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(71) Applicant *(for all designated States except US)*: **TOYOTA JIDOSHA KABUSHIKI KAISHA** [JP/JP]; 1, Toyota-cho, Toyota-shi, Aichi-ken, 471-8571 (JP).

(72) Inventor; and

(75) Inventor/Applicant *(for US only)*: **IMOTO, Rui** [JP/JP]; c/o Toyota Jidosha Kabushiki Kaisha, of 1, Toyota-cho, Toyota-shi, Aichi-ken, 471-8571 (JP).

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(54) **Title**: EXHAUST GAS CONTROL SYSTEM, EXHAUST GAS PURIFICATION CATALYST AND METHOD FOR THE PRODUCTION OF EXHAUST GAS PURIFICATION CATALYST

(57) **Abstract**: An exhaust gas purification catalyst which includes copper as an active species and in which particles of copper or an oxide of copper are supported on a $Ce0_2$-$Zr0_2$ carrier and the ratio of Ce to Zr (Ce/Zr, mass ratio) in the surface of the carrier is in the range of $0.5 < Ce/Zr < 2.5$, and a method for the production of an exhaust gas purification catalyst that includes the step of preparing a $Ce0_2$-$Zr0_2$ carrier in which the ratio of Ce to Zr (Ce/Zr, mass ratio) in the surface thereof is in the range of $0.5 < Ce/Zr < 2.5$.

EXHAUST GAS CONTROL SYSTEM, EXHAUST GAS PURIFICATION CATALYST AND METHOD FOR THE PRODUCTION OF EXHAUST GAS PURIFICATION CATALYST

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] The present invention relates to an exhaust gas control system, an exhaust gas purification catalyst, and a method for the production of the exhaust gas purification catalyst. More specifically, the present invention relates to an exhaust gas control system and an exhaust gas purification catalyst which use a specific base metal and a specific carrier in combination to achieve high NO_X purification performance at low temperature, and a method for the production of the exhaust gas purification catalyst.

2. Description of Related Art

[0002] In recent years, regulations on exhaust gas are becoming stricter worldwide from the standpoint of global environmental conservation. In response, an exhaust gas purification catalyst is used in internal combustion engines. In such an exhaust gas purification catalyst, a noble metal, such as Pt, Au or Rh, is used as a catalyst component that is supported on a carrier to remove HC, CO and NO_X in exhaust gas efficiently. However, these noble metals are produced only in some specific countries and face the risk of depletion. An exhaust gas purification catalyst that uses a base metal, instead of a noble metal, as the supported metal is also considered. However, a base metal-supported purification catalyst, in which a base metal is supported on a carrier, such as a metal oxide carrier, is poorer in exhaust gas purification performance, especially in NO_X conversion efficiency, than a noble metal-supported purification catalyst and has not been put into practice yet.

[0003] On the other hand, in automobiles, such as gasoline engine vehicles and diesel engine vehicles, that use an exhaust gas purification catalyst in which a noble metal is supported on a metal oxide carrier, various systems are used to improve not only catalytic activity but also fuel efficiency. For example, the engine is operated usually

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under lean air-fuel ratio (A/F) (oxygen-excess) conditions to improve fuel efficiency but occasionally under stoichiometric (theoretical air-fuel ratio, A/F = 14.6) to rich (fuel-excess) conditions to improve the catalytic activity of the exhaust gas purification catalyst.

[0004] When it comes to the particle size of the noble metal supported, it is known that a catalyst in which nanoparticles with a particle size of less than 10 nm are supported on a metal oxide carrier exhibits high catalytic activity. Thus, a catalyst in which fine nanoparticles of a noble metal and/or a base metal are supported on a metal oxide carrier is under consideration.

[0005] For example, Published Japanese Translation of PCT Application No. 2009-515679 discloses a catalyst for conversion of carbon monoxide that includes high-dispersion particles of metals that are selected from the group that consists of Au, Pt, Pd, Ag, Ni, Ru, Rh, Ir, Os, Co, Fe and Cu with a diameter of approximately 2 to 5 nm, a metal oxide carrier that is selected from the group that consists of Al_2O_3, TiO_2, Fe_2O_3, CeO_2, CuO, ZnO, SiO_2, V_2O_5, MgO, La_2O_3, ZrO_2, SnO_2, MnO_2, MoO_3, Mo_2O_5 and zeolite, and a capping agent, wherein the metal particles and the capping agent are supported on the carrier. As specific examples, catalysts in which Au particles are supported on various types of metal oxide carriers are shown.

[0006] As described above, a supported catalyst which uses nanoparticles of a base metal with a particle size of 10 nm or greater as a supported metal component and which exhibits high NO_X purification performance has not been known yet as a specific technique.

SUMMARY OF THE INVENTION

[0007] The present invention provides an exhaust gas purification catalyst which uses nanoparticles of a base metal with a particle size of 10 nm or greater as a supported metal component and which exhibits high NO_X purification performance. The present invention also provides an exhaust gas control system that includes the exhaust gas purification catalyst. The present invention also provides a method for the

production of an exhaust gas purification catalyst which uses a base metal as the supported metal component and which exhibits high NO_X purification performance.

[0008] A first aspect of the present invention relates to an exhaust gas purification catalyst that includes copper as an active species. The exhaust gas purification catalyst includes a CeO_2-ZrO_2 carrier, and particles of copper or an oxide of copper, that are supported on the CeO_2-ZrO_2 carrier. The mass ratio of Ce to Zr (Ce/Zr, mass ratio) in a surface of the CeO_2-ZrO_2 carrier is in a range of $0.5 < Ce/Zr < 2.5$ (the CeO_2-ZrO_2 carrier may be abbreviated to "CZ").

[0009] It is possible to achieve high NO_X purification performance using nanoparticles of a base metal, copper, with a particle size of 10 nm or greater as supported copper particles.

[0010] A second aspect of the present invention relates to an exhaust gas control system which includes an exhaust pipe that is connected to an engine, and an exhaust gas control apparatus that is provided in the exhaust pipe. The exhaust gas control apparatus includes the exhaust gas purification catalyst and is controlled to contain a rich atmosphere.

[0011] A third aspect of the present invention relates to a method for a production of an exhaust gas purification catalyst that includes copper as an active species. The production method includes preparing a CeO_2-ZrO_2 carrier in which a mass ratio of Ce to Zr (Ce/Zr, mass ratio) at least in a surface thereof is in a range of $0.5 < Ce/Zr < 2.5$, preparing a mixture of the CeO_2-ZrO_2 carrier and an aqueous solution that contains a copper compound, and depositing copper or an oxide of copper on the CeO_2-ZrO_2 carrier by removing water from the mixture by heating. The "ratio of Ce to Zr in the surface (Ce/Zr, mass ratio)" that is used in the present invention is a value that is measured by XPS (X-ray photoelectron spectroscopy) as described in detail later in the section of Examples.

[0012] According to the present invention, it is possible to obtain an exhaust gas purification catalyst which exhibits high NO_X purification performance using nanoparticles of a base metal with a particle size of 10 nm or greater as a supported metal

component. In addition, according to the present invention, it is possible to obtain an exhaust gas purification catalyst which exhibits high NO_X purification performance easily using a base metal as the supported metal component.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] Features, advantages, and technical and industrial significance of exemplary embodiments of the invention will be described below with reference to the accompanying drawings, in which like numerals denote like elements, and wherein:

FIG. 1 is a schematic diagram that illustrates an exhaust gas purification catalyst of the present invention in a reducing atmosphere;

FIG. 2 is a graph that shows NO_X conversion efficiencies of exhaust gas purification catalysts according to embodiments of the present invention and outside the scope of the present invention for comparison;

FIG. 3 is a graph that shows oxygen desorption temperatures of exhaust gas purification catalysts according to embodiments of the present invention and outside the scope of the present invention for comparison;

FIG. 4 is a schematic diagram that illustrates an example of a system in which an exhaust gas purification catalyst according to an embodiment of the present invention is applied to exhaust gas purification;

FIG. 5 is a graph that shows a temperature pattern that is used to evaluate the activity of an exhaust gas purification catalyst;

FIG. 6 is a schematic diagram that illustrates an experiment that is conducted to evaluate the catalytic activity of an exhaust gas purification catalyst;

FIG. 7 is a graph that shows processing conditions to measure the particle size of Cu particles of an exhaust gas purification catalyst by a CO pulse method; and

FIG. 8 is a graph that shows a temperature pattern that is used to measure the oxygen desorption temperature of an exhaust gas purification catalyst.

DETAILED DESCRIPTION OF EMBODIMENTS

[0014] The present invention includes the following embodiments.

1) An exhaust gas purification catalyst, wherein the particles of copper (Cu) or an oxide of copper are nanoparticles with a particle size of 10 to 30 nm as measured by a CO pulse method in a reducing atmosphere.

2) An exhaust gas purification catalyst, wherein the ratio of Ce to Zr (Ce/Zr, mass ratio) in the surface of the CeO_2-ZrO_2 carrier is in the range of $0.5 < Ce/Zr \leq 1.5$.

3) An exhaust gas purification catalyst, wherein the particles of copper (Cu) or an oxide of copper are nanoparticles with a particle size of 20 to 30 nm as measured by a CO pulse method in a reducing atmosphere.

4) An exhaust gas purification catalyst which is placed in a rich atmosphere in an exhaust gas flow path from an engine.

5) An exhaust gas purification catalyst, wherein the ratio of copper supported to the CeO_2-ZrO_2 carrier [the content of Cu in the particles to the CeO_2-ZrO_2 carrier (% by mass)] is 1 to 10% by mass.

6) The method for the production of an exhaust gas purification catalyst that includes copper as an active species further includes the step of calcining the CeO_2-ZrO_2 carrier on which copper or an oxide of copper has been deposited.

[0015] Description is hereinafter made of an embodiment of the present invention in detail with reference to the drawings. As shown in FIG. 1 and FIG. 2, an exhaust gas purification catalyst according to an embodiment of the present invention, which includes copper as an active species, is composed of a CeO_2-ZrO_2 carrier and particles of copper or an oxide of copper that are supported on the carrier, and is understood to exhibit specifically high NO_X purification performance at 300°C because the ratio of Ce to Zr (Ce/Zr, mass ratio) in the surface of the carrier is in the range of $0.5 < Ce/Zr < 2.5$.

[0016] FIG. 3 shows that catalysts which include copper as an active species and are composed of a CeO_2-ZrO_2 carrier and particles of copper or an oxide of copper that are supported on the carrier, and in which the ratio of Ce to Zr (Ce/Zr, mass ratio) in the surface of the carrier is in the range of $0.5 < Ce/Zr < 2.5$ have a specifically low oxygen

desorption peak temperature. The Ce/Zr range of $0.5 < Ce/Zr < 2.5$ in which the oxygen desorption temperatures in a reducing atmosphere (which indicate the oxygen desorption peak temperatures) are included in FIG. 3 is equal to the Ce/Zr range in which high NO_X purification performance is achieved in FIG. 2. The decrease in oxygen desorption temperature promotes regeneration (removal of oxygen from the Cu component including an oxide of copper) of the exhaust gas purification catalyst of this embodiment. The NO_X purification performance is improved accordingly.

[0017] As described above, the exhaust gas purification catalyst of this embodiment, which exhibits a low oxygen desorption peak temperature in a reducing atmosphere, is assumed to be suitable to be disposed in a rich atmosphere in an exhaust gas flow path from an engine. Thus, the exhaust gas purification catalyst of this embodiment is placed in an exhaust gas flow path in a system that purifies exhaust gas from an internal combustion engine as shown in FIG. 4, and a known catalyst member, such as Fe/Al_2O_3, is placed upstream of the exhaust gas purification catalyst of this embodiment. The air-fuel ratio of the exhaust gas is controlled to be rich by a control device (not shown) and the oxygen that remains in the exhaust gas is consumed by the known catalyst member. Then, the exhaust gas, which has been turned rich in air-fuel ratio, is introduced into the exhaust gas purification catalyst of this embodiment. The control device introduces air into the exhaust gas downstream of the exhaust gas purification catalyst to control the air-fuel ratio of the exhaust gas to be lean. The exhaust gas is discharged after being passed through a catalyst member, such as Ag/Al_2O_3, which can oxidize HC and CO that remain in the exhaust gas.

[0018] The exhaust gas purification catalyst of this embodiment is produced by a method that includes, for example, the steps of preparing a CeO_2-ZrO_2 carrier in which the ratio of Ce to Zr (Ce/Zr, mass ratio) in the surface thereof is in the range of $0.5 < Ce/Zr < 2.5$, preparing a mixture of the CeO_2-ZrO_2 carrier and an aqueous solution that contains a Cu salt, and depositing copper or an oxide of copper on the CeO_2-ZrO_2 carrier by removing water from the mixture to obtain a solid matter. The obtained solid matter is usually transformed into a catalyst powder by calcination at 500 to 800°C for one to

five hours in a vacuum or air. The carrier with a Ce to Zr ratio in the above range that is prepared in advance in this method can keep the Ce to Zr ratio in the range even after the step of depositing copper or an oxide of copper.

[0019] Examples of the Cu salt include nitrates, sulfates, acetates, sulfates and phosphates of Cu. Above all, nitrates, sulfates and acetates are preferred. These Cu salts may be provided in the form of a hydrate. In the exhaust gas purification catalyst of this embodiment, the amount of Cu supported [the ratio of Cu to the CeO_2-ZrO_2 carrier (% by mass)] is preferably in the range of approximately 1 to 10% by mass.

[0020] In the exhaust gas purification catalyst of this embodiment, the copper or an oxide of copper that is supported or formed on the CeO_2-ZrO_2 carrier by calcination can be an active species of Cu when contacted with a reducing gas, such as hydrogen, CO or C_3H_6, in an exhaust gas flow path.

[0021] The CeO_2-ZrO_2 carrier in this embodiment may be uniform solid solution type CeO_2-ZrO_2 composite oxide particles or core-shell type CeO_2-ZrO_2 composite oxide particles. In the case of the latter, the particles may have a core layer of ZrO_2 and a shell layer of a mixed system of CeO_2 and ZrO_2. In either case, a CeO_2-ZrO_2 carrier in which the ratio of Ce to Zr (Ce/Zr, mass ratio) in the surface thereof is in the range of $0.5 < Ce/Zr < 2.5$ can be used.

[0022] The CeO_2-ZrO_2 carrier can be obtained in the form of a powder by dissolving a cerium compound and a zirconium compound in water at a predetermined ratio, adding a pH adjuster, such as ammonia water, to neutralize the aqueous solution or adding a precipitant liquid, such as hexamethylenetetramine, to form a precipitate, and then filtering and washing the precipitate, and then drying and calcining the precipitate. Examples of the cerium compound include cerium nitrate. Examples of the zirconium compound include zirconium oxynitrate and zirconium nitrate. These salts may be provided in the form of a hydrate.

[0023] By this production method, an exhaust gas purification catalyst can be produced which is composed of a CeO_2-ZrO_2 carrier and nanoparticles of copper or an oxide of copper that are supported on the carrier and preferably have a copper particle

size of 10 to 30 nm as measured by a CO pulse method in a reducing atmosphere and in which the ratio of Ce to Zr (Ce/Zr, mass ratio) in the surface of the carrier is in the range of $0.5 < Ce/Zr < 2.5$.

[0024] In the exhaust gas purification catalyst of this embodiment, the nanoparticles of copper or an oxide of copper that are supported on the CeO_2-ZrO_2 carrier do not necessarily have to have a specific particle size of less than 10 nm. Thus, the exhaust gas purification catalyst of this embodiment exhibits stable performance without strict control of manufacturing conditions during preparation, and can be suitably used as an exhaust gas purification catalyst for an internal combustion engine, such as an engine of an automobile.

[0025] The exhaust gas purification catalyst of this embodiment is usually used in the form of a layer on a substrate, such as a honeycomb. The honeycomb that is used as the substrate may be formed of a ceramic material, such as cordierite, or stainless steel. The exhaust gas purification catalyst of this embodiment may be used in any shape.

[0026] Examples of the present invention are described below. In each of the following examples, the catalyst was evaluated by the measuring methods that are described below. The measuring methods that are described below are illustrative and can be replaced by any method which is considered to be equivalent by those who are skilled in the art.

[0027] 1. Evaluation of catalytic activity using model gas

Measurement was made under a temperature condition for evaluation of exhaust gas purification catalyst activity which follows a pattern that is shown in FIG. 5 using a catalyst carrier transient performance evaluation apparatus (manufactured by BEST INSTRUMENTS Co., Ltd.), which carries out an experiment in a manner as illustrated in FIG. 6, as an evaluation apparatus under the following conditions.

Conditions: NO: 0.3%, CO: 0.9%, O_2: 0.3%, H_2O: 3% (gas composition: vol%)

Gas flow rate: 15 L/min

Amount of catalyst pellets used: 3 g

[0028] 2. Measurement of Ce/Zr concentration ratio in carrier surface by XPS

Apparatus used: scanning X-ray photoelectron spectrometer (manufactured by ULVAC-PHI INCORPORATED)

Measurement method: the electron binding energy of each element of the carrier was measured and the surface Ce/Zr concentration ratio was calculated.

[0029] 3. Measurement of Cu particle size by CO pulse method

After a pretreatment including oxidation with O_2 gas, purge with He gas and reduction with H_2 gas at 400°C was carried out according to the temperature rise and gas supply conditions as shown in FIG. 7, the catalyst was cooled to 0°C and allowed to adsorb CO. The particle size (diameter) of the copper was calculated based on the amount of gas that was adsorbed by the Cu.

[0030] 4. Measurement of oxygen desorption temperature in reducing atmosphere

Measurement was made under a temperature condition for evaluation of oxygen desorption peak temperature which follows a pattern that is shown in FIG. 8 using Thermoplus TG8120 (manufactured by Rigaku Corporation) as an evaluation apparatus under the following conditions.

Conditions: H_2: 1%, He: balance (gas composition: vol%)

Catalyst powder: approximately 12 mg (pellets were pulverized in a mortar)

[0031] Example 1

Cerium nitrate and zirconium oxynitrate were dissolved in water such that a ratio of Ce to Zr that is shown in Table 1 was obtained. Ammonia water as a pH adjuster was added to the ingredient aqueous solution with stirring to neutralize the aqueous solution and form a precipitate. The precipitate was filtered and washed, and the residue was dried at 120°C and calcined at 800°C to obtain a uniform solid solution type CZ powder. Copper nitrate trihydrate was dissolved in water in a beaker, and the uniform solid solution type CZ carrier powder was added to the aqueous solution. The mixture was heated and stirred at 150°C to deposit copper on the CZ carrier powder by an evaporation-to-dryness method. The CZ carrier powder was dried at 120°C and then calcined at 600°C for two hours to prepare catalyst pellets (amount of Cu supported: 5%

by mass, calculated based on the composition of the ingredients added). The obtained catalyst pellets were evaluated. The results are summarized in Tables 1 and 2 and FIGs. 1 to 3 together with other results.

[0032] Example 2

Cerium nitrate and zirconium oxynitrate were dissolved in water such that a ratio of Ce to Zr that is shown in Table 1 was obtained, and the ingredient aqueous solution was stirred. The ingredient aqueous solution was placed in a separable beaker, and hexamethylenetetramine was added as a precipitant liquid. Then, the mixture was stirred. The mixture was subjected to an aging treatment at 80°C for one hour in a drier and filtered. The residue was washed and dried at 120°C, and was then calcined at 800°C to obtain a core-shell type CZ powder. Catalyst pellets were prepared in the same manner as Example 1 except that this CZ powder was used. The obtained catalyst pellets were evaluated. The results are summarized in Tables 1 and 2 and FIGs. 1 to 3 together with other results.

[0033] Examples 3 to 5

A CZ powder was obtained in the same manner as in Example 1 except that the ratio of Ce to Zr was changed to the value that is shown in Table 1. Catalyst pellets were prepared in the same manner as Example 1 except that this CZ powder was used. The obtained catalyst pellets were evaluated. The results are summarized in Tables 1 and 2 and FIGs. 1 to 3 together with other results.

[0034] Comparative Example 1

A carrier powder was obtained in the same manner as in Example 1 except that only zirconium oxynitrate was used. Catalyst pellets were prepared in the same manner as Example 1 except that this carrier powder was used. The obtained catalyst pellets were evaluated. The results are summarized in Tables 1 and 2 and FIGs. 1 to 3 together with other results.

[0035] Comparative Example 2

A carrier powder was obtained in the same manner as in Example 1 except that only cerium nitrate was used. Catalyst pellets were prepared in the same manner as Example

1 except that this carrier powder was used. The obtained catalyst pellets were evaluated. The results are summarized in Tables 1 and 2 and FIGs. 1 to 3 together with other results.

[0036] Comparative Examples 3 and 4

A carrier powder was obtained in the same manner as in Example 1 except that the ratio of Ce to Zr was changed to the value that is shown in Table 1. Catalyst pellets were prepared in the same manner as Example 1 except that this carrier powder was used. The obtained catalyst pellets were evaluated. The results are summarized in Tables 1 and 2 and FIGs. 1 to 3 together with other results.

[Table 1]

	Carrier		Surface Ce/Zr concentration ratio	Amount of Ce added [mol%]	Amount of Zr added [mol%]
Comparative Example 1	Only ZrO_2	Related Art	0	0	100
Comparative Example 3	CeO_2-ZrO_2		0.22	30	70
Example 1		Present invention	0.57	50	50
Example 2			0.61	30	70
Example 3			0.82	60	40
Example 4			1.19	70	30
Example 5			2.35	80	20
Comparative Example 4			5.17	90	10
Comparative Example 2	Only CeO_2	Related Art	-	100	0

[Table 2]

	Carrier		Surface Ce/Zr concentration ratio	NO_X conversion efficiency [%] at 300°C	Cu particle size [nm]
Comparative Example 1	Only ZrO_2	Related Art	0	16	6
Comparative Example 3	CeO_2-ZrO_2		0.22	18	40
Example 1		Present invention	0.57	28	30
Example 2			0.61	30	28
Example 3			0.82	38	24
Example 4			1.19	42	20

Example 5			2.35	26	30
Comparative Example 4			5.17	22	32
Comparative Example 2	Only CeO_2	Related Art	-	25	8

[0037] As shown in Table 2 and FIGs. 1 to 3, the catalyst in which copper or an oxide of copper is supported on a CeO_2 carrier as in a related art has a high temperature at which Ce is reduced, and the catalyst in which copper or an oxide of copper is supported on a ZrO_2 carrier has low activity probably because oxygen is not released from the carrier. In either case, the NO_X purification performance is poor. The catalysts in which the ratio of Ce to Zr (Ce/Zr, mass ratio) of $Ce/Zr \leq 0.5$ or $2.5 \leq Ce/Zr$ in the surface of the carrier have low activity and exhibit poor NO_X purification performance, whereas the exhaust gas purification catalysts of Examples exhibit high NO_X purification performance.

[0038] According to the exhaust gas purification catalyst of this embodiment, it is possible to achieve high NO_X purification performance using a base metal. In addition, according to the method for the production of an exhaust gas purification catalyst of this embodiment, it is possible to obtain an NO_X purification catalyst for internal combustion engines including engines for automobiles.

CLAIMS

1. An exhaust gas purification catalyst that includes copper as an active species, comprising:

a CeO_2-ZrO_2 carrier, and

particles of copper or an oxide of copper, that are supported on the CeO_2-ZrO_2 carrier,

wherein a mass ratio of Ce to Zr in a surface of the CeO_2-ZrO_2 carrier is in a range of $0.5 < Ce/Zr < 2.5$.

2. The exhaust gas purification catalyst according to claim 1,

wherein the particles are nanoparticles with a particle size of 10 to 30 nm as measured by a CO pulse method in a reducing atmosphere.

3. The exhaust gas purification catalyst according to claim 2,

wherein the particles are nanoparticles with the particle size of 20 to 30 nm as measured by the CO pulse method in the reducing atmosphere.

4. The exhaust gas purification catalyst according to any one of claims 1 to 3,

wherein the mass ratio of Ce to Zr in the surface of the CeO_2-ZrO_2 carrier is in the range of $0.5 < Ce/Zr \leq 1.5$.

5. The exhaust gas purification catalyst according to any one of claims 1 to 4,

wherein a ratio of copper in the particles to the CeO_2-ZrO_2 carrier is 1 to 10% by mass.

6. An exhaust gas control system comprising:

an exhaust pipe that is connected to an engine, and

an exhaust gas control apparatus that is provided in the exhaust pipe,

wherein the exhaust gas control apparatus includes the exhaust gas purification catalyst according to any one of claims 1 to 5 and is controlled to contain a rich atmosphere.

7. A method for a production of an exhaust gas purification catalyst that includes copper as an active species, comprising:

preparing a CeO_2-ZrO_2 carrier in which a mass ratio of Ce to Zr at least in a surface thereof is in a range of $0.5 < Ce/Zr < 2.5$,

preparing a mixture of the CeO_2-ZrO_2 carrier and an aqueous solution that contains a copper compound, and

depositing copper or an oxide of copper on the CeO_2-ZrO_2 carrier by removing water from the mixture by heating.

8. The method according to claim 7,

further comprising: calcining the CeO_2-ZrO_2 carrier on which copper or the oxide of copper has been deposited.

FIG. 1

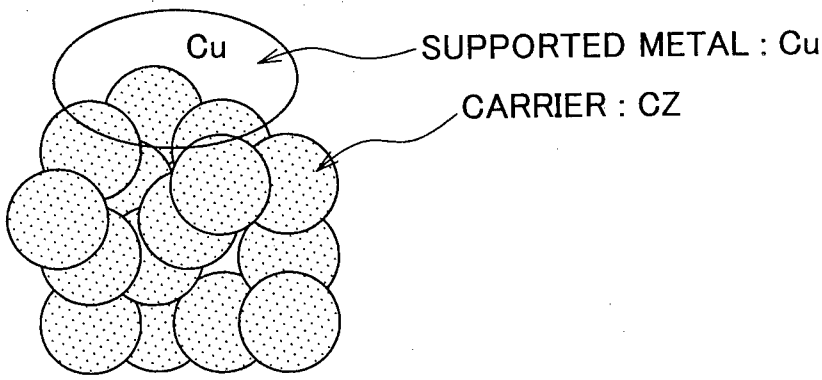


FIG. 2

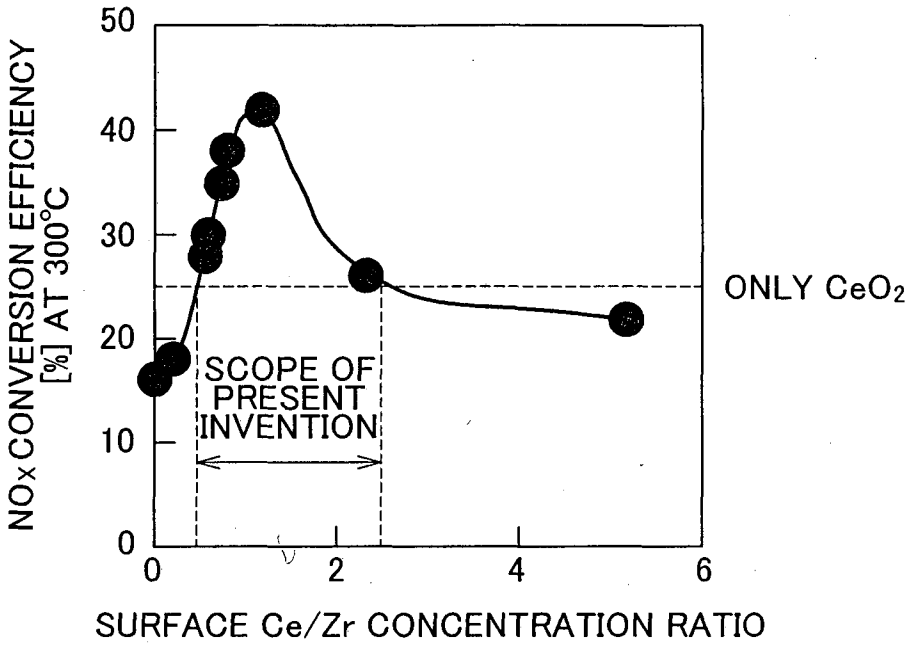

NOx CONVERSION EFFICIENCY [%] AT 300°C
50
40
30
20
10
0
0
2
4
6
SCOPE OF PRESENT INVENTION
ONLY CeO2
SURFACE Ce/Zr CONCENTRATION RATIO

FIG. 3

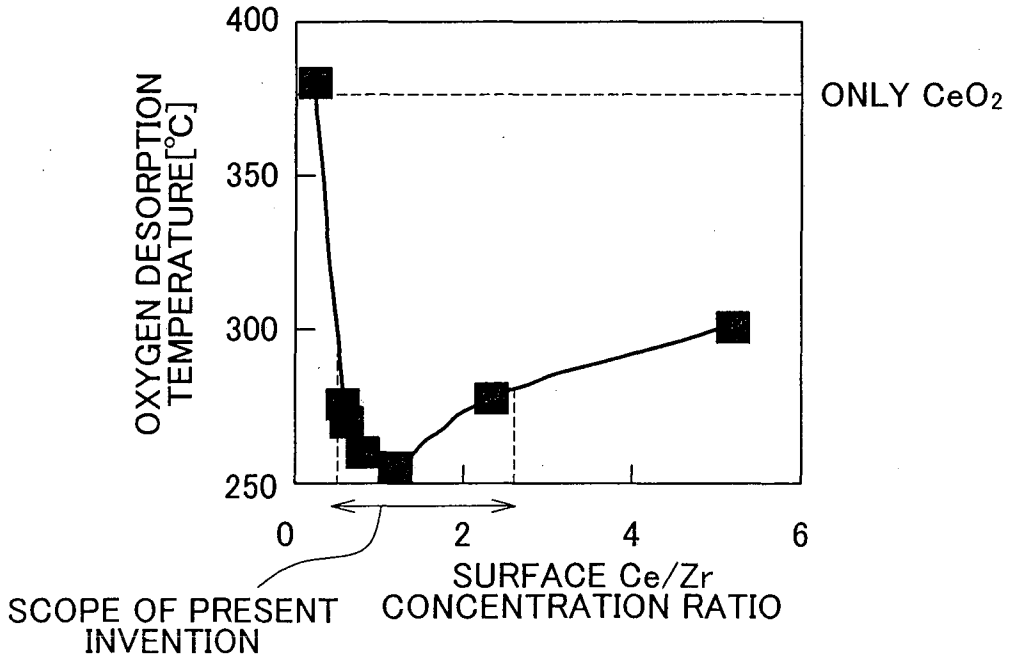

OXYGEN DESORPTION TEMPERATURE[°C]
400
350
300
250
0
2
4
6
ONLY CeO2
SURFACE Ce/Zr CONCENTRATION RATIO
SCOPE OF PRESENT INVENTION

FIG. 4

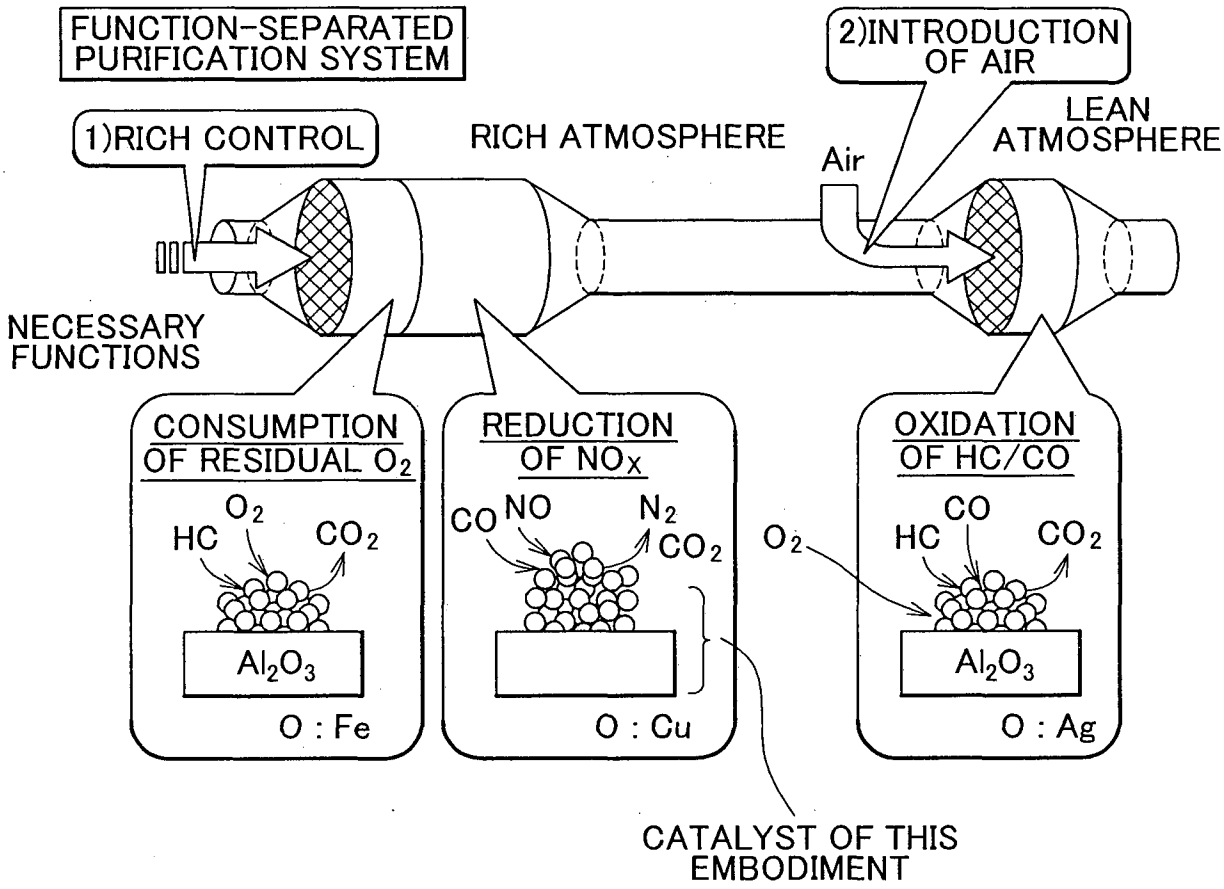

FUNCTION-SEPARATED PURIFICATION SYSTEM
1)RICH CONTROL
RICH ATMOSPHERE
2)INTRODUCTION OF AIR
Air
LEAN ATMOSPHERE
NECESSARY FUNCTIONS
CONSUMPTION OF RESIDUAL O_2
O_2
HC
CO_2
Al_2O_3
O : Fe
REDUCTION OF NO_X
CO NO
N_2
CO_2
O : Cu
O_2
OXIDATION OF HC/CO
HC
CO
CO_2
Al_2O_3
O : Ag
CATALYST OF THIS EMBODIMENT

FIG. 5

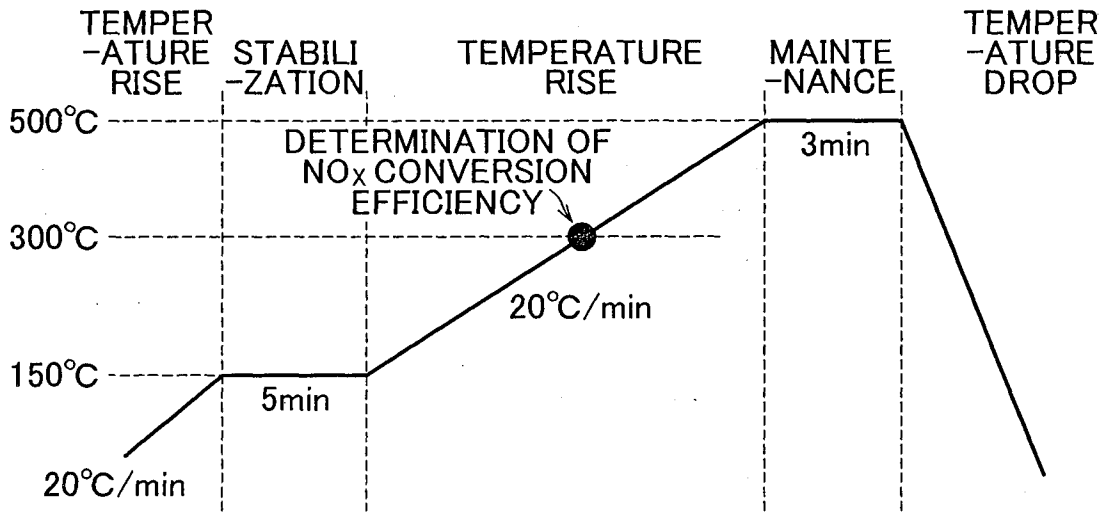

TEMPER
-ATURE
RISE
STABILI
-ZATION
TEMPERATURE
RISE
MAINTE
-NANCE
TEMPER
-ATURE
DROP
500°C
300°C
150°C
20°C/min
5min
DETERMINATION OF
NOx CONVERSION
EFFICIENCY
20°C/min
3min

FIG. 6

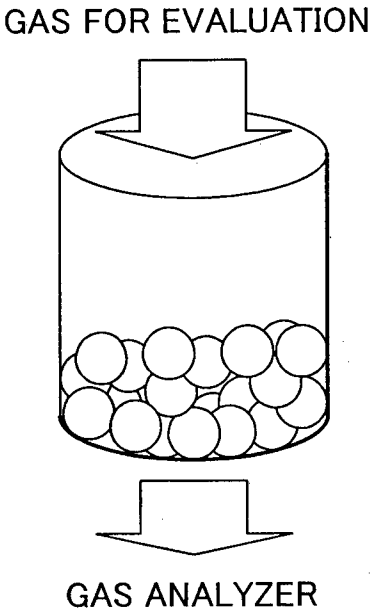

GAS FOR EVALUATION
GAS ANALYZER

FIG. 7

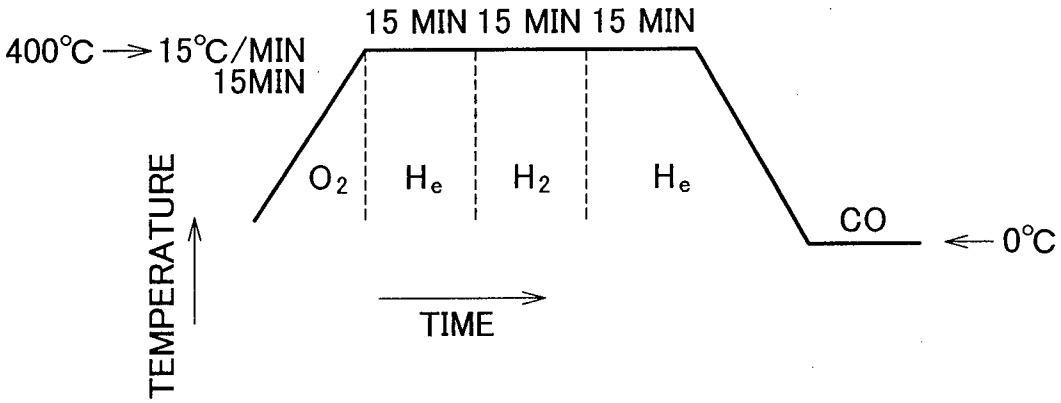
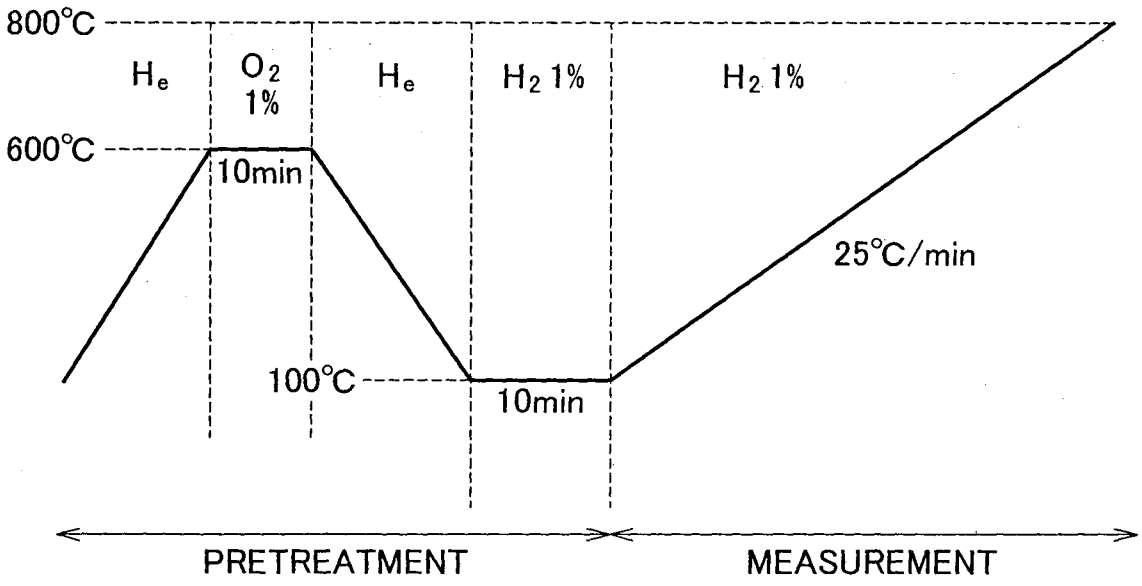

400°C → 15°C/MIN
15MIN
15 MIN 15 MIN 15 MIN
O2
He
H2
He
CO
← 0°C
TEMPERATURE
TIME

FIG. 8


800°C
600°C
100°C
He
O2 1%
He
H2 1%
H2 1%
10min
10min
25°C/min
PRETREATMENT
MEASUREMENT

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2012/001001

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01D53/94 B01J23/72 B01J35/00 B01J21/06 B01J23/00
ADD.

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

B. FIELDS SEARCHED

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

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 504 805 A1 (RADICI CHIMICA SPA [IT]) 9 February 2005 (2005-02-09) paragraphs [0013], [0015], [0019], [0020]; claims; example 2	1,4,5,7, 8
X	WO 92/05861 A1 (ENGELHARD CORP [US]) 16 April 1992 (1992-04-16) page 1, line 14 page 5, lines 3-22 page 10; claims	1,4-8
X	US 2004/092395 A1 (HASE TOMOMI [JP] ET AL) 13 May 2004 (2004-05-13) paragraphs [0004], [0047], [0048]	1-8
X	US 4 927 799 A (MATSUMOTO SHINICHI [JP] ET AL) 22 May 1990 (1990-05-22) column 3, line 50 - column 6, line 20; claims	1,6,7

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
10 September 2012	26/09/2012

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Polesak, Helmut

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
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