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(57) Abstract

A platinum group metal three-way conversion catalyst composition containing a high temperature catalytic component and a low temperature catalytic component has each catalytic component present as separate distinct particles in the same washcoat layer. The catalyst composition is prepared from a washcoat slurry containing a high temperature catalyst support material, and a low temperature catalyst support material, each support material being of sufficiently large particle size so as to prevent each support material forming a solution or a sol with the liquid medium of the slurry. The platinum group metal or metals can be impregnated into each support material either after formation of the washcoat on a non-porous refractory, metallic or pelletised substrate or before forming the washcoat slurry.

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THREE-WAY CONVERSION CATALYSTS AND METHODS FOR THE PREPARATION THEREOF

This invention relates to catalysts used to remove undesirable components in the exhaust gas from internal combustion engines. More particularly, the invention is concerned with improved catalysts of the type generally referred to as three-way conversion or TWC catalysts.

The exhaust from internal combustion engines contains hydrocarbons, carbon monoxide and nitrogen oxides which must be removed to levels established by various government regulations. The aforementioned three-way catalysts are polyfunctional in that they have the capability of substantially simultaneously catalysing the oxidation of hydrocarbons and carbon monoxide and the reduction of nitrogen oxides.

Typical three-way catalysts which exhibit good catalytic activity and long life contain one or more platinum group metals (*eg* Pt, Pd, Rh, Ru and Ir) located upon a high surface area porous refractory oxide support, *eg* a high surface area alumina coating. The porous refractory oxide support is carried on a suitable non-porous refractory substrate such as a monolithic carrier comprising a refractory ceramic or metal honeycomb structure or refractory particles such as spheres, pellets or short extruded segments of a suitable refractory material.

Three-way catalysts are currently formulated with complex washcoat compositions containing stabilised alumina, an oxygen storage component (primarily stabilised ceria) and precious metal catalytic components. The term "oxygen storage component" is used to designate a material which is capable of being oxidised during oxygen-rich (lean) cycles of the exhaust gas being treated and reduced during oxygen-poor (rich) cycles of the exhaust gas being treated.

Three-way catalysts typically have been based on platinum/rhodium catalysts in preference to palladium which suffered from certain disadvantages including the high sensitivity of palladium to poisoning by sulphur and lead. However, with increased use of lead free petrol around the world, palladium is an extremely promising substitute for the traditionally used platinum/rhodium catalysts. Furthermore, the much lower cost of palladium makes it a highly desirable alternative to platinum/rhodium in three-way catalysts, provided the desired catalytic performance can be achieved.

The art has devoted a great deal of effort in attempts to improve the efficiency of palladium containing three-way catalysts. Thus, in an article in Third Int. Cong. Catal. and Auto Poll. Controls, Pre-print Vol. 1, pages 125 to 135, the authors, Dettling et al, describe the inclusion of a low temperature catalyst component ($Pd/Al_2 0_3$) and a high temperature catalyst component ($Pd/Ce0_2$) in the same catalyst composition for high activity under both low and high operating temperatures.

W0 95/00235 (Engelhard Corporation) also describes a palladium containing catalyst composition containing low and high temperature catalyst components structured as two washcoat layers

W0 95/07600 (Allied Signal) describes a palladium containing three-way catalyst as a single layer. However, according to the method of preparation. the finished catalyst only has the high temperature $Pd/Ce0_2$ component.

US Patent Nos 4,727,052, 5,057,483, 5,008,090 and 5,010,051; GB Patent 1495637; and European Patent Applications 92302928.4 and 0427293A2 also describe three-way conversion catalysts based on platinum group metal catalytic components.

We have found that platinum group metal three-way catalysts containing a high temperature functional component and a low temperature functional component when prepared by the unique methods of the present invention exhibit greatly improved three-way catalytic activity even after extended high temperature aging.

In this specification, by high temperature functional catalytic component is meant a catalytic component which exhibits catalytic activity at higher temperatures (*eg* above about 500°C) and by low temperature functional catalytic component is meant a catalytic component which exhibits catalytic activity at lower temperatures (*eg* in the range 200 to 400°C)

According to the present invention there is provided a method of making a platinum group metal three-way catalyst composition which contains a high temperature catalytic component and a low temperature catalytic component with each catalytic component being present in the catalyst composition as separate distinct particles in the same washcoat layer, which method comprises:

(a) forming on a non-porous substrate a combined washcoat of a high temperature catalyst support material and a low temperature catalyst support material from a slurry in which each of the catalyst support materials is of sufficiently large particle size so as to prevent each catalyst support material from forming a solution or a sol with the liquid medium of the slurry; and

(b) impregnating a platinum group metal or metals into each catalyst support material either after formation of the washcoat on the non-porous substrate or before forming the washcoat slurry.

Preferably, separate slurries of the high temperature support material and the low temperature support material are prepared and the two slurries are then blended together and coated onto the non-porous substrate.

The non-porous substrate may be a refractory ceramic or metal honeycomb structure or refractory particles such as spheres, pellets or short extruded segments of a suitable refractory material.

Further according to the present invention, the proportions of the high temperature catalytic component and the low temperature catalytic component required in the catalyst composition are determined by the respective water absorption capabilities of each catalyst support material and the respective amounts of each catalyst support material present in the washcoat.

Preferably, the water absorption capabilities of the high temperature catalyst support material and the low temperature catalyst support material are respectively 0.2 to 1.0ml/g and 0.5 to 2.5ml/g.

Suitably, the catalyst support materials have a mean particle size of less than 20 microns, preferably between 1 and 20 microns and more preferably about 5 microns.

The platinum group metal is selected from platinum, palladium, rhodium, ruthenium, iridium or any combination thereof.

Preferably, the high temperature catalyst support material is an oxygen storage material.

Suitable oxygen storage materials include ceria, perovskites, NiO, MnO_2 and Pr_2O_3 with stablised ceria being the preferred material.

Suitable stabilisers for ceria include zirconium, lanthanum, alumina, yttrium, praeseodymium and neodymium with zirconium being preferred.

Suitably, the zirconium stablised ceria contains 2 to 50% ZrO_2, a preferred composition being about 58% by weight CeO_2 and about 42% by weight ZrO_2.

Suitable low temperature catalyst support materials are stabilised alumina and unstabilised alumina.

Suitable stabilisers for alumina include lanthanum, barium and zirconium with lanthanum being preferred.

Preferably, the lanthanum stabilised alumina contains 2 to 7% lanthanum oxide.

The method of the invention may utilise a catalyst promoter, preferably selected from Nd, Ba, Ce, La, Pr, Mg, Ca and Sr with Nd and Ba being particularly suitable. The catalyst promoters may be added to the slurry or separately impregnated.

Further preferably, the method of the invention utilises a compound effective for the suppression of hydrogen sulphide emissions from the catalyst composition. Suitable such compounds include NiO, Fe_2O_3 and BaO with NiO being preferred.

Suitably, the method according to the invention utilises a compound which is effective in preventing preferential absorption of the platinum group metal in one or other of the high temperature or low temperature catalyst support materials. Preferred such compounds include citric acid, acetic acid and oxalic acid.

From another aspect, the present invention is a platinum group metal three-way catalyst composition made by any of the methods described above.

From yet another aspect, the present invention is a platinum group metal three-way catalyst composition comprising a high temperature catalytic component and a low temperature catalytic component wherein each catalytic component is present in the catalyst composition as separate distinct particles in the same washcoat layer.

Suitably, the high temperature and low temperature catalytic components in the catalyst composition have a mean particle size of less than 20 microns, preferably between 1 and 20 microns and more preferably about 5 microns.

As can be seen from the foregoing discussion of the prior art, the concept of combining a high temperature catalytic component and a low temperature catalytic component in the same three-way conversion catalyst is known. The present invention, however, enables both catalytic components to be advantageously incorporated into a single washcoat layer by utilising a unique preparation technique. This preparation technique entails incorporating two distinct and separate catalyst support materials into the same washcoat slurry so that the final catalyst composition has both the high temperature catalytic function and the low temperature catalytic function in a single washcoat layer.

A key feature of the invention is that the catalyst support materials should not be in solution in the washcoat slurry or present as very small particles as found in a sol (the order of magnitude of the size of sol particles being in the nanometer range). In order to obtain the benefits of the present invention, the insoluble catalyst support materials in the washcoat slurry preferably should have a mean particle size of at least 1 micron, more preferably about 5 microns. However, if the particle size is too large (*eg* greater than 20 microns) there may be difficulty in getting the washcoat to adhere to a non-porous substrate.

Another important feature of the invention is that to maintain separation of the catalyst support materials they should be ball-milled in separate slurries followed by blending of these slurries. The final blend is coated onto the non-porous substrate.

Yet another important feature of the invention is the incipient wetness water absorption capabilities of the high temperature catalyst support material and the low temperature catalyst support material because these water absorption capabilities relate not only to the process for making the catalyst composition but also to the specification of the catalyst formulation. The catalyst contains two oxide support materials, exemplified by zirconium-stablilised ceria and lanthanum- stabilised alumina, although unstabilised alumina may be used. The platinum group metal (exemplified by palladium) is split between the two oxide support materials. In one embodiment of the invention, the palladium is impregnated from an aqueous solution into the washcoat consisting of a mixture of the two oxide support materials and the way in which the palladium is split between the two oxides depends on the fraction of the aqueous impregnation solution absorbed by the respective oxides. For example, if it is required that 50% of the available palladium is to be supported on the zirconium-stabilised ceria and the other 50% of available palladium is to be supported on the lanthanum-stabilised alumina then the washcoat would be formulated so that the water absorption of the zirconium-stabilised ceria in the catalyst composition (*ie* (ml water absorbed/g) x (g in catalyst)) is equal to the water absorption of the lanthanum-stabilised alumina in the catalyst composition. Thus, the ratio of the oxide support materials is specified by their relative water absorptions and the absolute amounts of the oxide support materials is specified by the amount of support needed in the catalyst composition (more specifically, a certain amount of Zr-stabilised ceria is needed for adequate performance). The desired split of the palladium depends on the duty required of the catalyst composition. In some applications, equal amounts of high temperature catalytic component and low temperature catalytic component is required. In other applications, more high temperature compound than low temperature compound is required (or *vice versa*). For example, catalyst compositions having palladium splits ranging from (a) 27% of Pd as $Pd/ZrCeO_2$ - 73% of Pd as $Pd/La\ Al_2O_3$ to (b) 73% of Pd as $Pd/ZrCeO_2$ - 27% of Pd as $Pd/LaAl_2O_3$ have been prepared according to the methods of the invention.

In an alternative method of making the catalyst composition, a portion of the total palladium is impregnated into a bulk form of the high temperature catalyst support material and the remaining portion of the palladium is impregnated into a bulk form of the low temperature catalyst support material prior to the formation of the washcoat slurry. Since the impregnated palladium is essentially insoluble in the washcoat it remains interacted with its associated oxide support material in the final catalyst composition. In this embodiment also, the ratio of the two oxide support materials is chosen on the basis of their relative water absorptions and the desired split between the palladium intimately interactive with, for example, the zirconium stabilised ceria and the palladium intimately interactive with the lanthanium stabilised alumina.

Certain embodiments of the invention and the efficacy thereof are demonstrated by the following Examples.

EXAMPLE 1

La-stabilised Al_2O_3 with an incipient wetness water absorption of about 1.85ml/g was slurried in water at a composition of about 55% by weight solids to form slurry A. Slurry A was then wet milled to a mean particle size of about 5 microns. Separately, bulk NiO was slurried in water at a composition of about 4% by weight solids and wet milled to a mean particle size of about 5 microns. After the NiO slurry was wet milled, Zr-stabilised ceria with an incipient wetness water absorption of about 0.5ml/g and was added to the NiO slurry and the resulting slurry was wet milled further to a mean particle size of about 5 microns to form slurry B. Slurry A and slurry B were blended in a specific ratio (1:2.36 as dictated by the desired catalyst composition) and coated on a monolithic cordierite substrate by dipping or alternatively passing through a washcoat curtain. After blowing off the excess washcoat with compressed air, the coated substrate was then dried at 60°C and fired at 500°C in flowing air. The fired coated substrate was then dipped in an aqueous solution of $Pd(NO_3)_2$/citric acid/$Nd(NO_3)_3$ or alternatively passed through a curtain of the same solution and excess solution was blown off with compressed air (Impregnation 1). The $Pd(NO_3)_2$/citric acid/$Nd(NO_3)_3$ solution was absorbed such that the quantity of solution which just filled the pores of the washcoat contained sufficient Pd and Nd to give the desired loadings. The resulting impregnated block was dried at 60°C and fired at 500°C in flowing air. Finally, the fired block was dipped in an aqueous solution of barium acetate (about 150g Ba/l) or alternatively passed through a curtain of the same solution and the excess solution was blown off with compressed air (Impregnation 2). The barium acetate solution was absorbed such that the quantity of solution which just filled the washcoat contained sufficient barium to give the desired loading. Finally, the barium-impregnated block was dried at 60°C and fired at 500°C in flowing air.

The catalyst composition prepared in accordance with this Example 1 had the palladium split approximately 62% on the stabilised alumina and 38% on the stabilised ceria.

In a modification of this Example 1, slurry B could be prepared by co-milling NiO and Zr-stabilised ceria as opposed to pre-milling the NiO and then adding the Zr-stabilised ceria.

EXAMPLE 2

An aqueous solution of $Pd(NO_3)_2$ was impregnated into La-stabilised Al_2O_3 with an incipient wetness water absorption of about 1.85ml/g and the wet powder was dried at 60°C and fired at 500°C in static air. The thus obtained Pd/La-stabilised Al_2O_3 powder was substituted for some or all of the La-Stabilised Al_2O_3 used to make slurry A as in Example 1. Separately, an aqueous solution of $Pd(NO_3)_2$ was impregnated into Zr-stabilised CeO_2 with an incipient wetness water absorption of about 0.5ml/g and the resulting wet powder was dried at 60°C and fired at 500°C in static air. The thus obtained Pd/Zr-stabilised CeO_2 was substituted for some or all of the Zr-stabilised CeO_2 used to make slurry B as in Example 1. The rest of the catalyst preparation was identical to the method of Example 1 except that the Pd impregnation had already been carried out prior to the formation of the slurries.

NOTES:

(i) In a modified method of preparing the catalyst, barium can be included in the washcoating step by co-milling a barium compound (*eg* barium sulphate, barium nitrate or barium acetate) with La-stabilised Al_2O_3 during the preparation of slurry A. This change would reduce production costs by reducing the preparation from three steps to two steps.

(ii) Nitrates, acetates and chlorides are suitable impregnation salts.

(iii) The catalyst compositon may contain non-Pd-containing Zr-stabilised ceria and non-Pd-containing La-stabilised alumina.

(iv) Unstabilised ceria and unstabilised alumina can be used.

(v) The catalysts obtained in Examples 1, 2 and 3 above had the same composition, namely:

(a)	2.1%	Pd
(b)	52.5%	Zr-stabilised CeO_2
(c)	23.0%	La-stabilised Al_2O_3
(d)	6.9%	Nd_2O_3
(e)	13.4%	BaO
(f)	2.1%	NiO

All percentages are weight percentages.

(vi) Other useful catalyst compositions of the invention are as follows:

	(A)	(B)
Zr-stabilised CeO_2	55.8%	51.8%
La-stabilised Al_2O_3	24.4%	22.7%
Nd_2O_3	3.1%	6.8%
BaO	10.9%	13.3%
NaO	3.1%	2.9%
Pd	2.3%	1.0%
Rh	--	0.1%
Washcoat load	$0.13 g/cm^3$	$0.145 g/cm^3$

Again, all precentages are weight percentages.

(vii) As with all catalyst systems, the precious metal content of the catalyst can vary widely. Also, similar composition ranges with washcoat loads up to 0.274g/cm^3 have been tested and found to be successful.

EXAMPLE 3

(Comparative Example)

This Example is directed to a comparative catalyst, not in accordance with the present invention, in which soluble ceria is present in the washcoat.

Cerium carbonate was slurried in water. A 10% excess amount of glacial acetic acid was added to this slurry to completely convert the cerium carbonate to cerium acetate. Zirconium acetate was then added to the aforementioned mixture. Finally, La-stabilised alumina and NiO were added to form a slurry with approximately 50% solids. The slurry was milled to a mean particle size of about 5 microns and coated on a smooth monolith substrate by dipping (or alternatively passing through a washcoat curtain). After blowing off the excess washcoat with compressed air, the coated substrate was then dried at 60°C and fired at 500°C in flowing air. This process may have to be repeated to achieve the desired washcoat loading. The fired catalyst was dipped in an aqueous solution of $Pd(NO_3)_2$/citric acid/$Nd(NO_3)_2$ (or alternatively it can be passed through a washcoat curtain of the same solution) and the excess solutions was blown off with compressed air (Impregnation 1). This impregnation solution was absorbed such that the quantity of solution which just filled the pores of the washcoat contained sufficient Pd and Nd to give the desired loadings. The resulting impregnated block was dried at 60°C and fired at 500°C in flowing air. Finally, the fired block was dipped in an aqueous solution of barium acetate (or alternatively it can be passed through a curtain of the same solution) and the excess solution was blown off with compressed air (Impregnation 2). The solution was absorbed such that the quantity of solution which just filled the pores of the washcoat contained sufficient barium to give the desired loading. The impregnated block was dried at 60°C and fired at 500°C in flowing air.

EXAMPLE 4

(Test Results)

Laboratory tests of the catalysts of Examples 1, 2 and 3 were conducted in the following manner.

A cylindrical core of 2.54cm diameter and 30mm length was cut from each of the impregnated blocks of Examples 1, 2 and 3. Each core was placed in an oven which had a controlled atmosphere capable of cycling between 1% CO/10% H_2O/20ppm SO_2/balance N_2 and 0.5% O_2/10% H_2O/20ppm SO_2/balance N_2 every five minutes. The furnace was heated to 1050°C and held at that temperature for 12 hours. Each core was removed and tested in a laboratory reactor under lean/rich cycled conditions with the following average simulated exhaust gas composition:

200ppm	C_3H_8
200ppm	C_3H_6
1%	CO

2000ppm	NO
0.33%	H_2
0.755%	O_2
14%	CO_2
10%	H_2O
balance	N_2

with a total flow rate of 23.8 SLPM. After establishing this inlet gas composition, the inlet gas temperature was raised to 550°C and the total HC, CO and NOx percentage conversions were measured. The temperature was then lowered to 450°C and the conversions were measured again, and finally the temperature was lowered to 350°C and the conversions were measured yet again.

The following table contains the data for the catalysts of Examples 1, 2 and 3.

TABLE

	550°C			450°C			350°C		
Catalyst	HC	CO	NOx	HC	CO	NOx	HC	CO	NOx
Example 1	72	79	63	68	75	58	46	53	35
Example 2	66	87	59	59	71	47	41	49	31
Example 3	63	68	52	59	61	45	38	41	28

It can be seen from the above Table that the catalysts prepared in accordance with Examples 1 and 2 are substantially better than the catalyst prepared according to Example 3 which has soluble ceria in the washcoat.

CLAIMS

1. A method of making a platinum group metal three-way catalyst composition which contains a high temperature catalytic component and a low temperature catalytic component with each catalytic component being present in the catalyst composition as separate distinct particles in the same washcoat layer which method comprises:

(a) forming on a non-porous substrate a combined washcoat of a high temperature catalyst support material and a low temperature catalyst support material from a slurry in which each of the catalyst support materials is of sufficiently large particle size so as to prevent each catalyst support material from forming a solution or a sol with the liquid medium of the slurry; and

(b) impregnating a platinum group metal or metals into each catalyst support material either after formation of the washcoat on the non-porous substrate or before forming the washcoat slurry.

2. A method as claimed in claim 1 wherein separate slurries of the high temperature support material and the low temperature support material are prepared and the two slurries are then blended together and coated onto the non-porous substrate.

3. A method as claimed in claim 1 or 2 wherein the proportions of the high temperature catalytic component and the low temperature catalytic component required in the catalyst composition are determined by the respective water absorption

capabilities of each catalyst support material and the respective amounts of each catalyst support material present in the washcoat.

4. A method as claimed in any of the preceding claims wherein the water absorption capabilities of the high temperature catalyst support material and the low temperature catalyst support material are respectively 0.2 to 1.0ml/g and 0.5 to 2.5ml/g.

5. A method as claimed in any one of the preceding claims wherein the catalyst support materials have a mean particle size of less than 20 microns.

6. A method as claimed in claim 5 wherein the mean particle size of the catalyst support materials is about 5 microns.

7. A method as claimed in any one of the preceding claims wherein the platinum group metal is selected from platinum, palladium, rhodium, iridium or any combination thereof.

8. A method as claimed in any one of the preceding claims wherein the high temperature catalyst support material is an oxygen storage material.

9. A method as claimed in claim 8 wherein the oxygen storage material is selected from ceria, perovskites, NiO, MnO_2 or Pr_2O_3.

10. A method as claimed in claim 8 or 9 wherein the oxygen storage material is stabilised with zirconium, lanthanum, alumina, yttrium, praesodymium or neodymium.

11. A method as claimed in claim 10 wherein the oxygen storage material is a zirconia-stabilised ceria.

12. A method as claimed in claim 11 wherein the zirconium stabilised ceria contains 2 to 50% zirconium oxide.

13. A method as claimed in claim 12 wherein the zirconium stabilised ceria has a composition of about 58% by weight CeO_2 and about 42% by weight ZrO_2.

14. A method according to any one of the preceding claims wherein the low temperature catalyst support material is a stabilised or unstabilised alumina.

15. A method as claimed in claim 14 wherein the stabiliser for the alumina is selected from lanthanum, barium or zirconium.

16. A method as claimed in claim 15 wherein the lanthanum stabilised alumina contains 2 to 7% by weight lanthanum oxide.

17. A method as claimed in any one of the preceding claims which utilises a catalyst promoter.

18. A method as claimed in claim 17 wherein the catalyst promoter is selected from Nd, Ba, Ce, La, Pr, Mg, Ca or Sr.

19. A method as claimed in any one of the preceding claims which utilises a compound effective for the suppression of hydrogen sulphide emissions from the catalyst composition.

20. A method as claimed in claim 19 wherein the hydrogen sulphide suppression compound is NiO, Fe_2O_3, CaO or BaO.

21. A method as claimed in any one of the preceding claims which utilises a compound which is effective in preventing preferential absorption of the platinum group metal in one or other of the high temperature or low temperature catalyst support materials.

22. A method as claimed in claim 21 wherein the compound preventing preferential absorption is citric acid, acetic acid or oxalic acid.

23. A platinum group metal three-way catalyst composition prepared by the method of any one of claims 1 to 22.

24. A platinum group metal three-way catalyst composition comprising a high temperature catalytic component and a low temperature catalytic component

wherein each catalytic component is present in the catalyst composition as separate distinct particles in the same washcoat layer.

25. A catalyst composition as claimed in claim 24 wherein the high temperature and low temperature catalytic components have a mean particle size of less than 20 microns.

26. A catalyst composition as claimed in claim 25 wherein the mean particle size of the catalytic components is about 5 microns.

27. A catalyst composition as claimed in any one of claims 23, 24, 25 or 26 wherein the high temperature catalytic component is an oxygen storage material impregnated with a platinum group metal or metals.

28. A catalyst composition as claimed in claim 27 wherein the oxygen storage material is selected from ceria, perovskites, NiO, MnO_2 or Pr_2O_3.

29. A catalyst composition as claimed in claim 28 wherein the oxygen storage material is a stabilised ceria.

30. A catalyst composition as claimed in claim 29 wherein the oxygen storage material is zirconium stabilised ceria.

31. A catalyst composition as claimed in claim 30 wherein the zirconium stabilised ceria contains 2 to 50% zirconium oxide.

32. A catalyst composition as claimed in claim 31 wherein the zirconium stabilised ceria has a composition of about 58% by weight CeO_2 and 42% by weight ZrO_2.

33. A catalyst composition as claimed in any one of claims 23 to 32 wherein the low temperature catalytic component is a stabilised or unstabilised alumina impregnated with a platinum group metal or metals.

34. A catalyst composition as claimed in claim 33 wherein the stabiliser for the alumina is selected from lanthanum, barium or zirconium.

35. A catalyst composition as claimed in claim 34 wherein the lanthanum stabilised alumina contains 2 to 7% by weight lanthanum oxide.

36. A catalyst composition as claimed in any one of claims 23 to 35 wherein the platinum group metal is selected from platinum, palladium, rhodium, ruthenium, iridium, or any combination thereof.

37. A catalyst composition as claimed in any one of claims 23 to 36 which contains a catalyst promoter.

38. A catalyst composition as claimed in claim 37 wherein the catalyst promoter is selected from Nd, Ba, Ce, La, Pr, Mg, Ca or Sr.

39. A catalyst composition as claimed in any one of the claims 23 to 38 which contains a compound effective for the suppression of emissions of hydrogen suplhide from the catalyst composition.

40. A catalyst composition as claimed in claim 39 wherein the compound effective for the suppression of emissions of hydrogen sulphide is NiO, Fe_2O_3, CaO or BaO.

41. An engine whose exhaust apparatus contains the catalyst defined in any one of claims 23 to 40.

INTERNATIONAL SEARCH REPORT

Interr ıal Application No
PCT/GB 97/01944

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B01D53/94 B01J37/04

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B01D B01J

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 93 10886 A (ENGELHARD CORP.) 10 June 1993 see the whole document ---	1
A	US 5 081 095 A (R. E. BEDFORD ET AL.) 14 January 1992 see the whole document ---	1
A	EP 0 244 127 A (JOHNSON MATTHEY, INC.) 4 November 1987 SEE ESPECIALLY EXAMPLE III PAGE 3 ---	1
A	EP 0 351 197 A (JOHNSON MATTHEY PUBLIC LTD.) 17 January 1990 see the whole document --- -/--	1

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

1

Date of the actual completion of the international search 23 October 1997	Date of mailing of the international search report 29. 10. 97
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Devisme, F

Intern. al Application No
PCT/GB 97/01944

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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A	WO 93 09146 A (ENGELHARD CORP.) 13 May 1993 see the whole document ---	1
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Inten ıal Application No
PCT/GB 97/01944

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