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(54) **Catalyst for purifying exhaust gases and method for manufacturing same**

(57) A catalyst for use in purifying exhaust gases by oxidation comprises a carrier made of calcium aluminate and titanium oxide and a catalytic component such as a platinum group metal, compound thereof, a metal oxide capable of oxidizing reductive gases or a mixture thereof. The carrier may be formed of a solid mass of desired form made of calcium aluminate and a layer of titanium oxide or may be a mixture of the two. Alternatively, the carrier may further comprise a transition metal oxide.

SPECIFICATION

Catalyst for purifying exhaust gases and method for manufacturing same

5 This invention relates to a catalyst for purifying exhaust gases generated from various burning or cooking appliances by oxidation of carbon monoxide and/or hydrocarbons contained in the exhaust gases into innocuous gases. Also, it relates to method for making the catalyst of the type just mentioned. 5

10 Recently, owing to increased air tightness in housing or building, it is required to purify exhaust gases from various burning devices or heaters. For instance, there have been already commercially sold petroleum stoves or heaters provided with catalysts therein or table roasters in which catalysts are set in position to eliminate oil and smoke generated during cooking. It is the general practice that catalysts have been employed under control of the technical expert, however, as is apparently seen from the above instances, it is a recent trend that ordinary consumers make use of catalyst positively. The requirements for catalyst to be used by ordinary users can be summarized as follows. 15

- (1) Inexpensiveness
- (2) Harmlessness
- (3) Long lifetime
- 20 (4) No side reactions involved. 20
- (5) Solidity and firmness.
- (6) Moldability in any desired form.

As catalysts which meet the above requirements, we have proposed catalysts which comprise a binder or carrier made of calcium aluminate and manganese oxide or copper oxide supported on the carrier with or without being further supported with platinum group metals (U.S. Patent Nos. 3,905,917, 4,065,406 and 4,211,672). It is sure that the catalyst using calcium alumina as a base material can satisfy the above requirements to a certain extent but is not necessarily satisfactory from a viewpoint of lifetime. As a matter of course, proper control of the amount of a catalyst to be supported or applying conditions will ensure long lifetime but is accompanied by problems such as high price and limitation in the range of use. Especially the catalyst using calcium aluminate as a base material shows a tendency of being deteriorated, when applied under relatively high temperature conditions, such as by sintering of calcium aluminate, reduction of the specific surface area caused by aggregation of a supported metal or metal oxide or poisoning with SO_2 gas. 30

35 Hitherto, alumina has been widely used as a carrier for catalyst. Further, there is known a carrier of a specific construction in which a monolithic molding of a honey-comb structure made of a cordierite mineral is applied with a $\gamma\text{-Al}_2\text{O}_3$ layer thereon. Moreover, diatomaceous earth or magnesia has been applied as a carrier. However, these materials can not overcome the drawbacks described above. 35

40 For instance, $\gamma\text{-Al}_2\text{O}_3$ is considered excellent as a carrier for catalyst, i.e. it exhibits a great surface area and large dispersability of catalyst, thus being one of the most widely employed carriers at present. However, the drawback of $\gamma\text{-Al}_2\text{O}_3$ is that it is so low in heat resistance that when employed at high temperatures, the compound is sintered to reduce its specific surface area and converted into more stable $\alpha\text{-Al}_2\text{O}_3$. On the other hand, according to recent studies on the mechanism of deterioration of Pt catalyst, the following growing theories of metal particles have been reported. 45

- (1) A mechanism in which one — several atoms separate from metal particles and move along the surface of carrier (atom-moving theory).
- (2) A mechanism in which entire particles of the metal move along the carrier surface by the intermetallic action while overcoming a strong interaction between the carrier and metal (particle moving theory). 50
- (3) A mechanism in which platinum changes into atoms or molecules and moves in a gas phase or on carrier.

55 In any of these theories, the metal catalyst on the carrier gradually aggregates or gathers and thus the specific surface area is reduced with the attendant lowering of its activity. The carrier which serves to expedite the growth of metal particles includes, aside from $\gamma\text{-Al}_2\text{O}_3$ or ZrO_2 , calcium aluminate which we have proposed for use as a carrier for the platinum group metals. 55

60 In contrast thereto, titanium oxide or barium oxide has attracted special interest recently as a carrier which does hardly cause the growth of metal particles thereon. The reason why these materials show the growth-suppressing effect is not known at the present stage of investigation but it is a fact that a catalyst using particularly titanium oxide as a carrier does hardly involve the growth of metal particles thereon and is stable in heat resistance and lifetime. In addition, titanium oxide is excellent in resistance to SO_2 poisoning and is thus a favourable material for a catalyst for purifying exhaust gas. 60

65 Accordingly, it is considered convenient to prepare a carrier from titanium oxide but titanium 65

oxide has drawbacks that titanium oxide is difficult to mold monolithically because of its high melting point of above 1800°C and that even though the molding is obtained, the specific surface area is so small that the molding becomes inactive as a carrier. Thus, although titanium oxide is recognized to be effective as a carrier, it involves some difficulties in practical

5 applications. 5

It is therefore an object of the present invention to provide a catalyst for purifying exhaust gases which overcomes the prior art difficulties or problems described above.

It is another object of the invention to provide a catalyst of the just-mentioned type which comprises titanium oxide as one of carrier components so as to impart excellent characteristic 10 properties of titanium oxide to the catalyst. 10

It is a further object of the invention to provide a catalyst for oxidizing reducing gases such as carbon monoxide and/or hydrocarbons into innocuous gases under relatively high temperature conditions, which catalyst being excellent in heat resistance and long in lifetime.

It is a still further object of the invention to provide a catalyst which involves little thermal 15 deterioration over a long period even when applied at high temperatures. 15

It is another object of the invention to provide a method for making a catalyst of the just-mentioned type.

In a broad aspect of the invention, there is provided a catalyst which comprises a carrier 20 substantially composed of calcium aluminate and 5 to 90 wt% of titanium oxide based on the carrier, and a catalytic component of a platinum group metal or a metal oxide capable of 20 oxidizing reductive gases into innocuous gases and supported on the carrier in an amount of 0.001 to 0.1 wt% of the carrier when the platinum group metal is used and in an amount of 0.1 to 10 wt% when the metal oxide is used. In the catalyst of this arrangement, the carrier 25 itself shows little or no catalytic activity and the catalytic performance depends on the type of a 25 supported catalyst. However, because of excellency in resistances to heat and poisoning of TiO_2 , 25 the amount of the catalytic component to be supported is sufficient to be very small. The amount of titanium oxide is in the range of 5 to 90wt% as defined above. Less amounts are unfavorable since the effect of addition of the titanium oxide can not be expected. On the 30 contrary, larger amounts result in a reduced amount of calcium aluminate and as a consequence 30 the carrier becomes so weak in binding force that it can not stand use. 30

In another aspect, there is provided a catalyst in which the carrier further comprises a 35 transition metal oxide, i.e. the carrier is substantially composed of 10 to 70 wt% of calcium aluminate, 5 to 50 wt% of titanium oxide and 5 to 70 wt% of a transition metal oxide. Most of 35 transition metal oxides show high catalytic activity and have been long used as a hopcalite 35 catalyst. This catalyst is characterized by its high activity at low temperatures but has a 35 drawback that it suffers thermal deterioration to a great degree and is poor in resistance to poisoning. This is partly due to a fact that transition metal oxides are thermally unstable and can 40 readily be converted into lower oxides and partly due to a fact that active sites disappear or the specific surface area is reduced owing to sintering thereof. This sintering becomes considerable 40 especially when particles of the oxide come close to one another. We have succeeded in 40 preventing the occurrence of the sintering to some extent by binding the particles of the metal oxide with calcium aluminate. However, there arises a problem that CaO of the calcium 45 aluminate reacts with the metal oxide to form, for example, $CaMn_2O_4$ thereby lowering the 45 activity of the oxide. This problem is overcome in accordance with the invention by incorporat- 45 ing titanium oxide in the mixture of calcium aluminate and a transition metal oxide. That is, 45 titanium oxide which has excellent resistances to heat and poisoning is admixed with calcium aluminate and a transition metal to form a barrier layer between particles of the metal oxide 50 thereby preventing occurrence of the sintering. Furthermore, it has been found that the metal 50 oxide itself does scarcely suffer from sulfur poisoning by the influence of titanium oxide which is 50 resistant to sulfur poisoning. The reason for this is that a sulfur compound is first caught by 50 calcium aluminate and is diffused into the inside of a carrier by which the metal oxide is 50 poisoned, but the barrier layer of titanium oxide protects the metal oxide from the sulfur 50 compound. 50

As described above, the catalyst composed of a mixture of calcium aluminate, a transition 55 metal oxide and titanium oxide shows a catalytic activity by itself to some extent differently from 55 the first-mentioned catalyst, but is unsatisfactory for use as a catalyst. Accordingly it is convenient that this carrier is further supported or deposited with a catalytic metal or metal 55 oxide on the surface thereof. In the case, a more excellent catalytic performance can be attained by the synergistic effect of a transition metal oxide and the catalytic metal or metal oxide. 55

In accordance with a further aspect of the invention, the carrier of the first-mentioned type is 60 made of a solid mass or core of calcium aluminate and a titanium oxide layer formed on part or 60 all of the surface of the mass, the amount of the titanium oxide being controlled to be in the range of 0.05 to 10 wt% of the solid mass. By this, the catalyst becomes more stable in lifetime 60 and more excellent in resistance to SO_2 poisoning without causing growth of catalytic particles 60 on the carrier surface. This type of catalyst is very advantageous in that calcium aluminate can 65 65

be molded in any desired form and titanium oxide having excellent properties as carrier can be readily applied as a layer on the molded mass or core. The covering layer of titanium oxide is tenacious and satisfactory in bonding strength even when treated at temperatures below 800°C.

This type of catalyst can be prepared by a method which comprises providing a mass of calcium aluminate, applying a slurry of titanium oxide or a solution of a titanium compound on the mass, thermally treating the thus applied mass at temperatures above 500°C to form a titanium oxide layer on part or all of the surface of the mass thereby obtaining a carrier, and depositing on the carrier a platinum group metal or a metal oxide capable of oxidizing reductive gases into innocuous ones in an amount of 0.001 to 0.1 wt% based on the carrier when the metal is used and in an amount of 0.1 to 10 wt% when the metal oxide is used.

The present invention will be described in more detail.

Calcium aluminate which is used as a binder for carrier or a carrier core in the practice of the invention is typically alumina cement of high heat resistance, which is distinct from Portland cement. Alumina cement is generally represented by $m\text{Al}_2\text{O}_3 \cdot n\text{CaO}$ while Portland cement is represented by $m'\text{SiO}_2 \cdot n'\text{CaO}$. Although large in demand and low in cost, Portland cement has drawbacks that it is poor in heat and spalling resistances and low in speed of hardening and is liable to be attacked by sulfate ions. In contrast, alumina cement is excellent in heat resistance and high in hardening speed and is thus preferable from a viewpoint of catalyst preparation.

The alumina cement has such a composition as indicated above and when the CaO component exceeds 40 wt%, its heat resistance becomes poorer although mechanical strengths increase, coupled with another disadvantage that such alumina cement readily reacts with a heavy metal oxide at high temperatures, e.g. it reacts with manganese oxide at temperatures of 650°C or more to form CaMn_2O_4 , thus giving rise to thermal breakage of catalyst. On the other hand, less contents of CaO component result in improved heat resistance but mechanical strengths are lowered with the aging time being prolonged at the time of molding, thus leading to reduced productivity. Additionally, when a content of the alumina component is below 35 wt%, the heat resistance is lowered. On the other hand, larger contents of alumina component can improve that heat resistance.

When an iron oxide component to be incorporated in the alumina cement exceed 20 wt%, mechanical strengths under heating conditions are lowered with the attendant lowering of the heat resistance. The iron oxide exhibits catalytic activity for purifying gases such as, for example, carbon monoxide, at temperatures higher than 300°C. In order to develop such a promoting effect, it is preferable that iron oxide is contained in an amount of 2 wt% or more.

Preferable compositions of the alumina cement are comprised of 15 to 40 wt%, preferably 30 to 40 wt%, of CaO component, 35 to 80 wt%, preferably 40 to 60 wt%, of alumina component and 0.3 to 20 wt%, preferably 2 to 10 wt% of iron oxide component.

When the calcium aluminate is used in admixture with titanium oxide, its content is 10 to 95 wt% of a total of calcium aluminate and titanium oxide. Further, when a transition metal is further incorporated in the calcium aluminate and titanium oxide, the content of calcium aluminate is the range 10 to 70 wt% so as to impart a satisfactory binding strength to the article formed from the mixture of these three components.

As described hereinbefore, Portland cement is poor in heat resistance and can not withstand temperatures higher than 300°C and this is not suitable for the gas purification purpose of household burning appliances in which temperatures of the catalyst are likely to exceed approximately 300°C. Although the alumina cement can satisfactorily withstand temperatures higher than 300°C, it is preferable that when a catalyst is allowed to withstand temperatures higher than 700°C, high alumina cement is employed.

Then, titanium oxide to be an essential component of the carrier will be described. In the practice of the invention titanium oxide is intended to mean not only simple metal oxides but also compound oxides containing titanium oxide. Titanium oxides include Ti_2O , TiO , Ti_2O_3 , Ti_3O_5 and TiO_2 , of which TiO_2 is a stable one and is preferable. TiO_2 includes crystal modifications called anatase, brookite and rutile. All of the three modifications naturally occur or can be artificially prepared. Of these, the rutile compound is stable even at high temperatures and the temperature at which the conversion of an anatase into rutile structure takes place is about 700°C. In practice, any types of TiO_2 may be used, of which the rutile compound showing excellent heat stability is preferably used.

On the other hand, examples of the compound oxides of titanium oxide include $\text{TiO}_2\text{-ZrO}_2$, $\text{TiO}_2\text{-SiO}_2$, $\text{TiO}_2\text{-MgO}$, $\text{TiO}_2\text{-Bi}_2\text{O}_3$, $\text{TiO}_2\text{-CdO}$, $\text{TiO}_2\text{-SnO}_2$ and the like, which are within the scope of the present invention. TiO_2 of the rutile structure has a tetragonal crystal structure and a melting point of 1855°C. Naturally occurring TiO_2 has a specific surface area of about 10 m²/g. It is believed that though not so high in the specific surface area, the compound has such a high melting point that the reduction of the surface area by sintering or the growth of particles of a metal catalyst can be suppressed in a usual manner of application.

TiO_2 partially reacts with calcium aluminate and thus shows high bonding force. In addition,

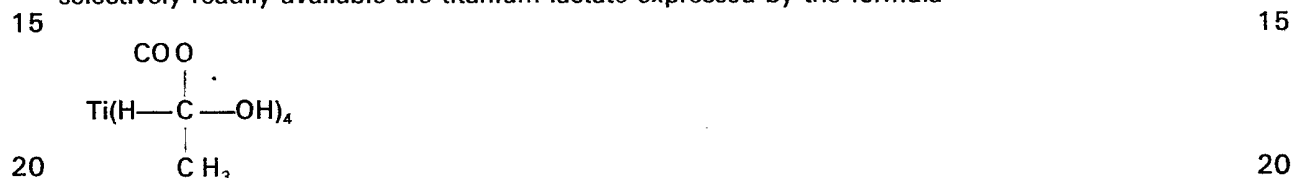
TiO₂ itself is high in mechanical strength. Accordingly, it is possible to form a carrier which is much more excellent than prior art counterparts.

When the titanium oxide is used in admixture with calcium aluminate, its content should be in the range of 5 wt% to 90 wt% for the reason described hereinbefore.

5 As described hereinbefore, the titanium oxide may be applied as a layer on a solid mass or core made of calcium aluminate. The procedure of formation of the titanium oxide layer will be described. 5

In order to form the titanium oxide layer on the solid mass, it is convenient to use a slurry of TiO₂ which is readily available. This slurry is commercially sold and is merely applied onto or immersed with the solid mass and subsequently heat treated to form a layer of TiO₂. 10

Alternatively, TiOSO₄ or (NH₄)₂TiCl₆·2H₂O which is soluble in water may be used in the form of an aqueous solution. Further, titanium can form salts in combination with various organic materials and solutions of these salts may be used. Examples of the organic salts which are selectively readily available are titanium lactate expressed by the formula 15



These solutions may be applied similarly to the slurry, i.e. either the solution or slurry is applied to the solid mass made of calcium aluminate by the coating or immersing technique. Then, the applied mass is dried and cured or sintered at a predetermined temperature thereby depositing a TiO₂ layer on the solid mass. In this manner, the titanium oxide layer can be deposited on part or all of the surface of the solid mass of calcium aluminate. Since the deposition is limited only to the surface area, the titanium oxide used is very small in amount. Nevertheless, the excellent properties of titanium oxide can be imparted to the carrier and the carrier may be shaped in any desired form because the core is made of calcium aluminate which is readily moldable. The effective amount of titanium oxide to be deposited or formed as a layer is in the range of 0.05 to 10 wt% based on the solid mass. Less amounts can not reflect the purpose of the invention while larger amounts are unfavourable since a bonding force to the calcium aluminate mass becomes weak and thus a tenacious titanium oxide layer can not be formed. 25

30 Then, the thermal treatment of the deposited titanium oxide layer is described. The heat treating conditions are important so as to determine the crystal form of TiO₂ and increase the bonding force to the calcium aluminate mass. In order to form a thermally stable TiO₂ layer, it is necessary to heat at temperatures above 700°C but where such a high temperature is not used in practical applications of catalyst, the heat treatment at 500 to 700°C is sufficient. However, the heat treatment at temperature below 500°C is not favorable since TiO₂ may not be completely deposited and its bonding force to calcium aluminate does not reach a satisfactory level the carrier of this type in which a TiO₂ layer is formed on part or all of the surface of calcium aluminate mass is rather preferable to that made of a mixture of calcium aluminate and titanium oxide for a reason that excellent properties of titanium oxide are effectively reflected on the carrier. 35

The transition metal oxide is then described. The transition metal oxides include oxides of a metal selected from Mn, Co, Ni, Cr, Cu and Fe. The transition metal oxides used herein mean at least one metal oxide mentioned above or a compound oxide containing the above metal oxide as one component. Of these transition metal oxide, manganese oxide is most preferable. The manganese oxide is a main component constituting the hopcalite catalyst and is relatively high in catalytic activity. The manganese oxide involves various types of crystal modification, of which γ-MnO₂ prepared from electrolysis is preferable for the purpose of the invention. 40

Simple metal oxides are high in activity but in view of heat stability, compound oxides are preferable. Various compound oxides are usable including, for example, MnFe₂O₄, ZnFe₂O₄, CoFe₂O₄, BaFe₂O₄ and the like. These compound oxides may be used singly or in combination with the simple metal oxides. 45

The amount of the transition metal oxide shows a close relation to an improved characteristic of catalytic performance and is necessary to be in the range of at least 5 wt% of the mixture of calcium aluminate, titanium oxide and the transition metal oxide. Less amounts are unfavorable since the effect of the addition can not be expected, whereas larger amounts than 70 wt% are also unfavorable since mechanical strengths of the catalyst are lowered and particles of the metal oxide naturally come too close to one another and thus the effect of titanium oxide can not be expected. For the reason described above, an optimum range is 5 to 70 wt% of the mixture. 60

65 The three types of carrier have been described above including one type in which a mixture of 65

calcium aluminate and titanium oxide is used, another type in which a solid mass of calcium aluminate is coated with titanium oxide on part or all of the surface of the solid mass, and a further type using a mixture of calcium aluminate, titanium oxide and a transition metal oxide.

5 These types of carrier may be used satisfactorily as they are. In order to increase mechanical strengths, deflective strength and resistance against thermal destruction or breakage, heat resistance aggregates may be added. Examples of the heat-resistant aggregate include silica aggregates, silica-alumina aggregates and alumina aggregates and, in mineral phase, it is preferable to employ silica minerals, millite, corundum, silimanite, β -alumina, and minerals of magnesia, chrome, dolomite, magnesite-chrome and chrome-magneiste. Moreover, it is preferable to use ordinary particulate or granular aggregates at low temperatures (300 to 700°C) and heat-resistant granular aggregates at high temperatures (above 700°C) depending on the working temperature of catalyst. 10

More particularly, the silica aggregates include siliceous stone and are mainly composed of SiO_2 . The silica-alumina aggregates include chamotte, agalmatolite, high alumina and the like, in which SiO_2 - Al_2O_3 is a main component. The alumina aggregates include α - Al_2O_3 , β - Al_2O_3 , γ - Al_2O_3 , ρ - Al_2O_3 and the like. As ordinarily employed minerals mentioned are silicate minerals, mullite, corundum, silimanite, β -alumina and the like. In practice, materials obtained by roughly crushing the above-mentioned aggregates to some extent or commercially available aggregates of coinchalcite, siliceous sand, alumina, chamotte and the like may be used, and for general purpose it is convenient to employ siliceous sand or chamotte commercially sold on the market. 20

In order to improve the heat resistance of carrier, there may be optionally added alkali-resistant glass fibers, fibrous iron wires, silica-alumina fibers, asbestos and the like.

Further, the molding of carrier is feasible more easily by adding as a molding aid such as carboxymethyl cellulose, methyl cellulose, polyvinyl alcohol, alcohols, and clay minerals such as bentonite. 25

Catalytic components to be supported or deposited on the carrier constituted of the afore-described compositions are described.

Catalytic components to be supported are those which are capable of oxidizing reductive gases such as carbon monoxide and hydrocarbons into innocuous ones and are mainly platinum group metals which include platinum, palladium, ruthenium, rhodium, and iridium. In practice, these metals are applied in the form of salts, of which chlorides are preferable. Typical salts include tetrachloroplatinate H_2PtCl_4 , hexachloroplatinate H_2PtCl_6 , platinum diamminodinitrile $\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$, palladium chloride PdCl_2 , ruthenium chloride RuCl_3 , and rhodium chloride. These metal salts are used by being dissolved in a solvent such as water or an alcohol. The concentration may vary depending on the amount or manner of deposition but use of a much concentrated solution results in poor dispersability of catalytic particles, an optimum concentration should be determined depending on the purpose in end use and the shape of carrier. 35

Especially when the platinum group metals are employed, there can be obtained a catalyst which is more excellent both in initial performance and in lifetime as compared with known platinum catalysts even when the deposition amount of is in the range of as small as 0.001 to 0.1 wt% of the carrier. That is, known platinum catalysts make use of a carrier such as of alumina or cordierite and platinum is usually deposited in an amount of 0.5 to 0.1 wt%. Less amounts that 0.1 wt% involve much deteriorated lifetime and thus it is generally accepted that the above-indicated range of the deposition amount should be used. On the other hand, when the carrier for catalyst of the invention is used, high catalytic performance can be expected even when the amount of deposited platinum is very small. 40

Thus, when any types of carrier in accordance with the invention is used, a catalyst of high performance can be obtained using only a very small amount of platinum group metals. This is believed for a reason which follows. That is, part of calcium aluminate constituting the carrier absorbs moistures, in which $\text{Al}_2\text{O}_3 \cdot n\text{CaO}$ is partially dissolved to release part of CaO and the solution thus shows alkalinity. On the other hand, a starting material for a noble metal catalyst is in most cases in the form of a chloride such as, for example, RuCl_3 , RhCl_3 , PdCl_2 , H_2PtCl_4 , or H_2PtCl_6 . When the hexachloroplatinate is dissolved in water, PtCl_6^{2-} ions are released and react with the dissolved CaO to form $\text{PtCl}_6(\text{OH})$. This $\text{PtCl}_6(\text{OH})$ salt is formed on or around the surface of the carrier and does not arrive at the depth of pores. Accordingly, the catalytic metal of the invention is distributed chiefly on the surface of the carrier and does not diffuse into the inside of the carrier. As described above, the catalytic metal ions are converted into a corresponding hydroxide on the carrier surface and attached also to TiO_2 as they are. Further, the carrier is alkaline in nature, so that a compound is formed by a reaction between the catalytic metal anions and part of the carrier surface and thus the catalytic metal is fixedly deposited on the carrier. 50

Thus, the catalytic component can be deposited only on the surface layer of the carrier, with the result that there can be obtained a catalyst of high performance even when the deposited amount is very small. 55

60 Aside from the platinum group metals, there may be supported as a catalytic component 65

oxides of iron, cobalt and nickel to be iron family elements, chromium and molybdenum to be chromium family elements, tin and lead to be carbon family elements, manganese to be a manganese family element, lanthanum to be a rare earth metal, zinc and cadmium to be zinc family elements, and vanadium to be a vanadium family element. Of these, a metal such as Pt, Pd, Mn, Fe, Cu or Ag or an oxide thereof are preferable in consideration of environmental pollution and most preferably Pt is used. These catalytic metals and metal oxides may be used singly or in combination. 5

There is a close relation between the amount of deposited catalytic component and the performance. In general, a greater amount of deposited catalyst results in more improved performance. Too much amount will cause problems such as falling-off and partial distribution of the catalytic component. Independently of the amount of catalytic component, the ranges of application, shape, activity at low temperatures and lifetime of the catalyst can be improved by applying two or more catalytic metals or metal oxides on the carrier. 10

An optimum amount of the catalytic metal oxide is in the range of 0.1 to 10 wt% of the carrier. The metal oxide is lower in activity as compared with noble metals such as platinum and is necessary to be used in so much large amount. With less amounts than 0.1 wt%, satisfactory catalytic activity can not be expected, whereas larger amounts than 10 wt% will cause a problem that the catalytic component may be falled off. In the practice of the invention, catalytic metal oxide and noble metal may be used in combination, in which case a total amount of the catalytic components is in the range of 0.1 to 10 wt% provided that the noble metal is used within the range defined hereinbefore. 15 20

The metal oxide can be supported on a carrier similarly to the case of the noble metal by applying an aqueous solution of salts such as a nitrate, chloride and the like onto the carrier or immersing the carrier in the solution. In case where a metal oxide and a metal catalytic components are allowed to coexist, a mixture of two solutions of corresponding metal salts may be used but it is preferable that a metal oxide is first supported, on which a metal component is subsequently a applied. 25

The present invention will be illustrated by way of examples.

30 Example 1 30

Calcium aluminate (alumina cement), titanium oxide of the rutile structure and siliceous sand serving as a heat-resistant aggregate were mixed in such ratios as indicated in Table 1 to obtain compositions of different formulations. Each mixture was further admixed by a wet process with 30 to 40 part by weight of water, 4 parts by weight of an alkali-resistant glass fiber and 0.5 parts by weight of methyl cellulose each based on 100 parts by weight of the mixture and then press molded. The molding was dried, aged in a water bath of 90°C and then dried to obtain a sample carrier. This carrier was in the form of a disc of a honey-comb structure having a diameter of 154 mm and a thickness of 15 mm and provided with 745 through-holes having a diameter of 4.1 mm. 35

Platinum was used as a catalytic metal, i.e. an aqueous solution of chloroplatinate having a concentration of 1g/100 cc was applied to a carrier in an amount of 70 mg (0.028 wt%) calculated as platinum, dried and thermally treated at 500°C for 1 hour to deposit platinum on the carrier. 40

The performance of each catalyst thus obtained was determined to measure its CO purification rate under conditions of a space velocity of 10,000 hr⁻¹, a CO concentration of 300 ppm and an atmospheric temperature of 200 °C. The heat resistance of each sample was determined by comparing the catalytic performances obtained after heating of the sample at 500 °C for 1 hour and after heating at 700°C for 50 hours. The test results are shown in Table 1. 45

Table 1

5	Composition of Carrier (wt%)			CO Purification Rate (200°C, SV 10,000 hr ⁻¹)		5	
	Test No.	alumina cement	TiO ₂	SiO ₂	after heat treatment at 500°C for hour		after heat treatment at 700°C for hours
10	1	50	—	50	100%	72%	10
	2	70	3	27	100%	73%	
	3	70	5	25	100%	94%	
	4	70	10	20	100%	98%	
15	5	50	30	20	100%	100%	15
	6	40	50	10	100%	100%	
	7	20	70	10	100%	100%	
	8	10	90	—	100%	100%	
20	9	5	95	—	Impossible to mold		20

As is clearly seen from the above results, the effect of TiO₂ appears when the TiO₂ content in the carrier is in the range of 5 to 90 wt%. When the content exceeds 90 wt%, the molding is infeasible since the alumina cement becomes too small in amount.

In this examples, the test Nos. 1, 2 and 9 are shown for reference only.

25 Example 2

The procedure of No. 6 of Example 1 was repeated using TiO₂ of the anatase structure, with the results that the catalytic performance was 100% after heat treatment at 500°C and 96% after heat treatment at 700°C.

30 Example 3

The procedure of Example 1 using the composition No. 5 in which TiO₂ was replaced by compound oxides including TiO₂-ZrO₂, TiO₂-SiO₂ and TiO₂-MgO was repeated. As a result, it was found the CO purification rates after heat treatment at 500°C were 100% for all the catalysts and those after heat treatment at 700°C were 98%, 100%, and 100%, respectively.

40 Example 4

The carrier of the composition indicated by No. 5 of Example 1 was used and applied with platinum in different ratios to know a relation between the deposited amount and the catalytic performance. Pt(NH₃)₂(NO₂)₂ was used as a starting material for platinum. That is, 1 g of the salt was dissolved in 100 cc of water and applied onto the carrier in amounts indicated in Table 2 (weight by percent after drying). The performance was evaluated in the same manner as in Example 1.

45 Table 2

50	No.	Deposition amount of Pt (wt%)	CO Purification Rate		50
			after heat treatment at 500°C for 1 hour	after heat treatment at 700°C for 50 hours	
	1	0.0008	71%	63%	
	2	0.001	98%	90%	
55	3	0.01	100%	100%	55
	4	0.05	100%	100%	
	5	0.10	100%	100%	
	6	0.12	100%	89%	
60	7	0.20	94%	83%	60

As is apparent from the above results, an optimum amount of the platinum is in the range of 0.001 to 0.1 wt%. When the amount exceeds 0.1 wt%, the dispersability of the catalyst becomes poor because of the too large amount of the catalytic metal and aggregation is rather likely to occur, resulting in a lowering of the performance.

In the table, test nos. 1, 6 and 7 are for reference.

When the above procedure was repeated using other platinum group metals, similar results were obtained. From this, an optimum amount of the platinum group metals is found to be in the range of 0.001 to 0.1 wt%.

5 Example 5 5

The carrier of No. 6 of Example 1 was used and deposited with a metal oxide. That is, the carrier was immersed in an aqueous 20 wt% $Mn(NO_3)_2$ solution, dried at 120°C and heat treated at 500°C for 1 hour to convert the manganese salt into a corresponding oxide. The amount of the deposition was controlled by repeating the cycle of the immersion and drying at 120°C. 10

The catalytic performance was evaluated similarly to Example 1 with the results shown in Table 3.

15 Table 3 15

No.	Amount of deposited manganese oxide (wt%)	CO Purification Rate at 200°C	
		after heat treatment at 500°C for 1 hour	after heat treatment at 700°C for 50 hours
1	0.08	68%	48%
2	0.10	84%	65%
25 3	0.23	86%	68%
4	3.24	88%	74%
5	8.32	90%	84%
6	10.0	93%	80%
30 7	12.5	Falling-off of manganese oxide	

As is apparent from the above results, an optimum amount of the metal oxide catalyst is in the range of 0.1 to 10 wt%. Less amounts lead to poor performance while larger amounts are unfavorable because of the falling-off of the oxide from the carrier. 35

In the table Nos. 1 and 7 are shown for reference.

Example 6

Example 5 was repeated using a 20 wt% $Cu(NO_3)_2$ solution instead of the $Mn(NO_3)_2$ solution thereby depositing 5.7 wt% of copper oxide. The resulting catalyst had CO purification rates of 89% and 80% after the heat treatment 500°C for 1 hour and at 700°C for 50 hours, respectively. 40

Example 7

The sample of No. 5 of Example 5 was applied with the Pt salt solution of Example 4 so that the amount of Pt deposited was 0.05 wt% and then heat treated at 500°C for 1 hour to obtain a catalyst. The thus obtained catalyst showed CO purification rates of 100% both after the heat treatment at 500°C for 1 hour and after the heat treatment at 700°C for 50 hours. 45

50 Example 8 50

The carrier of No. 5 of Example 1 was applied with mixed solutions of a $Pt(NH_3)_2(NO_2)_2$ aqueous solution and solutions of $PdCl_2$, $RuCl_3$ and $RhCl_3$ in mixing ratios indicated in Table 4, and then the procedure of Example 1 was repeated to obtain catalysts deposited with different catalytic compositions. Further, Pd alone was deposited on the carrier. The test results are shown in Table 4 below. 55

Table 4

No.	Composition Ratio by Wt.	Amount of Deposition (wt%)	CO Purification Rate at 200°C	
			after heat treatment at 500°C for 1 hour	after heat treatment at 700°C for 50 hours
1	Pt + Pd 2:1	0.03	100%	98%
2	Pt + Pd 3:1	0.08	100%	100%
3	Pt + Ru 5:1	0.06	100%	99%
4	Pt + Rh 5:1	0.08	100%	98%
5	Pt + Pd + Ru 5:2:1	0.09	100%	100%
6	Pd	0.05	100%	94%

Example 9

25 Calcium aluminate, manganese oxide ($\gamma\text{-MnO}_2$) and titanium oxide of the rutile structure were mixed in different ratios indicated in Table 5, to which was further added siliceous sand as a heat-resistant aggregate to give base compositions. Each base composition which had been dry mixed was admixed by a wet process with 30 to 40 parts by weight of water, 4 parts by weight of an alkali-resistant glass fiber and 0.5 parts by weight of methyl cellulose each based on 100 parts by weight of the base composition and press molded to obtain a disc of a honey-comb structure having a diameter of 154 mm and a thickness of 15 mm and provided with 745 through-holes with a diameter of 4.1 mm, followed by drying, aging in a water bath of 90°C and drying to give a carrier sample.

30 The samples were each applied with a chloroplatinate solution having a concentration of 1 g/100 ccH₂O in an amount of 70 mg (0.028 wt%) calculated as Pt, dried and thermally treated at 500°C for 1 hour thereby depositing Pt on the sample.

35 The catalytic performances of these catalysts were evaluated by measuring their CO purification rate at 200°C under conditions of a space velocity of 10,000 hr⁻¹ and a CO concentration of 300 ppm. The heat resistance of the samples was determined by comparing the CO purification rates after heating of the catalyst at 500°C for 1 hour and after heating at 700°C for 50 hours.

40 The test results are shown in Table 5 below.

Table 5

No.	Composition (wt%)				CO Purification Rate	
	alumina cement	TiO ₂	$\gamma\text{-MnO}_2$	SiO ₂	after heating at 500°C for 1 hour	after heating at 700°C for 50 hours
1	40	—	50	10	100%	46%
2	40	3	50	7	100%	53%
3	50	5	40	5	100%	73%
4	50	10	30	10	100%	92%
5	30	30	30	10	100%	100%
6	25	50	20	5	100%	100%
7	10	80	10	—	Impossible to mold.	

60 As is clearly seen from the above results, the effect of TiO₂ appears when the amount is in the range of 5 to 50 wt%. Larger amounts lead to a reduced amount of calcium aluminate serving as a binder, making it impossible to mold.

In the table, test Nos. 1, 2 and 7 are for reference.

65 Reference

The sample Nos. 1-6 of Example prior to the deposition of Pt were subjected to the measurement of the CO purification rate with the results shown in Table 6.

Table 6

5		CO Purification Rate (200°C)		5
10		after heating at 500°C for 1 hour	after heating at 700°C for 50 hours	10
1	92%	35%		
2	91%	42%		
3	90%	75%		
4	88%	85%		
15	5	85%	83%	15
6	82%	81%		

20 As is clear from the above results, sample Nos. 1 and 2 having larger contents of manganese dioxide and show a better catalytic activity after the heat treatment at 500°C for 1 hour but exhibit greater degrees of deterioration than sample Nos. 3 to 6 when treated at 700°C. 20

Example 10

25 Example 9 was repeated using the composition of Nos. 6 in which TiO₂ was changed to that of the anatase type. The CO purification rate of the resulting catalyst was 100% after heating at 500°C for 1 hour and 96% after heating at 700°C for 50 hours. 25

Example 11

30 Example 9 was repeated using the composition of No. 5 in which TiO₂ was replaced by compound oxides, i.e. TiO₂-ZrO₂, TiO₂-SiO₂ and TiO₂-MgO. The CO purification rates of these samples were 100% in all the cases after heating at 500°C for 1 hour and were 98%, 100% and 100%, respectively, after heating at 700°C for 50 hours. 30

Example 12

35 In Example 9, instead of 30 wt% of γ -MnO₂ of the composition of No. 5 were used transition metal oxides shown in Table 7 thereby obtaining catalyst samples. Similarly to examples 9 and 10 the CO purification rates of the samples with or without depositing Pt were measured after heat treatments at 500°C for 1 hour and at 700°C for 50 hours. The measurement of the purification rate was conducted under conditions of a temperature of 200°C and a space 40 velocity of 10,000 hr⁻¹. 40

Table 7

5	CO Purification Rate					5		
	10	Transition Metal Oxide	No deposition of Pt		Pt deposited		10	
			after heating at 500°C for 1 hour	after heating at 700°C for 50 hours	after heating at 500°C for 1 hour			after heating at 700°C for 50 hours
No.								
1	MnFe ₂ O ₄	90%	85%	100%	92%			
15	2	CuO	93%	86%	100%	93%	15	
	3	MnO ₂ + NiO (1:1)	95%	89%	100%	98%		
	4	Co ₂ O ₃ + Fe ₂ O ₃ (1:1)	94%	88%	100%	95%		
20	5	Co ₂ O ₃ + Fe ₂ O ₃ (1:1)	91%	85%	100%	98%	20	
	6	ZnFe ₂ O ₄	90%	87%	100%	99%		
	7	MnO ₂ + CuO (1:1)	97%	90%	100%	100%		
25						25		

Example 13

The carrier of the composition shown by No. 7 of Example 9 was used and the amount of Pt deposited on the carrier was varied and the CO purification rates were measured. A starting material for Pt was a solution of 1 g of Pt(NH₃)₂(NO₂)₂ in 100 cc of water and applied in such amounts (% by weight after drying) as indicated in Table 8. The performance was evaluated in the same manner as in Example 9.

Table 8

35	CO Purification Rate at 200°C			35	
	40	Deposited Amount of Pt (wt%)	after heating at 500°C for 1 hour		after heating at 700°C for 50 hours
	1	0.0008	71%	63%	
	2	0.001	98%	90%	
	3	0.01	100%	100%	
45	4	0.05	100%	100%	45
	5	0.10	100%	100%	
	6	0.12	100%	89%	
	7	0.20	94%	83%	

50 As is apparent from the above results, in this case an optimum amount of the metal catalyst supported on the carrier is in the range of 0.001 to 0.10 wt%. Larger amounts of Pt is in excess and show a tendency of aggregation, lowering the catalytic performance. In the table Nos. 1, 6 and 7 are for reference.

55

Example 14

The carrier of No. 5 of Example 9 was used and supported with various types of platinum group metals using mixtures of an aqueous solution of Pt(NH₃)(NO₂)₂ and solutions of PdCl₂, RuCl₃ and/or RhCl₃. The CO purification rates of these catalysts are shown in Table 9.

Table 9

10 No.	Composition Ratio	Amount of Deposition (wt%)	CO Purification Rate at 200°C		10
			after heating at 500°C for 1 hour	after heating at 700°C for 50 hours	
5					5
1	Pt + Pd 2:1	0.03	100%	98%	
2	Pt + Pd 3:1	0.08	100%	100%	
15					15
3	Pt + Ru 5:1	0.06	100%	99%	
4	Pt + Rh 5:1	0.08	100%	98%	
20					20
5	Pt + Pd + Ru 5:2:1	0.09	100%	100%	
6	Pd	0.05	100%	94%	

25 Example 15 25

One hundred parts by weight of a mixture of 50 wt% of calcium aluminate and 50 wt% of siliceous stone were admixed with 4 parts by weight of an alkali-resistant glass fiber, and 25 parts by weight of water. The mixture was press molded into a disc having a diameter of 154 mm and a thickness of 15 mm and provided with 745 through-holes having a diameter of 4.1 mm. After drying, the disc sample was aged in a water bath of 90°C for 1 hour and then dried at 120°C for 1 hour. 30

The resulting solid mass was applied with a slurry of rutile type TiO₂ in different ratios, dried and heated at 600°C for 1 hour to obtain a carrier.

Each carrier was applied with an aqueous solution of chloroplatinate having a concentration of 1 g/100 cc in an amount of 70 mg (0.028 wt%) calculated at Pt, dried and heat treated at 500°C for 1 hour to deposit Pt on the carrier. 35

The CO purification rate of the catalysts at 200°C was measured under conditions of a space velocity of 10,000 Hr⁻¹ and a CO concentration of 300 ppm. The heat resistance of the samples was determined by comparing the catalytic performances measured after heating at 500°C for 1 hour and after heating at 700°C for 50 hours. The results are shown in Table 10. 40

Table 10

50 No.	Deposited Amount of TiO ₂ (wt%)	Deposited State of TiO ₂	CO Purification Rate at 200°C		50
			after heating at 500°C for 1 hour	after heating at 700°C for 50 hours	
45					45
1	0.03	o	100%	73%	
2	0.05	o	100%	90%	
3	0.12	o	100%	93%	
55					55
4	3.2	o	100%	94%	
5	5.3	o	100%	97%	
6	6.7	o	100%	100%	
7	8.4	o	100%	100%	
8	10.0	Δ	100%	100%	
60					60
9	10.2	x	—	—	

In the table, the deposited state of TiO₂ is evaluated as follows: When the carrier was rubbed by fingers, a case where no TiO₂ is attached to the fingers is indicated as "o", a case where a slight degree of the attachment is observed is indicated as "Δ", and a case where a fair degree 65

of the attachment is observed and TiO_2 is fallen off from the carrier is indicated as "x".

As is clearly seen from the table, an optimum amount of deposition of the TiO_2 layer is in the range of 0.05 to 10 wt% based on the solid mass. Within the above range, little or no deterioration in performance is observed even after heating of the catalysts at $700^\circ C$ for 50 hours. When the amount exceeds 10 wt%, the falling off of TiO_2 undesirably takes place, making it impossible to use such a carrier.

It will be noted that Nos. 1 and 9 are for reference.

Example 16

The solid mass containing calcium aluminate as used in Example 15 was immersed in a 10 wt% $TiSO_4$ solution and heated at $700^\circ C$ for 1 hour to deposit a TiO_2 layer on the surface of the solid mass. The deposited amount of TiO_2 was 3.5%. The resulting carrier was treated in the same manner as in Example 15 to deposit Pt thereon. The CO purification rate of the catalyst was 100% after heating at $500^\circ C$ for 1 hour and 98% after heating at $700^\circ C$ for 50 hours.

Example 17

Example 16 was repeated using a 10 wt% $(NH_4)_2TiCl_6 \cdot 2H_2O$ solution to deposit TiO_2 in an amount of 4.2 wt% after the heat treatment. Then, the procedure of Example 16 was repeated to obtain a catalyst showing a CO purification rate of 100% after heating at $500^\circ C$ for 1 hour and 96% after heating at $700^\circ C$ for 50 hours.

Example 18

Example 16 was repeated using a 10 wt% titanium lactate ($Ti(C_3H_5O_3)_4$) to deposit TiO_2 in an amount of 5.4 wt% after the heat treatment. Then, the procedure of Example 16 was repeated to obtain a catalyst showing a CO purification rate of 100% after heating at $500^\circ C$ for 1 hour and 97% after heating at $700^\circ C$ for 50 hours.

Example 19

The carrier of the composition indicated by No. 5 of Example 1 was deposited with platinum in different amounts to give catalysts. A starting material for platinum used was $Pt(NH_3)_2(NO_2)_2$ and was dissolved in water at a concentration of 1 g/100 cc. Then, the solution was applied so that the amount of the deposited platinum was as indicated in Table 11 below. The catalytic performance of these catalysts was evaluated in the same manner as in Example 15.

Table 11

No.	Amount of Deposited Pt (wt%)	CO Purification Rate at $200^\circ C$	
		after heating at $500^\circ C$ for 1 hour	after heating at $700^\circ C$ for 50 hours
1	0.0008	71%	63%
2	0.001	98%	90%
3	0.01	100%	100%
4	0.05	100%	100%
5	0.10	100%	100%
6	0.12	100%	89%
7	0.20	94%	83%

As is clearly seen from the above results, an optimum amount of the metal catalyst is also found to be in the range of 0.001 to 0.1 wt%. When the amount exceeds 0.1 wt%, the catalytic metal is so large in amount that its dispersability becomes poor and the metal is rather likely to aggregate, showing a lowering of the catalytic performance.

Example 20

The carrier of No. 6 of Example 15 was used for deposition with a metal oxide. That is, the carrier was immersed in a 20 wt% solution of $Mn(NO_3)_2$, dried at $120^\circ C$ and heat treated at $500^\circ C$ for 1 hour to convert the manganese salt into a corresponding oxide. The deposited amount was controlled by repeating the procedure of the immersion and the drying at $120^\circ C$. The catalytic performance was evaluated in the same manner as in Example 15. The results are shown in Table 12.

Table 12

5	No.	Deposited Amount of Pt (wt%)	CO Purification Rate at 200°C		5
			after heating at 500°C for 1 hour	after heating at 700°C for 50 hours	
10	1	0.08	68%	48%	10
	2	0.10	84%	65%	
	3	0.23	86%	68%	
	4	3.24	88%	74%	
	5	8.32	90%	84%	
15	6	10.0	93%	80%	15
	7	12.5	falling-off of manganese oxide		

It will be noted that, in the foregoing examples, the catalytic performance of catalysts is evaluated by virtue of CO purification rate but a similar tendency is observed when hydrocarbons are used instead of CO.

As seen from the foregoing examples, there can be obtained according to the invention catalysts which are excellent in heat resistance and lifetime. This is considered to result from the addition of TiO₂ as one component of the carrier. In addition, a major proportion of the catalyst of the invention is constituted of inexpensive materials, i.e. calcium aluminate and titanium oxide, so that the catalyst can be manufactured inexpensively.

CLAIMS

1. A catalyst for purifying an exhaust gas, which catalyst comprises a carrier comprising calcium aluminate and 5 to 90 wt% of titanium oxide based on the weight of the carrier, and a catalytic component of a platinum group metal or compound thereof or of a metal oxide capable of oxidizing reductive gases into harmless gases and supported on said carrier in an amount of 0.001 to 0.1 wt% based on the weight of the carrier when said platinum group metal or compound thereof is used and in an amount of 0.1 to 10 wt % based on the weight of the carrier when said metal oxide is used.

2. A catalyst according to claim 1, wherein said carrier is made of a mixture of calcium aluminate and titanium oxide.

3. A catalyst according to claim 1, wherein said carrier is made of a solid mass of calcium aluminate with a titanium oxide layer formed on part or all of the surface of said mass, the amount of the titanium oxide being in the range of 0.05 to 10 wt% based on the weight of said solid mass.

4. A catalyst according to any one of claims 1 to 3, wherein said titanium oxide is TiO₂ of an anatase or rutile structure.

5. A catalyst according to any one of claims 1 to 3, wherein said titanium oxide is a compound oxide containing titanium oxide.

6. A catalyst according to any one of the preceding claims, wherein said catalytic component is a mixture of the platinum group metal or compound thereof and the metal oxide and is used in an amount of 0.1 to 10 wt% based on the weight of said carrier provided that said platinum group metal or compound thereof is used in an amount of 0.001 to 0.1 wt% based on the weight of the carrier.

7. A catalyst according to any one of the preceding claims, wherein said platinum group metal is Pt, Ru, Rh, Pd, Ir or a mixture thereof.

8. A catalyst according to claim 7, wherein said platinum group metal is platinum.

9. A catalyst according to any one of the preceding claims, wherein said metal oxide is an oxide of Fe, Co, Ni, Cr, Mo, Sn, Pb, Mn, Cu, Ag, La, Zn, Cd, V or a mixture thereof.

10. A catalyst according to any one of the preceding claims, wherein said carrier further comprises alumina aggregate, aluminasilica aggregate, silica aggregate or a mixture thereof.

11. A catalyst according to any one of the preceding claims, wherein said carrier further comprises an alkali-resistant glass fiber, fibrous iron wire, asbestos or a mixture thereof.

12. A catalyst according to any one of the preceding claims, wherein said carrier further comprises a molding aid to facilitate the moulding of carrier.

13. A catalyst according to any one of the preceding claims, wherein said carrier comprises a mixture of 10 to 70 wt% of calcium aluminate, 5 to 50 wt% of titanium oxide, and 5 to 70 wt% of a transition metal oxide.

14. A catalyst according to claim 13, wherein said transition metal oxide is an oxide of Mn,

Co, Ni, Cr, Cu, or Fe.

15. A catalyst according to claim 13 or 14, wherein said transition metal oxide is γ - MnO_2 .
16. A catalyst according to claim 13, wherein said transition metal oxide is a compound oxide.
- 5 17. A catalyst for use in purifying an exhaust gas said catalyst being substantially as hereinbefore described in any one of Examples 2, 6, 7, 10, 16, 17 or 18 or of Test Nos. 3 to 8 of Example 1, 2 to 5 of Example 4, 2 to 6 of Example 5, 1 to 6 of Example 8, 3 to 6 of Example 9, 1 to 7 of Example 12, 2 to 5 of Example 13, 1 to 6 of Example 14, 2 to 8 of Example 15, 2 to 5 of Example 19 or 2 to 6 of Example 20 or with reference to any one of the 10 compound oxides of Example 3 to 11.
18. A method of manufacturing a catalyst for purifying an exhaust gas, which method comprises applying a slurry of titanium oxide or a solution of a titanium compound on a mass of calcium aluminate, thermally treating the thus applied mass at temperatures above 500°C to form a titanium oxide layer on part or all of the surface of said mass thereby obtaining a carrier, 15 and depositing on said carrier a catalytic component of a platinum group metal or compound thereof or of a metal oxide capable of oxidizing reductive gases into harmless gases in an amount of 0.001 to 0.1 wt% based on the weight of said carrier when the platinum group metal or compound thereof is used and in an amount of 0.1 to 10 wt% based on the weight of the carrier when the metal oxide is used.
- 20 19. A method according to claim 18, wherein the titanium oxide is applied in an amount of 0.05 to 10 wt% based on the weight of said mass of calcium aluminate.
20. A method according to claim 18, wherein the titanium compound is TiOSO_4 or $(\text{NH})_2\text{TiCl}_6 \cdot 2\text{H}_2\text{O}$.
- 25 21. A method for manufacturing a catalyst for purifying an exhaust gas, said method being substantially as hereinbefore described in any one of Examples 2, 6, 7, 10, 16, 17, or 18 or of Test Nos. 3 to 8 of Example 1, 2 to 5 of Example 4, 2 to 6 of Example 5, 1 to 6 of Example 8, 3 to 6 of Example 9, 1 to 7 of Example 12, 2 to 5 of Example 13, 1 to 6 of Example 14, 2 to 8 of Example 15, 2 to 5 of Example 19 or 2 to 6 of Example 20 or with reference to any one of the compound oxides of Example 3 or 11.