500°C
Example Catalyst 48	NaMgMnPd0.1Ti-RhPt/Al ₂ O ₃	61	68	58
Example Catalyst 49	NaMgMnPd0.1Si-RhPt/Al ₂ O ₃	59	62	55
Example Catalyst 50	LiNaKMnPd0.1Ti-RhPt/Al ₂ O ₃	70	75	71
Example Catalyst 51	LiNaKMnPd0.1Si-RhPt/Al ₂ O ₃	65	70	58
Comp. Ex. Catalyst 1	0.8NaPd-RhPt/Al ₂ O ₃	28	32	15
Comp. Ex. Catalyst 3	0.8KPd-RhPt/Al ₂ O ₃	20	24	32

[Example 4]

In the same manner as in Example 1, Example
 5 Catalysts 52 to 60 were prepared by adding 0.2 parts by mole of Ce, La or Nd in terms of metal elements to Example Catalysts 36, 48 and 50, respectively, on the basis of 1.5 parts by mole of alumina. Test was the same as in Test Example 2.

10

(Test Results)

NOx elimination efficiencies determined
 according to Test Example 2 are shown in Table 5. Example
 Catalysts 52 to 60 had evidently higher NOx elimination
 15 efficiencies than those of Comparative Example Catalysts shown in Table 2 and had good high temperature durabilities.



Table 5

Catalyst		NOx elimination efficiency (%)		
		300°C	400°C	500°C
Example Catalyst 52	LiNaKMnPd-RhPt-0.2Ce/Al ₂ O ₃	88	95	91
Example Catalyst 53	LiNaKMnPd-RhPt-0.2La/Al ₂ O ₃	83	96	89
Example Catalyst 54	LiNaKMnPd-RhPt-0.2Nd/Al ₂ O ₃	85	93	90
Example Catalyst 55	NaMgMnPdTi-RhPt-0.2Ce/Al ₂ O ₃	93	95	85
Example Catalyst 56	NaMgMnPdTi-RhPt-0.2La/Al ₂ O ₃	88	92	87
Example Catalyst 57	NaMgMnPdTi-RhPt-0.2Nd/Al ₂ O ₃	90	91	91
Example Catalyst 58	LiNaKMnPdTi-RhPt-0.2Ce/Al ₂ O ₃	95	97	94
Example Catalyst 59	LiNaKMnPdTi-RhPt-0.2La/Al ₂ O ₃	82	91	91
Example Catalyst 60	LiNaKMnPdTi-RhPt-0.2Nd/Al ₂ O ₃	80	91	80

[Example 5]

In the same manner as in Example 1, Example Catalysts 61 to 66 were prepared by omitting one of the noble metals from Example Catalysts 52 and 58. Test was the same as in Test Example 2.

(Test Results)

NOx elimination efficiencies determined according to Test Example 2 are shown in Table 6. Example Catalysts 61 to 66 had evidently higher NOx elimination efficiencies than those of Comparative Example catalysts shown in Table 2 and had good high temperature durabilities.



Table 6

Catalyst		NOx elimination efficiency (%)		
		300°C	400°C	500°C
Example Catalyst 61	LiNaKMnPd-Pt-Ce/Al ₂ O ₃	79	86	73
Example Catalyst 62	LiNaKMnPd-RhCe/Al ₂ O ₃	73	86	77
Example Catalyst 63	LiNaKMn-RhPt-Ce/Al ₂ O ₃	70	86	80
Example Catalyst 64	LiNaKMnPdTi-Pt-ce/Al ₂ O ₃	86	90	78
Example Catalyst 65	LiNaKMnPdTi-Rh-Ce/Al ₂ O ₃	89	90	80
Example catalyst 66	LiNaKMnTi-RhPt-Ce/Al ₂ O ₃	79	91	83

[Example 6]

In the same manner as in Example 1, Example
 5 Catalysts 67 to 72 were prepared by adding 0.1 part by
 mole of at least one of P and B in terms of elements to
 Example Catalysts 52 and 58, respectively, on the basis of
 1.5 parts by mole of alumina. Test was the same as in Test
 Example 2.

10

(Test Results)

NOx elimination efficiencies determined
 according to Test Example 2 are shown in Table 7. Example
 Catalysts 67 to 72 had higher NOx elimination efficiencies
 15 than those of Comparative Example Catalysts shown in Table
 2 and had good high temperature durabilities.



Table 7

Catalyst		NOx elimination efficiency (%)		
		300°C	400°C	500°C
Example Catalyst 67	LiNaKMnPd0.1P-RhPt-Ce/Al ₂ O ₃	88	87	94
Example Catalyst 68	LiNaKMnPd0.1B-RhPt-Ce/Al ₂ O ₃	83	82	95
Example Catalyst 69	LiNaKMnPd0.1P0.1B-RhPt-Ce/Al ₂ O ₃	85	81	92
Example Catalyst 70	LiNaKMnPdTi0.1P-RhPt-Ce/Al ₂ O ₃	81	93	92
Example Catalyst 71	LiNaKMnPdTi0.1B-RhPt-Ce/Al ₂ O ₃	80	83	87
Example Catalyst 72	LiNaKMnPdTi0.1P0.1B-RhPt-Ce/Al ₂ O ₃	80	86	97

[Example 7]

In the same manner as in Example 1, Catalysts
 5 containing 0.1 part by mole of Ti in terms of metal
 element on the basis of 1.5 parts by mole of alumina were
 prepared by adding Ti to Example Catalysts 11 and 33 and
 catalysts were also prepared by changing Mn contents of
 Example Catalysts 36 and 48. Test was the same as in Test
 10 Example 1.

(Test Results)

NOx elimination efficiencies determined at 400°C
 according to Test Example 1 are shown in Table 8. The
 15 catalysts containing 0.05 to 2 parts by mole of supported
 Mn in terms of metal element had high NOx elimination
 efficiencies than 80%, showing good NOx elimination
 efficiencies.



Table 8

Catalysts	NOx elimination efficiency (%), 400°C	Catalysts	NOx elimination efficiency (%), 400°C
LiKPtTi-RhPt/Al ₂ O ₃	73	LiNaKPt-RhPt/Al ₂ O ₃	70
LiKO.02MnPdTi-RhPt/Al ₂ O ₃	75	LiNaKO.02MnPd-RhPt/Al ₂ O ₃	75
LiKO.05MnPdTi-RhPt/Al ₂ O ₃	83	LiNaKO.05MnPd-RhPt/Al ₂ O ₃	82
LiKO.2MnPdTi-RhPt/Al ₂ O ₃	92	LiNaKO.2MnPd-RhPt/Al ₂ O ₃	99
LiKO.4MnPdTi-RhPt/Al ₂ O ₃	98	LiNaKO.4MnPd-RhPt/Al ₂ O ₃	99
LiKl.4MnPdTi-RhPt/Al ₂ O ₃	90	LiNaKl.4MnPdRhPt/Al ₂ O ₃	93
LiK2MnPdTi-RhPt/Al ₂ O ₃	82	LiNaK2MnPd-RhPt/Al ₂ O ₃	86
LiK3MnPdTi-RhPt/Al ₂ O ₃	68	LiNaK3MnPd-RhPt/Al ₂ O ₃	71
SrMgPdTi-RhPt/Al ₂ O ₃	69	NaMgPdTi-RhPt/Al ₂ O ₃	71
SrMg0.02MnPdTi-RhPt/Al ₂ O ₃	75	NaMg0.02MnPdTi-RhPt/Al ₂ O ₃	73
SrMg0.05MnPdTi-RhPt/Al ₂ O ₃	81	NaMg0.05MnPdTi-RhPt/Al ₂ O ₃	81
SrMg0.2MnPdTi-RhPt/Al ₂ O ₃	85	NaMg0.2MnPdTi-RhPt/Al ₂ O ₃	96
SrMg0.4MnPdTi-RhPt/Al ₂ O ₃	93	NaMg0.4MnPdTi-RhPt/Al ₂ O ₃	93
SrMgl.4MnPdTi-RhPt/Al ₂ O ₃	88	NaMgl.4MnPdTi-RhPt/Al ₂ O ₃	88
SrMg2MnPdTi-RhPt/Al ₂ O ₃	83	NaMg2MnPdTi-RhPt/Al ₂ O ₃	83
SrMg3MnPdTi-RhPt/Al ₂ O ₃	62	NaMg3MnPdTi-RhPt/Al ₂ O ₃	65

[Example 8]

In the same manner as in Example 1, catalysts
 5 containing 0.1 part by mole of Ti in terms of metal
 element on the basis of 1.5 parts by mole of alumina were
 prepared by adding Ti to Example Catalysts 11 and 33, and
 catalysts whose K and Sr contents were further changed in
 the prepared catalysts and catalysts whose K and Na
 10 contents were changed in Example Catalysts 36 and 48 were
 also prepared. Test was the same as in Test Example 1.



(Test Results)

NOx elimination efficiencies determined at 400°C according to Test Example 1 are shown in Table 9. The catalysts having K, Sr and Na contents of 0.05 to 3 parts by mole each had higher NOx elimination efficiencies than 80% at 400°C, showing good NOx elimination efficiencies.

Table 9

Catalysts	NOx elimination efficiency (%), 400°C	Catalysts	NOx elimination efficiency (%), 400°C
Li0.02KMnPdTi-RhPt/Al ₂ O ₃	72	LiNa0.02KMnPd-RhPt/Al ₂ O ₃	70
Li0.05KMnPdTi-RhPt/Al ₂ O ₃	81	LiNa0.05KMnPd-RhPt/Al ₂ O ₃	84
Li0.4KMnPdTi-RhPt/Al ₂ O ₃	92	LiNa0.4KMnPd-RhPt/Al ₂ O ₃	99
Li1.5KMnPdTi-RhPt/Al ₂ O ₃	96	LiNa0.6KMnPd-RhPt/Al ₂ O ₃	99
Li2.2KMnPdTi-RhPt/Al ₂ O ₃	89	LiNa1.5KMnPd-RhPt/Al ₂ O ₃	90
Li3KMnPdTi-RhPt/Al ₂ O ₃	83	LiNa3KMnPd-RhPt/Al ₂ O ₃	82
Li4KMnPdTi-RhPt/Al ₂ O ₃	69	LiNa4KMnPd-RhPt/Al ₂ O ₃	73
0.02SrMgMnPdTi-RhPt/Al ₂ O ₃	73	0.02NaMgMnPdTi-RhPt/Al ₂ O ₃	62
0.05SrMgMnPdTi-RhPt/Al ₂ O ₃	81	0.05NaMgMnPdTi-RhPt/Al ₂ O ₃	81
0.4SrMgMnPdTi-RhPt/Al ₂ O ₃	85	0.5NaMgMnPdTi-RhPt/Al ₂ O ₃	88
0.6SrMgMnPdTi-RhPt/Al ₂ O ₃	88	0.8NaMgMnPdTi-RhPt/Al ₂ O ₃	96
1.5SrMgMnPdTi-RhPt/Al ₂ O ₃	83	2NaMgMnPdTi-RhPt/Al ₂ O ₃	90
3SrMgMnPdTi-RhPt/Al ₂ O ₃	81	3NaMgMnPdTi-RhPt/Al ₂ O ₃	84
4SrMgMnPdTi-RhPt/Al ₂ O ₃	62	4NaMgMnPdTi-RhPt/Al ₂ O ₃	76

10 [Example 9]

In the same manner as in Example 1, catalysts whose Rh, Pt and Pd contents were changed in Example Catalyst 48 were prepared. Test was the same as in Test Example 1.



(Test Results)

NOx elimination efficiencies determined at 400°C according to Test Example 1 are shown in Table 10. The catalysts containing 0.002 to 0.05 parts by mole of Pt, 0.0003 to 0.01 part by mole of Rh and 0.001 to 0.2 parts by mole of Pd in terms of metal elements as amounts of supported Rh, Pt and Pd had higher NOx elimination efficiencies than 80% at 400°C, showing good NOx elimination efficiencies.

10

Table 10

Catalysts	NOx elimination efficiency (%), 400°C	Catalysts	NOx elimination efficiency (%), 400°C
NaMgMn0.001PdTi-0.0003Rh0.001Pt/Al ₂ O ₃	60	NaMgMn0.014PdTi-0.0003Rh0.001Pt/Al ₂ O ₃	76
NaMgMn0.001PdTi-0.01Rh0.001Pt/Al ₂ O ₃	68	NaMgMn0.014PdTi-0.01Rh0.001Pt/Al ₂ O ₃	74
NaMgMn0.001PdTi-0.0001Rh0.002Pt/Al ₂ O ₃	62	NaMgMn0.014PdTi-0.0001Rh0.002Pt/Al ₂ O ₃	73
NaMgMn0.001PdTi-0.0003Rh0.002Pt/Al ₂ O ₃	84	NaMgMn0.014PdTi-0.0003Rh0.002Pt/Al ₂ O ₃	83
NaMgMn0.001PdTi-0.0022Rh0.002Pt/Al ₂ O ₃	90	NaMgMn0.014PdTi-0.0022Rh0.002Pt/Al ₂ O ₃	92
NaMgMn0.001PdTi-0.01Rh0.002Pt/Al ₂ O ₃	81	NaMgMn0.014PdTi-0.01Rh0.002Pt/Al ₂ O ₃	84
NaMgMn0.001PdTi-0.02Rh0.002Pt/Al ₂ O ₃	73	NaMgMn0.014PdTi-0.02Rh0.002Pt/Al ₂ O ₃	76
NaMgMn0.001PdTi-0.0003Rh0.014Pt/Al ₂ O ₃	85	NaMgMn0.014PdTi-0.0003Rh0.014Pt/Al ₂ O ₃	86
NaMgMn0.001PdTi-0.0022Rh0.014Pt/Al ₂ O ₃	95	NaMgMn0.014PdTi-0.0022Rh0.014Pt/Al ₂ O ₃	96
NaMgMn0.001PdTi-0.01Rh0.014Pt/Al ₂ O ₃	84	NaMgMn0.014PdTi-0.01Rh0.014Pt/Al ₂ O ₃	87
NaMgMn0.001PdTi-0.0001Rh0.05Pt/Al ₂ O ₃	75	NaMgMn0.014PdTi-0.0001Rh0.05Pt/Al ₂ O ₃	75
NaMgMn0.001PdTi-0.0003Rh0.05Pt/Al ₂ O ₃	81	NaMgMn0.014PdTi-0.0003Rh0.05Pt/Al ₂ O ₃	82
NaMgMn0.001PdTi-0.0022Rh0.05Pt/Al ₂ O ₃	88	NaMgMn0.014PdTi-0.0022Rh0.05Pt/Al ₂ O ₃	95
NaMgMn0.001PdTi-0.01Rh0.05Pt/Al ₂ O ₃	84	NaMgMn0.014PdTi-0.01Rh0.05Pt/Al ₂ O ₃	88
NaMgMn0.001PdTi-0.02Rh0.05Pt/Al ₂ O ₃	75	NaMgMn0.014PdTi-0.02Rh0.05Pt/Al ₂ O ₃	75



Catalysts	NOx elimination efficiency (%), 400°C	Catalysts	NOx elimination efficiency (%), 400°C
NaMgMn0.001PdTi-0.0003Rh0.07Pt/Al ₂ O ₃	72	NaMgMn0.014PdTi-0.0003Rh0.07Pt/Al ₂ O ₃	73
NaMgMn0.001PdTi-0.01Rh0.07Pt/Al ₂ O ₃	73	NaMgMn0.014PdTi-0.01Rh0.07Pt/Al ₂ O ₃	71
NaMgMn0.2PdTi-0.0003Rh0.001Pt/Al ₂ O ₃	63	NaMgMn0.2PdTi-0.0001Rh0.05Pt/Al ₂ O ₃	74
NaMgMn0.2PdTi-0.01Rh0.001Pt/Al ₂ O ₃	66	NaMgMn0.2PdTi-0.0003Rh0.05Pt/Al ₂ O ₃	82
		NaMgMn0.2PdTi-0.0022Rh0.05Pt/Al ₂ O ₃	88
NaMgMn0.2PdTi-0.0001Rh0.002Pt/Al ₂ O ₃	68	NaMgMn0.2PdTi-0.01Rh0.05Pt/Al ₂ O ₃	81
NaMgMn0.2PdTi-0.0003Rh0.002Pt/Al ₂ O ₃	81	NaMgMn0.2PdTi-0.02Rh0.05Pt/Al ₂ O ₃	77
NaMgMn0.2PdTi-0.0022Rh0.002Pt/Al ₂ O ₃	90		
NaMgMn0.2PdTi-0.01Rh0.002Pt/Al ₂ O ₃	83	NaMgMn0.2PdTi-0.0003Rh0.07Pt/Al ₂ O ₃	76
NaMgMn0.2PdTi-0.02Rh0.002Pt/Al ₂ O ₃	71	NaMgMn0.2PdTi-0.01Rh0.07Pt/Al ₂ O ₃	78
NaMgMn0.2PdTi-0.0003Rh0.014Pt/Al ₂ O ₃	84		
NaMgMn0.2PdTi-0.0022Rh0.014Pt/Al ₂ O ₃	93	NaMgMn0.0005PdTi-0.0022Rh0.014Pt/Al ₂ O ₃	70
NaMgMn0.2PdTi-0.01Rh0.014Pt/Al ₂ O ₃	87	NaMgMn0.3PdTi-0.0022Rh0.014Pt/Al ₂ O ₃	71

[Example 10]

In the same manner as in Example 1, catalysts were prepared by adding Ce, La or Nd to Example Catalysts 36 and 48 and by further changing their contents. Test was the same as in Test Example 2.

(Test Results)

NOx elimination efficiencies determined at 400°C according to Test Example 2 are shown in Table 11. The catalysts containing 0.02 to 0.5 parts by mole of supported Ce, La and Nd in terms of metal elements had higher NOx elimination efficiencies than 80% at 400°C after



heating at 800°C for 5 hours, showing good NOx elimination efficiencies.

Table 11

Catalysts	NOx elimination efficiency (%), 400°C	Catalysts	NOx elimination efficiency (%), 400°C
LiNaKMnPd-RhPt-0.01Ce/Al ₂ O ₃	75	NaMgMnPdTi-RhPt-0.01Ce/Al ₂ O ₃	76
LiNaKMnPd-RhPt-0.02Ce/Al ₂ O ₃	82	NaMgMnPdTi-RhPt-0.02Ce/Al ₂ O ₃	87
LiNaKMnPd-RhPt-0.2Ce/Al ₂ O ₃	95	NaMgMnPdTi-RhPt-0.2Ce/Al ₂ O ₃	95
LiNaKMnPd-RhPt-0.5Ce/Al ₂ O ₃	91	NaMgMnPdTi-RhPt-0.5Ce/Al ₂ O ₃	94
LiNaKMnPd-RhPt-0.8Ce/Al ₂ O ₃	73	NaMgMnPdTi-RhPt-0.8Ce/Al ₂ O ₃	71
LiNaKMnPd-RhPt-0.01La/Al ₂ O ₃	75	NaMgMnPdTi-RhPt-0.01La/Al ₂ O ₃	76
LiNaKMnPd-RhPt-0.02La/Al ₂ O ₃	85	NaMgMnPdTi-RhPt-0.02La/Al ₂ O ₃	85
LiNaKMnPd-RhPt-0.2La/Al ₂ O ₃	96	NaMgMnPdTi-RhPt-0.2La/Al ₂ O ₃	92
LiNaKMnPd-RhPt-0.5La/Al ₂ O ₃	88	NaMgMnPdTi-RhPt-0.5La/Al ₂ O ₃	82
LiNaKMnPd-RhPt-0.8La/Al ₂ O ₃	74	NaMgMnPdTi-RhPt-0.8La/Al ₂ O ₃	63
LiNaKMnPd-RhPt-0.01Nd/Al ₂ O ₃	66	NaMgMnPdTi-RhPt-0.01Nd/Al ₂ O ₃	70
LiNaKMnPd-RhPt-0.02Nd/Al ₂ O ₃	81	NaMgMnPdTi-RhPt-0.02Nd/Al ₂ O ₃	82
LiNaKMnPd-RhPt-0.2Nd/Al ₂ O ₃	93	NaMgMnPdTi-RhPt-0.2Nd/Al ₂ O ₃	91
LiNaKMnPd-RhPt-0.5Nd/Al ₂ O ₃	84	NaMgMnPdTi-RhPt-0.5Nd/Al ₂ O ₃	84
LiNaKMnPd-RhPt-0.8Nd/Al ₂ O ₃	69	NaMgMnPdTi-RhPt-0.8Nd/Al ₂ O ₃	75

5

[Example 11]

In the same manner as in Example 1, catalysts were prepared by adding Cu, Co or Ni to Example Catalysts 36 and 48 and by further changing their contents.

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(Test Results)

NOx elimination efficiencies determined at 400°C



according to Test Example 1 are shown in Table 12. The catalysts containing 0.01 to 2 parts by mole of Cu, Co or Ni in terms of metal elements had higher NOx elimination efficiencies than 80% at 400°C, showing good NOx elimination efficiencies.

Table 12

Catalysts	NOx elimination efficiency (%), 400°C	Catalysts	NOx elimination efficiency (%), 400°C
LiNaKMnPd-RhPt-0.005Cu/Al ₂ O ₃	75	NaMgMnPdTi-RhPt-0.005Cu/Al ₂ O ₃	76
LiNaKMnPd-RhPt-0.01Cu/Al ₂ O ₃	85	NaMgMnPdTi-RhPt-0.01Cu/Al ₂ O ₃	82
LiNaKMnPd-RhPt-0.1Cu/Al ₂ O ₃	92	NaMgMnPdTi-RhPt-0.1Cu/Al ₂ O ₃	87
LiNaKMnPd-RhPt-0.2Cu/Al ₂ O ₃	96	NaMgMnPdTi-RhPt-0.2Cu/Al ₂ O ₃	91
LiNaKMnPd-RhPt-2Cu/Al ₂ O ₃	81	NaMgMnPdTi-RhPt-2Cu/Al ₂ O ₃	83
LiNaKMnPd-RhPt-3Cu/Al ₂ O ₃	70	NaMgMnPdTi-RhPt-3Cu/Al ₂ O ₃	74
LiNaKMnPd-RhPt-0.005Co/Al ₂ O ₃	71	NaMgMnPdTi-RhPt-0.005Co/Al ₂ O ₃	71
LiNaKMnPd-RhPt-0.01Co/Al ₂ O ₃	81	NaMgMnPdTi-RhPt-0.01Co/Al ₂ O ₃	88
LiNaKMnPd-RhPt-0.1Co/Al ₂ O ₃	94	NaMgMnPdTi-RhPt-0.1Co/Al ₂ O ₃	94
LiNaKMnPd-RhPt-0.2Co/Al ₂ O ₃	97	NaMgMnPdTi-RhPt-0.2Co/Al ₂ O ₃	98
LiNaKMnPd-RhPt-2Co/Al ₂ O ₃	81	NaMgMnPdTi-RhPt-2Co/Al ₂ O ₃	83
LiNaKMnPd-RhPt-3Co/Al ₂ O ₃	77	NaMgMnPdTi-RhPt-3Co/Al ₂ O ₃	71
LiNaKMnPd-RhPt-0.005Ni/Al ₂ O ₃	71	NaMgMnPdTi-RhPt-0.005Ni/Al ₂ O ₃	74
LiNaKMnPd-RhPt-0.01Ni/Al ₂ O ₃	83	NaMgMnPdTi-RhPt-0.01Ni/Al ₂ O ₃	81
LiNaKMnPd-RhPt-0.1Ni/Al ₂ O ₃	84	NaMgMnPdTi-RhPt-0.1Ni/Al ₂ O ₃	82
LiNaKMnPd-RhPt-0.2Ni/Al ₂ O ₃	86	NaMgMnPdTi-RhPt-0.2Ni/Al ₂ O ₃	83
LiNaKMnPd-RhPt-2Ni/Al ₂ O ₃	83	NaMgMnPdTi-RhPt-2Ni/Al ₂ O ₃	83
LiNaKMnPd-RhPt-3Ni/Al ₂ O ₃	76	NaMgMnPdTi-RhPt-3Ni/Al ₂ O ₃	76



[Example 12]

In the same manner as in Example 1, catalysts were prepared by adding Ti or Si to Example Catalyst 36 while changing its contents, and also by changing Ti content of Example Catalyst 48 or by adding Si to Example Catalyst 48 while changing its content.

(Test Results)

NOx elimination efficiencies determined at 400°C according to Test Example 3 are shown in Table 13. The catalysts containing 0.01 to 2 parts by mole of supported Ti or Si in terms of metal elements had a higher NOx elimination efficiency than 50% at 400°C after SOx poisoning, showing high NOx elimination efficiencies.

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Table 13

Catalysts	NOx elimination efficiency (%), 400°C	Catalysts	NOx elimination efficiency (%), 400°C
LiNaKMnPd-0.005Ti-RhPt/Al ₂ O ₃	39	NaMgMnPd0.005Ti-RhPt/Al ₂ O ₃	43
LiNaKMnPd0.01Ti-RhPt/Al ₂ O ₃	54	NaMgMnPd0.01Ti-RhPt/Al ₂ O ₃	57
LiNaKMnPd0.1Ti-RhPt/Al ₂ O ₃	75	NaMgMnPd0.1Ti-RhPt/Al ₂ O ₃	68
LiNaKMnPd0.2Ti-RhPt/Al ₂ O ₃	79	NaMgMnPd0.2Ti-RhPt/Al ₂ O ₃	76
LiNaKMnPd2Ti-RhPt/Al ₂ O ₃	58	NaMgMnPd2Ti-RhPt/Al ₂ O ₃	51
LiNaKMnPd3Ti-RhPt/Al ₂ O ₃	43	NaMgMnPd3Ti-RhPt/Al ₂ O ₃	34
LiNaKMnPd0.005Si-RhPt/Al ₂ O ₃	46	NaMgMnPd0.005Si-RhPt/Al ₂ O ₃	41
LiNaKMnPd0.01Si-RhPt/Al ₂ O ₃	64	NaMgMnPd0.01Si-RhPt/Al ₂ O ₃	54
LiNaKMnPd0.1Si-RhPt/Al ₂ O ₃	70	NaMgMnPd0.1Si-RhPt/Al ₂ O ₃	62
LiNaKMnPd0.2Si-RhPt/Al ₂ O ₃	62	NaMgMnPd0.2Si-RhPt/Al ₂ O ₃	60
LiNaKMnPd2Si-RhPt/Al ₂ O ₃	53	NaMgMnPd2Si-RhPt/Al ₂ O ₃	56
LiNaKMnPd3Si-RhPt/Al ₂ O ₃	39	NaMgMnPd3Si-RhPt/Al ₂ O ₃	39



[Example 13]

In the same manner as in Example 1, catalysts were prepared by changing P and B contents of Example Catalysts 70 and 71. Test was the same as in Test Example 2.

(Test Results)

NOx elimination efficiencies determined at 500°C according to Test Example 2 are shown in Table 14. The catalyst containing 0.01 to 2 parts by mole of supported P or B in terms of elements on the basis of 1.5 parts by mole of alumina had higher NOx elimination efficiencies than 80% at 500°C after heating at 800°C for 5 hours, showing good NOx elimination efficiencies.

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Table 14

Catalysts	NOx elimination efficiency (%), 400°C	Catalysts	NOx elimination efficiency (%), 400°C
LiNaKMnPdTi0.01P-RhPt-Ce/Al ₂ O ₃	95	LiNaKMnPdTi0.01B-RhPt-Ce/Al ₂ O ₃	95
LiNaKMnPdTiP-RhPt-Ce/Al ₂ O ₃	92	LiNaKMnPdTi1B-RhPt-Ce/Al ₂ O ₃	88
LiNaKMnPdTi2P-RhPt-Ce/Al ₂ O ₃	86	LiNaKMnPdTi2B-RhPt-Ce/Al ₂ O ₃	81
LiNaKMnPdTi3P-RhPt-Ce/Al ₂ O ₃	73	LiNaKMnPdTi3B-RhPt-Ce/Al ₂ O ₃	71

[Example 14]

In the same manner as in Example 1, catalysts were prepared by changing only amounts of coating per l of the honeycomb in Example Catalysts 36 and 48 without changing amounts of other supported components on Al₂O₃.



(Test Results)

NOx elimination efficiencies determined at 400°C according to Test Example 1 are shown in Table 15. The catalysts containing 0.3 to 4 moles of Al₂O₃ coating/l of honeycomb in terms of Al₂O₃ had higher NOx elimination efficiencies than 80% at 400°C, showing good NOx elimination efficiencies.

Table 15

Catalysts	NOx elimination efficiency (%), 400°C	Catalysts	NOx elimination efficiency (%), 400°C
LiNaKMnPd-RhPt/0.1Al ₂ O ₃	64	NaMgMnPdTi-RhPt/0.1Al ₂ O ₃	77
LiNaKMnPd-RhPt/0.3Al ₂ O ₃	82	NaMgMnPdTi-RhPt/0.3Al ₂ O ₃	84
LiNaKMnPd-RhPt/1.5Al ₂ O ₃	99	NaMgMnPdTi-RhPt/1.5Al ₂ O ₃	96
LiNaKMnPd-RhPt/3Al ₂ O ₃	90	NaMgMnPdTi-RhPt/3Al ₂ O ₃	84
LiNaKMnPd-RhPt/4Al ₂ O ₃	86	NaMgMnPdTi-RhPt/4Al ₂ O ₃	81
LiNaKMnPd-RhPt/6Al ₂ O ₃	70	NaMgMnPdTi-RhPt/6Al ₂ O ₃	61

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[Example 15]

As a hydrocarbon and CO combustion catalyst, a catalyst containing only Rh and Pt supported on an alumina coat honeycomb was prepared in the same manner as in Example 1, where Rh and Pt contents were 0.002 parts by mole of Rh and 0.01 part by mole of Pt in terms of metal elements on the basis of 1.5 parts by mole of alumina. Test was the same as in Test Example 1, and hydrocarbon and CO elimination efficiencies were determined by providing the combustion catalyst upstream or downstream of Example Catalyst 36 or 48 or with no provision of the

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combustion catalyst. Test temperature was 400°C.

(Test Results)

NOx elimination efficiencies determined at 400°C according to Test Example 1 are shown in Table 16. Hydrocarbon and CO elimination efficiencies were improved by providing the combustion catalyst.

Table 16

Example Catalyst 36	C ₃ H ₈ elimination efficiency (%), 400°C	CO elimination efficiency (%), 400°C
Hydrocarbon and CO combustion catalyst not provided	93	94
Hydrocarbon and CO combustion catalyst provided upstream	98	99
Hydrocarbon and CO combustion catalyst provided downstream	99	100
Example Catalyst 48	C ₃ H ₈ elimination efficiency (%), 400°C	CO elimination efficiency (%), 400°C
Hydrocarbon and CO combustion catalyst not provided	92	94
Hydrocarbon and CO combustion catalyst provided upstream	99	97
Hydrocarbon and CO combustion catalyst provided downstream	99	100

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As described in detail above, nitrogen oxides can be eliminated with high efficiency in an oxygen excess atmosphere according to the present invention. The present catalyst has distinguished heat resistance and SOx resistance, so that a high elimination activity can be maintained for a long time.

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Industrial Applicability

Automobile exhaust gases are now on a trend toward global emission regulation and fuel economy

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regulation and it is expectable that the market for lean-burn automobiles will surely expand. For the automobile exhaust gas purification catalysts, ternary catalysts have been so far used, but have failed to eliminate NOx contained in the exhaust gases emitted from lean-burn automobiles. The present exhaust gas purification catalyst can eliminate NOx contained in the exhaust gases emitted from the lean-burn automobiles with high elimination efficiency and ensures a very high industrial applicability.

Throughout this specification and the claims which follow, unless the context requires otherwise, the word "comprise", and variations such as "comprises" and "comprising", will be understood to imply the inclusion of a stated integer or step or group of integers or steps but not the exclusion of any other integer or step or group of integers or steps.

The reference to any prior art in this specification is not, and should not be taken as, an acknowledgment or any form of suggestion that that prior art forms part of the common general knowledge in Australia.



THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. An internal combustion engine exhaust gas purification apparatus, which comprises an exhaust gas purification catalyst provided in an internal combustion engine exhaust gas passage through which an air/fuel ratio-lean exhaust gas and an air/fuel ratio-rich or stoichiometric exhaust gas flows, wherein the exhaust gas purification catalyst comprises a porous carrier and an active component supported on the porous carrier, the active component comprising Rh, Pt and Pd, at least one member selected from alkali metals, and Mn.
2. An internal combustion engine exhaust gas purification apparatus according to claim 1, wherein the active component further contains Ti.
3. An internal combustion engine exhaust gas purification apparatus according to claim 1, wherein the active component further contains at least one of Cu, Co and Ni.
4. An internal combustion engine exhaust gas purification apparatus according to claim 1, wherein the active component further contains at least one of rare earth metals.
5. An internal combustion engine exhaust gas purification apparatus according to claim 1, wherein the active component further contains at least one of P and B.
6. An internal combustion engine exhaust gas purification apparatus according to claim 1, wherein a combustion catalyst capable of combusting HC and CO contained in the exhaust gas is provided at least at one of position upstream and downstream of the exhaust gas purification catalyst in the exhaust gas passage.
7. An internal combustion engine exhaust gas purification apparatus according to claim 1, wherein the active component further comprises at least one member selected from alkaline earth metals.
8. An internal combustion engine exhaust gas purification apparatus according to claim 1, wherein the active component further comprises Si.



9. An internal combustion engine exhaust gas purification process, which comprises contacting an exhaust gas emitted from a lean-burn operated internal combustion engine with an exhaust gas purification catalyst, thereby purifying the exhaust gas, wherein the exhaust gas is contacted with a catalyst containing an active component comprising Rh, Pt and Pd, at least one member selected from alkali metals, and Mn, supported on a porous carrier.

10. An internal combustion engine exhaust gas purification process according to claim 9, wherein operation of the internal combustion engine is temporarily shifted from the lean-burn operation to a theoretical air/fuel ratio operation or a fuel excess operation, thereby bringing an air/fuel ratio of the exhaust gas into a stoichiometric or fuel-rich state to regenerate the exhaust gas purification catalyst.

11. An internal combustion engine exhaust gas purification process according to claim 9, wherein the exhaust gas is contacted with a combustion catalyst capable of combusting HC and CO and then with the exhaust gas purification catalyst.

12. An internal combustion engine exhaust gas purification process according to claim 9, wherein the exhaust gas purified by the exhaust gas purification catalyst is further contacted with a combustion catalyst capable of combusting HC and CO.

13. An internal combustion engine exhaust gas purification process according to claim 9, wherein the active component further comprises at least one member selected from alkaline earth metals.

14. An internal combustion engine exhaust gas purification process according to claim 9, wherein the active component further comprises Si.

15. A lean NOx elimination catalyst, which comprises a porous carrier and an active component supported on the porous carrier, wherein the active component comprises Rh,



Pt and Pd, at least one member selected from alkali metals, and Mn, amounts of supported active metals being 0.0003 to 0.01 part by mole of Rh, 0.002 to 0.05 parts by mole of Pt and 0.001 to 0.2 parts by mole of Pd, 0.05 to 3 parts by mole of each of the alkali metals and 0.05 to 2 parts by mole of Mn in terms of metal elements on the basis of 1.5 parts by mole of the porous carrier.

16. A lean NOx elimination catalyst according to claim 15, wherein the active component further contains Ti in an amount of 0.01 to 2 parts by mole in terms of metal element on the basis of 1.5 parts by mole of the porous carrier.

17. A lean NOx elimination catalyst according to claim 15, wherein the active component further contains at least one of Ni, Co and Cu, amounts of supported Ni, Co and Cu being 0.01 to 2 parts by mole each in terms of metal elements on the basis of 1.5 parts by mole of the porous carrier.

18. A lean NOx elimination catalyst according to claim 15, wherein the active component further contains at least one of rare earth metals, amounts of supported rare earth metals being 0.02 to 0.5 parts by mole each in terms of metal elements on the basis of 1.5 parts by mole of the porous carrier.

19. A lean NOx elimination catalyst according to claim 15, wherein the active component further contains at least one of P and B, amounts of supported P and B being 0.01 to 2 parts by mole each in terms of metal elements on the basis of 1.5 parts by mole of the porous carrier.

20. A lean NOx elimination catalyst according to claim 15, wherein the porous carrier is supported on a substrate, an amount of the supported porous carrier being 0.3 to 4 moles on the basis of 1l of the substrate.

21. A lean NOx elimination catalyst according to claim 15, wherein the active component further comprises at least one member selected from alkaline earth metals in an amount of 0.05 to 3 parts by mole in terms of each metal element on the basis of 1.5 parts by mole of the porous carrier.



22. A lean NOx elimination catalyst according to claim 15, wherein the active component further comprises Si in an amount of 0.01 to 2 parts by mole in terms of metal element on the basis of 1.5 parts by mole of the porous carrier.
- 5 23. An apparatus according to claim 1 and substantially as hereinbefore described with reference to the drawings and/or Examples.
24. A process according to claim 9 and substantially as hereinbefore described with reference to the drawings and/or
- 10 Examples.
25. A catalyst according to claim 15 and substantially as hereinbefore described with reference to the drawings and/or Examples.

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DATED this 9th day of APRIL, 2001

HITACHI, LTD.

by DAVIES COLLISON CAVE
Patent Attorneys for the Applicant

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FIG. 1

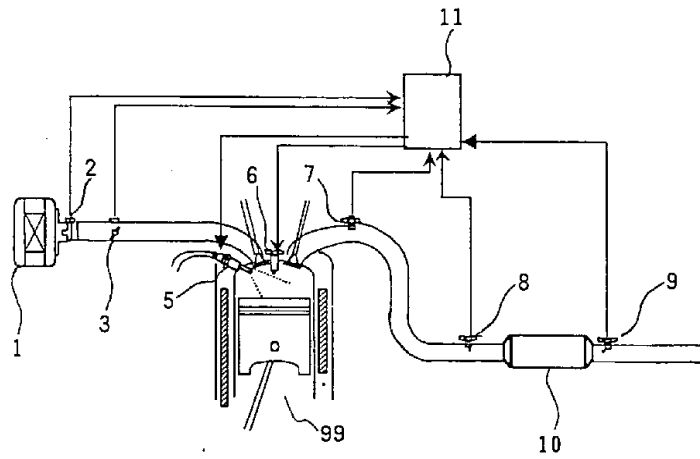


FIG. 2

