(19) **United States**
(12) **Patent Application Publication**
SATO et al.
(10) **Pub. No.: US 2015/0065334 A1**
(43) **Pub. Date: Mar. 5, 2015**

(54) **HONEYCOMB CATALYST AND EXHAUST GAS PURIFYING APPARATUS**

(71) Applicant: **IBIDEN CO., LTD.**, Ogaki-shi (JP)

(72) Inventors: **Masaya SATO**, Ibi-gun (JP); **Takehiro UMEMOTO**, Ibi-gun (JP); **Naoki ONAYA**, Ibi-gun (JP)

(73) Assignee: **IBIDEN CO., LTD.**, Ogaki-shi (JP)

(21) Appl. No.: **14/469,585**

(22) Filed: **Aug. 27, 2014**

(30) **Foreign Application Priority Data**

Aug. 27, 2013 (JP) 2013-175926

Publication Classification

(51) **Int. Cl.**
B01J 29/70 (2006.01)

(52) **U.S. Cl.**
CPC ***B01J 29/7015*** (2013.01); *B01J 2229/26* (2013.01)
USPC **502/64**; 502/60

(57) **ABSTRACT**

A honeycomb catalyst includes a honeycomb unit. The honeycomb unit has a plurality of through holes that are arranged in parallel in a longitudinal direction and partitions that are provided between the plurality of through holes. The honeycomb unit includes a zeolite, inorganic particles, and an inorganic binder. The zeolite includes a CHA-structured aluminosilicate having a Si/Al ratio of about 15 to about 50. The inorganic particles includes an oxide that has a positive coefficient of thermal expansion. A volume ratio of the zeolite to the inorganic particles is about 50:about 50 to about 90:about 10.

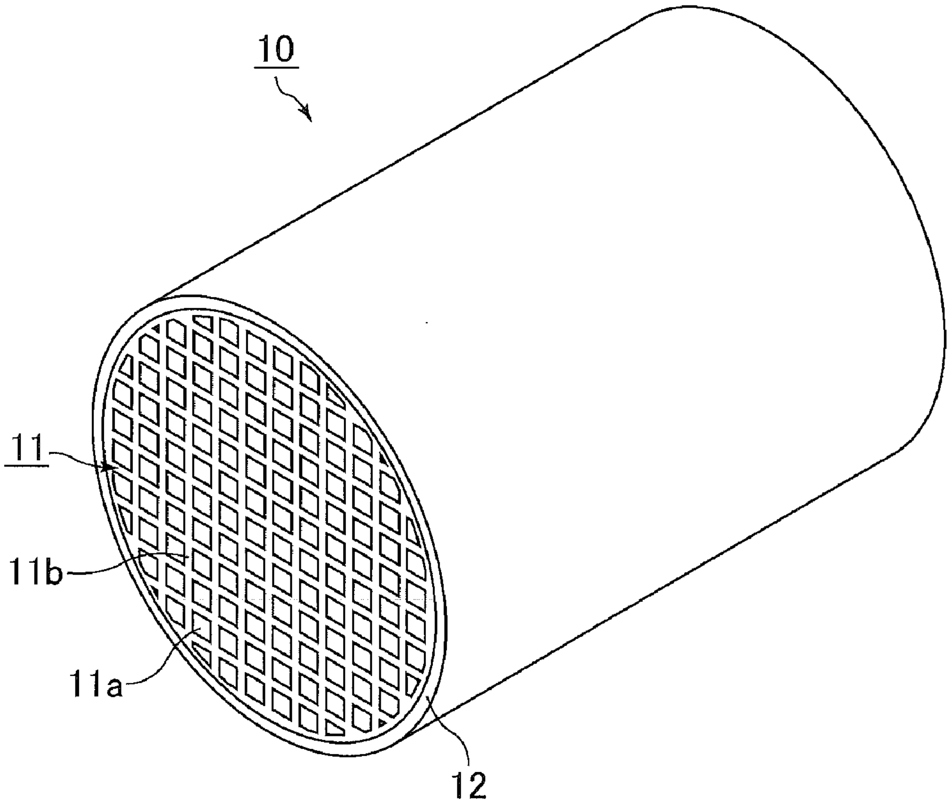


FIG.1

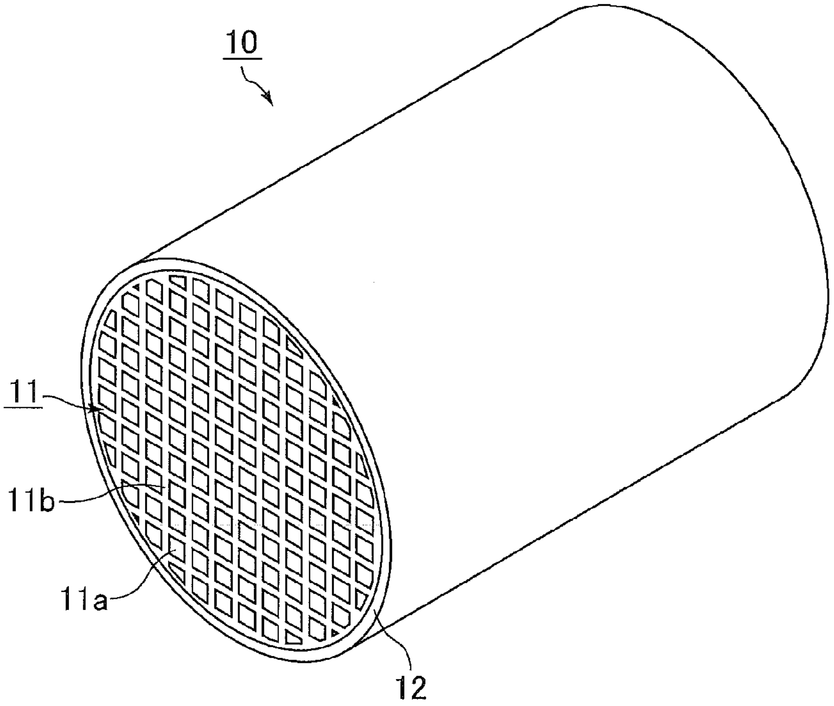


FIG.2

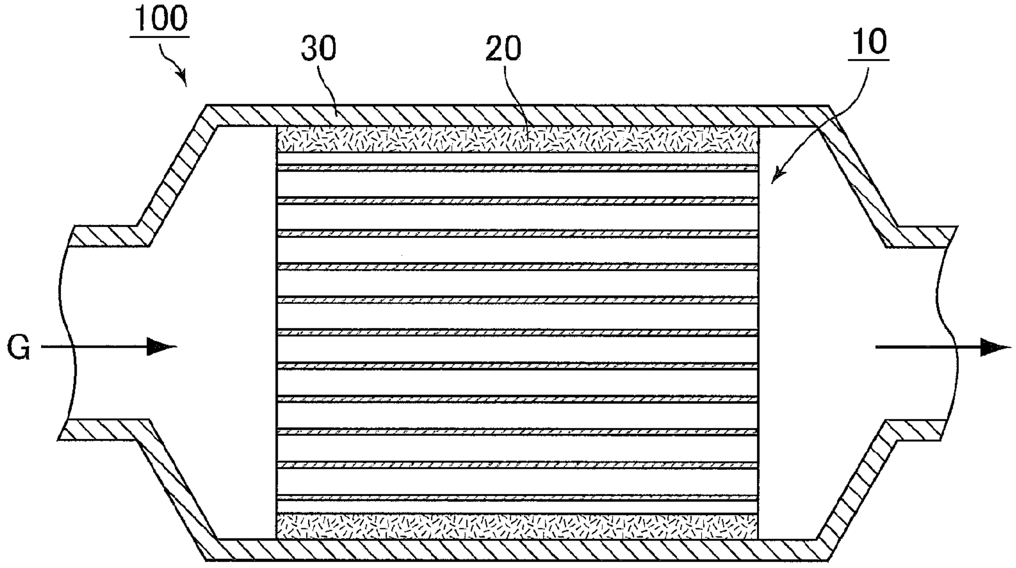


FIG.3

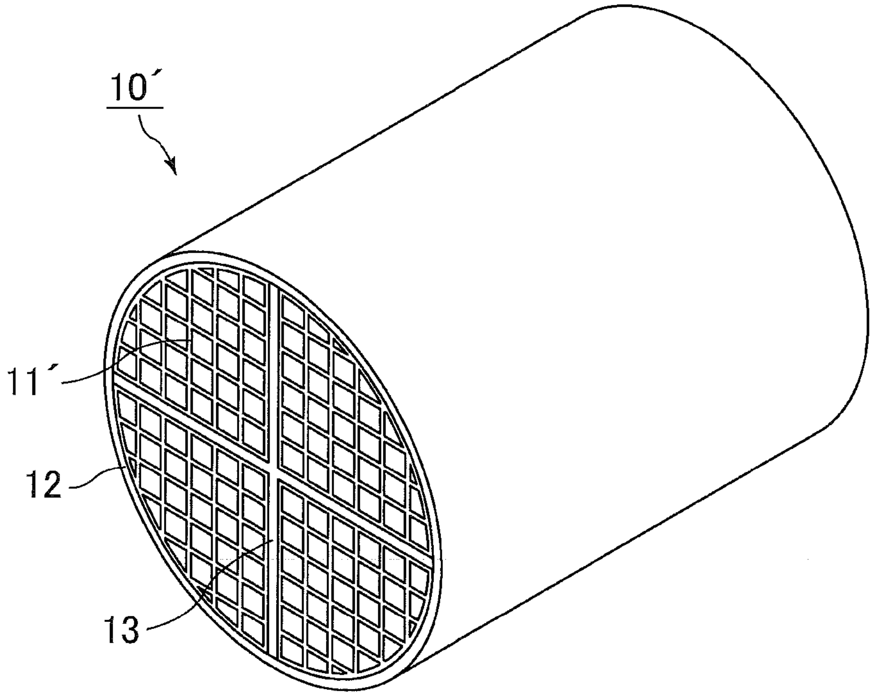


FIG.4

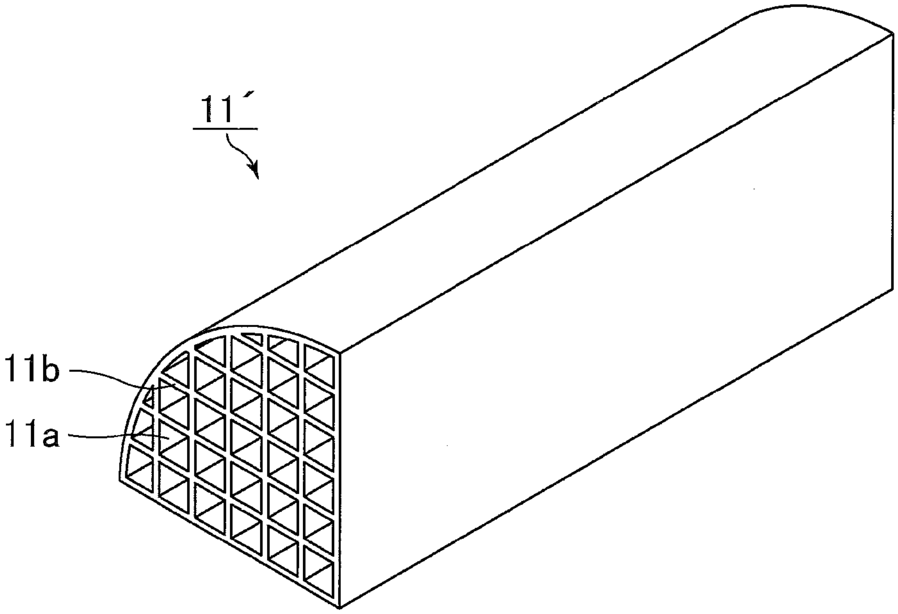
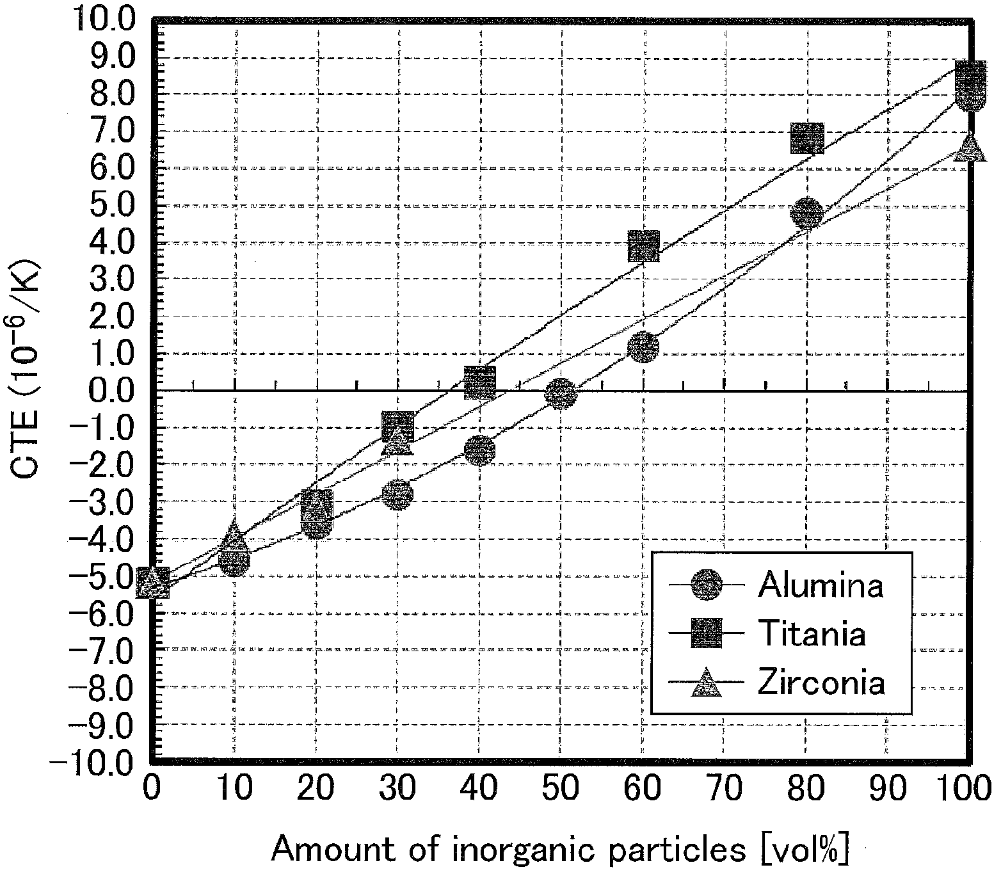


FIG.5


10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
−1.0
−2.0
−3.0
−4.0
−5.0
−6.0
−7.0
−8.0
−9.0
−10.0
CTE (10^{-6}/K)
0
10
20
30
40
50
60
70
80
90
100
Amount of inorganic particles [vol%]
Alumina
Titania
Zirconia

HONEYCOMB CATALYST AND EXHAUST GAS PURIFYING APPARATUS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] The present application claims priority under 35 U. S. C. §119 to Japanese Patent Application No. 2013-175926, filed Aug. 27, 2013. The contents of this application are incorporated herein by reference in their entirety.

BACKGROUND OF THE INVENTION

[0002] 1. Field of the Invention

[0003] The present invention relates to a honeycomb catalyst and an exhaust gas purifying apparatus.

[0004] 2. Discussion of the Background

[0005] Selective catalytic reduction (SCR) system is a known technology to purify exhaust gas from automobiles using ammonia to reduce NOx to nitrogen and water.

[0006] Zeolite-containing compositions molded into honeycomb shapes are known to be used as catalyst supports in the SCR system.

[0007] For example, WO 2009/141888 discloses a honeycomb structured body which includes a honeycomb unit containing a zeolite, inorganic fibers, and alumina. The honeycomb unit has an opening ratio Y(%) that satisfies the inequality “$57 \leq \leq 0.7X+25$” wherein X represents a zeolite content (% by mass) in the honeycomb unit. In the honeycomb structured body described in WO 2009/141888, the honeycomb unit contains alumina so that it has a higher strength. WO 2009/141888 mentions use of zeolites such as a β-zeolite and a ZSM-5 zeolite.

[0008] U.S. Pat. No. 7,601,662 discloses a CHA-structured zeolite that is ion-exchanged with a copper ion as a zeolite catalyst for the SCR system. U.S. Pat. No. 7,601,662 says that the zeolite catalyst described therein exerts higher NOx purifying performance after it is aged with hot water.

SUMMARY OF THE INVENTION

[0009] According to one aspect of the present invention, a honeycomb catalyst includes a honeycomb unit. The honeycomb unit has a plurality of through holes that are arranged in parallel in a longitudinal direction and partitions that are provided between the plurality of through holes. The honeycomb unit includes a zeolite, inorganic particles, and an inorganic binder. The zeolite includes a CHA-structured aluminosilicate having a Si/Al ratio of about 15 to about 50. The inorganic particles includes an oxide that has a positive coefficient of thermal expansion. A volume ratio of the zeolite to the inorganic particles is about 50:about 50 to about 90:about 10.

[0010] According to another aspect of the present invention, an exhaust gas purifying apparatus includes a honeycomb catalyst. The honeycomb catalyst includes a honeycomb unit. The honeycomb unit has a plurality of through holes that are arranged in parallel in a longitudinal direction and partitions that are provided between the plurality of through holes. The honeycomb unit includes a zeolite, inorganic particles, and an inorganic binder. The zeolite includes a CHA-structured aluminosilicate having a Si/Al ratio of about 15 to about 50. The inorganic particles includes an oxide that has a positive coefficient of thermal expansion. A volume ratio of the zeolite to the inorganic particles is about 50:about 50 to about 90:about 10.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011] A more complete appreciation of the invention and many of the attendant advantages thereof will be readily obtained as the same becomes better understood by reference to the following detailed description when considered in connection with the accompanying drawings.

[0012] FIG. **1** is a perspective view schematically illustrating one example of the honeycomb catalyst of an embodiment of the present invention.

[0013] FIG. **2** is a perspective view schematically illustrating one example of the exhaust gas purifying apparatus of an embodiment of the present invention.

[0014] FIG. **3** is a perspective view schematically illustrating another example of the honeycomb catalyst of an embodiment of the present invention.

[0015] FIG. **4** is a perspective view schematically illustrating one example of a honeycomb unit included in the honeycomb catalyst shown in FIG. **3**.

[0016] FIG. **5** is a graph showing relationships between the amounts of inorganic particles and the coefficients of thermal expansion of honeycomb units.

DESCRIPTION OF THE EMBODIMENTS

[0017] The embodiments will now be described with reference to the accompanying drawings, wherein like reference numerals designate corresponding or identical elements throughout the various drawings.

[0018] Specifically, the honeycomb catalyst of the embodiment of the present invention includes a honeycomb unit with a plurality of through holes that are arranged in parallel in a longitudinal direction and partitions that are provided between the through holes, wherein the honeycomb unit includes a zeolite, inorganic particles, and an inorganic binder; the zeolite is a CHA-structured aluminosilicate having a Si/Al ratio of 15 to 50; the inorganic particles include an oxide that has a positive coefficient of thermal expansion; and the volume ratio of the zeolite to the inorganic particles (zeolite:inorganic particles) is 50:50 to 90:10.

[0019] In the honeycomb catalyst of the embodiment of the present invention, the honeycomb unit manufactured using a CHA-structured aluminosilicate (hereinafter, also referred to as CHA) as a zeolite improves the NOx purifying performance. Too large an amount of the CHA causes thermal stress so that the honeycomb unit tends to be damaged. For preventing such damage, the honeycomb unit is allowed to include an oxide having a positive coefficient of thermal expansion so that the coefficient of thermal expansion of the entire honeycomb unit can be normalized. Thus, the honeycomb catalyst of the embodiment of the present invention is excellent in NOx purifying performance and is capable of suppressing damage of the honeycomb unit during use of the exhaust gas purifying apparatus.

[0020] The expression “having a positive coefficient of thermal expansion” herein means that “a material increases its volume as temperature rises”. The coefficient of thermal expansion is measured with a push-rod dilatometer at a temperature rising rate of 10° C./min in a temperature range of 50 to 700° C. with reference to the coefficient of thermal expansion, which is already known, of alumina.

[0021] The volume ratio of the zeolite to the inorganic particles (zeolite:inorganic particles) is 50:50 to 90:10, and preferably 60:40 to 80:20. Such a volume ratio can prevent a decrease of the NOx purifying performance due to oxidation of ammonia when the temperature of exhaust gas is high. Even in the case of a larger honeycomb catalyst, damage of the honeycomb unit caused by thermal stress can be suppressed.

[0022] The inorganic particles preferably include at least one selected from the group consisting of alumina, titania, and zirconia. The inorganic particles have a positive coefficient of thermal expansion. Thus, the coefficient of thermal expansion of the entire honeycomb unit can be normalized.

[0023] The zeolite preferably has an average particle size of 0.1 to 2.0 μm, and the inorganic particles preferably have an average particle size of 0.1 to 5.0 μm. This allows the honeycomb unit to have a large pore size, and thus higher NOx purifying performance due to gas diffusion can be achieved.

[0024] The average particle size of the inorganic particles is preferably ⅕ to 50 times the average particle size of the zeolite. This enables control of the pore size of the honeycomb unit.

[0025] The average particle size of the inorganic particles is preferably larger than the average particle size of the zeolite but is preferably not larger than four times the average particle size of the zeolite.

[0026] The zeolite is preferably ion-exchanged with a copper ion. This can improve the NOx purifying performance.

[0027] The honeycomb unit preferably contains the copper ion in an amount of 5.5 to 7.5 g per liter of an apparent volume of the honeycomb unit. The above copper ion content enables not only high NOx purifying performance when the temperature of exhaust gas is low but also prevention of a decrease of the NOx purifying performance due to oxidation of ammonia when the temperature of exhaust gas is high. Thus, the honeycomb unit exerts high NOx purifying performance over the entire temperature range.

[0028] The honeycomb unit preferably includes the zeolite in an amount of 150 to 250 g per liter of an apparent volume of the honeycomb unit. The above zeolite content enables not only high NOx purifying performance when the temperature of exhaust gas is low but also prevention of a decrease of the NOx purifying performance due to oxidation of ammonia when the temperature of exhaust gas is high. Thus, the honeycomb unit exerts high NOx purifying performance over the entire temperature range.

[0029] The honeycomb unit preferably further includes at least one selected from the group consisting of an inorganic fiber, a scaly material, a tetrapod-shaped material, and a three-dimensional needle-shaped material. This can increase the strength of the honeycomb catalyst.

[0030] The exhaust gas purifying apparatus of the embodiment of the present invention includes the honeycomb catalyst of the embodiment of the present invention.

[0031] The embodiment of the present invention enables to provide a honeycomb catalyst and an exhaust gas purifying apparatus which are excellent in NOx purifying performance and are capable of suppressing damage of the honeycomb unit during use of the exhaust gas purifying apparatus.

[0032] The embodiment of the present invention will now be specifically described below but is not limited to the described embodiment. These embodiments may be appropriately modified to an extent not changing the gist of the present invention.

[0033] The honeycomb catalyst of the embodiment of the present invention includes a honeycomb unit with a plurality of through holes that are arranged in parallel in a longitudinal direction and partitions that are provided between the through holes, wherein the honeycomb unit includes a zeolite, inorganic particles, and an inorganic binder; the zeolite is a CHA-structured aluminosilicate having a Si/Al ratio of 15 to 50; the inorganic particles include an oxide that has a positive coefficient of thermal expansion; and the volume ratio of the zeolite to the inorganic particles (zeolite:inorganic particles) is 50:50 to 90:10.

[0034] FIG. **1** shows one example of the honeycomb catalyst of the embodiment of the present invention. A honeycomb catalyst **10** shown in FIG. **1** includes a single honeycomb unit **11** with a plurality of through holes **11***a* that are arranged in parallel in a longitudinal direction and partitions **11***b* that are provided between the through holes **11***a*. A periphery coat layer **12** is formed on the outer peripheral face of the honeycomb unit **11**. The honeycomb unit **11** includes a zeolite, inorganic particles, and an inorganic binder.

[0035] In the honeycomb catalyst of the embodiment of the present invention, the zeolite in the honeycomb unit is a CHA-structured aluminosilicate (CHA). The expression "CHA-structured" means "having a structure represented by a code CHA, that defines the structure of zeolite, prescribed by International Zeolite Association (IZA)". The zeolite has a crystal structure equivalent to that of naturally produced chabazite.

[0036] The CHA has a Si/Al ratio of 15 to 50, preferably 20 to 40, and more preferably 25 to 35. If the Si/Al ratio is less than 15, the Al content is large so that thermal deterioration tends to occur. If the Si/Al ratio is more than 50, the zeolite has fewer acid sites. Thus, NOx purifying performance may decrease.

[0037] The CHA has an average particle size of preferably 0.1 to 2.0 μm, more preferably 0.3 to 1.8 μm, and still more preferably 0.7 to 1.7 μm. If the CHA has an average particle size of 0.1 to 2.0 μm, the honeycomb unit has a large pore size. Thus, the honeycomb catalyst has a low capillary stress when it has absorbed water, and also has higher NOx purifying performance due to gas diffusion.

[0038] The average particle size of the CHA is the average particle size of the primary particles measured with a scanning electron microscope (SEM).

[0039] The CHA has a specific surface area of preferably 500 to 650 m^2/g, and more preferably 550 to 630 m^2/g in view of the crystal structure.

[0040] The honeycomb unit has a CHA content of preferably 40 to 75 vol %, more preferably 45 to 70 vol %, and still more preferably 50 to 65 vol %. A CHA content of less than 40 vol % reduces the NOx purifying performance. A CHA content of more than 75 vol % tends to cause damage of the honeycomb unit due to absorption or desorption of water or thermal stress.

[0041] In the honeycomb catalyst of the embodiment of the present invention, the honeycomb unit may include a zeolite other than the CHA and a silicoaluminophosphate (SAPO) to an extent not impairing the effects of the embodiment of the present invention.

[0042] In the honeycomb catalyst of the embodiment of the present invention, the zeolite (CHA) is preferably ion-exchanged with a copper ion. In this case, the honeycomb unit contains a copper ion in an amount of preferably 5.5 to 7.5 g, and more preferably 6.0 to 7.5 g per liter of an apparent volume of the honeycomb unit. The above copper ion content enables not only high NOx purifying performance when the temperature of exhaust gas is low but also prevention of a decrease of the NOx purifying performance due to oxidation of ammonia when the temperature of exhaust gas is high. Thus, the honeycomb unit exerts high NOx purifying performance over the entire temperature range.

[0043] In the honeycomb catalyst of the embodiment of the present invention, the honeycomb unit includes the zeolite (CHA) in an amount of preferably 150 to 250 g, and more preferably 180 to 230 g per liter of an apparent volume of the honeycomb unit. The above zeolite content enables not only high NOx purifying performance when the temperature of exhaust gas is low but also prevention of a decrease of the NOx purifying performance due to oxidation of ammonia when the temperature of exhaust gas is high. Thus, the honeycomb unit exerts high NOx purifying performance over the entire temperature range.

[0044] In the honeycomb catalyst of the embodiment of the present invention, the inorganic particles included in the honeycomb unit may be particles of any oxide that has a positive coefficient of thermal expansion. Examples of the inorganic particles include particles of alumina, titania, zirconia, silica, ceria, or magnesia. Two or more kinds of the inorganic particles may be used in combination. The inorganic particles are preferably particles of at least one selected from the group consisting of alumina, titania and zirconia, and more preferably particles of one of alumina, titania and zirconia.

[0045] The inorganic particles have an average particle size of preferably 0.1 to 5.0 μm, more preferably 0.3 to 4.5 μm, and still more preferably 0.5 to 4.0 μm. The inorganic particles having an average particle size of 0.1 to 5.0 μm enables to control the pore size of the honeycomb unit.

[0046] The average particle size of the inorganic particles is a 50% cumulative particle size (Dv50) in a particle size distribution (volumetric basis) that is obtained by measurement according to the laser diffraction and scattering method.

[0047] In the honeycomb catalyst of the embodiment of the present invention, a combination of the average particle size of the CHA of 0.1 to 2.0 μm and the average particle size of the inorganic particles of 0.1 to 5.0 μm is preferable; a combination of the average particle size of the CHA of 0.3 to 1.8 μm and the average particle size of the inorganic particles of 0.3 to 4.5 μm is more preferable; and a combination of the average particle size of the CHA of 0.7 to 1.7 μm and the average particle size of the inorganic particles of 0.5 to 4.0 μm is still more preferable.

[0048] The average particle size of the inorganic particles is preferably ⅕ to 50 times, more preferably ⅓ to 30 times, and still more preferably ½ to 10 times the average particle size of the CHA within the ranges of the combinations mentioned above.

[0049] Particularly preferably, the average particle size of the inorganic particles is larger than the average particle size of the CHA but is not larger than four times the average particle size of the CHA.

[0050] For example, in the case of the CHA having an average particle size of 0.1 μm, the average particle size of the inorganic particles is preferably 0.1 to 0.4 μm; and in the case of the CHA having an average particle size of 1.5 μm, the average particle size of the inorganic particles is preferably 0.5 to 3.0 μm.

[0051] The honeycomb unit has an inorganic particle content of preferably 8 to 40 vol %, more preferably 10 to 35 vol %, and still more preferably 15 to 25 vol %. If the inorganic particle content is less than 8 vol %, the CHA content is too large so that the honeycomb unit is likely to be damaged by thermal stress. If the inorganic particle content is more than 40 vol %, the CHA content is small so that the NOx purifying performance decreases.

[0052] In the honeycomb catalyst of the embodiment of the present invention, the volume ratio of the CHA to the inorganic particles (CHA:inorganic particles) is 50:50 to 90:10, preferably 60:40 to 80:20, and more preferably 70:30 to 80:20. A volume ratio of the CHA to the inorganic particles within the above ranges enables to prevent not only a decrease of the NOx purifying performance but also damage of the honeycomb unit due to thermal stress.

[0053] In the honeycomb catalyst of the embodiment of the present invention, the honeycomb unit may include oxide particles having a negative coefficient of thermal expansion or non-oxide particles to an extent not impairing the effects of the embodiment of the present invention.

[0054] In the honeycomb catalyst of the embodiment of the present invention, the inorganic binder included in the honeycomb unit is not particularly limited. For allowing the honeycomb catalyst to maintain sufficient strength, preferable examples of the inorganic binder include solids contained in alumina sol, silica sol, titania sol, soluble glass, sepiolite, attapulgite, or boehmite. Two or more kinds of the inorganic binders may be used in combination.

[0055] The inorganic binder content in the honeycomb unit is preferably 3 to 30 vol %, and more preferably 5 to 20 vol %. An inorganic binder content of less than 3 vol % decreases the strength of the honeycomb unit. An inorganic binder content of more than 30 vol % reduces the zeolite content in the honeycomb unit so that the NOx purifying performance decreases.

[0056] In the honeycomb catalyst of the embodiment of the present invention, preferably the honeycomb unit further includes at least one selected from the group consisting of an inorganic fiber, a scaly material, a tetrapod-shaped material, and a three-dimensional needle-shaped material for increasing the strength.

[0057] The inorganic fiber included in the honeycomb unit is preferably formed of at least one selected from the group consisting of alumina, silica, silicon carbide, silica alumina, glass, potassium titanate, and aluminum borate. The scaly material included in the honeycomb unit is preferably formed of at least one selected from the group consisting of glass, muscovite, alumina, and silica. The tetrapod-shaped material included in the honeycomb unit is preferably formed of zinc oxide. The three-dimensional needle-shaped material included in the honeycomb unit is preferably formed of at least one selected from the group consisting of alumina, silica, silicon carbide, silica alumina, glass, potassium titanate, aluminum borate, and boehmite. The above materials have high heat resistance and are not eroded when they are used as a catalyst support in the SCR system. Thus, they can maintain the effect as reinforcing materials.

[0058] The inorganic fiber included in the honeycomb unit has an aspect ratio of preferably 2 to 300, more preferably 5 to 200, and still more preferably 10 to 100. The inorganic fiber having an aspect ratio of less than 2 reduces the effect of increasing the strength of the honeycomb unit. The inorganic fiber having an aspect ratio of more than 300 causes clogging or the like of the mold during extrusion molding for forming the honeycomb unit or causes bending of the inorganic fiber to reduce the effect of increasing the strength of the honeycomb unit.

[0059] The scaly material refers to a flat material which preferably has a thickness of 0.2 to 5.0 μm, a maximum length of 10 to 160 μm, and a ratio of the thickness to the maximum length of 3 to 250.

[0060] The tetrapod-shaped material refers to a material having a needle-shaped part extending three-dimensionally, the needle-shaped part preferably having an average needle length of 5 to 30 μm and an average diameter of 0.5 to 5.0 μm.

[0061] The three-dimensional needle-shaped material refers to a material including needle-shaped parts that are combined to each other by an inorganic compound (e.g., glass) at and near the center area of each needle-shaped part. Each needle-shaped part preferably has an average needle length of 5 to 30 μm, and an average diameter of 0.5 to 5.0 μm.

[0062] The three-dimensional needle-shaped material may include a plurality of three-dimensionally-connected needle-shaped parts. Each needle-shaped part preferably has a diameter of 0.1 to 5.0 μm, a length of 0.3 to 30.0 μm, and a ratio of the diameter to the length of 1.4 to 50.0.

[0063] The amount of the inorganic fiber, scaly material, tetrapod-shaped material, and/or three-dimensional needle-shaped material in the honeycomb unit is preferably 3 to 50 vol %, more preferably 3 to 30 vol %, and still more preferably 5 to 20 vol %. An amount of less than 3 vol % reduces the effect of increasing the strength of the honeycomb unit. An amount of more than 50 vol % reduces the zeolite content in the honeycomb unit so that the NOx purifying performance decreases.

[0064] In the honeycomb catalyst of the embodiment of the present invention, the honeycomb unit preferably has a porosity of 40 to 70%. The honeycomb unit having a porosity of less than 40% would not allow exhaust gas to easily permeate into the partitions of the honeycomb unit. Thus, the zeolite is not effectively utilized for NOx purification. The honeycomb unit having a porosity of more than 70% leads to an insufficient strength of the honeycomb unit.

[0065] The porosity of the honeycomb unit can be measured by the Archimedes method.

[0066] In the honeycomb catalyst of the embodiment of the present invention, a cross section of the honeycomb unit perpendicular to the longitudinal direction preferably has an aperture ratio of 50 to 75%. If the cross section of the honeycomb unit perpendicular to the longitudinal direction has an aperture ratio of less than 50%, the zeolite is not effectively utilized for NOx purification. If the cross section of the honeycomb unit perpendicular to the longitudinal direction has an aperture ratio of more than 75%, the honeycomb unit has an insufficient strength.

[0067] In the honeycomb catalyst of the embodiment of the present invention, the cross section of the honeycomb unit perpendicular to the longitudinal direction preferably has a through hole density of 31 to 155 pcs/cm^2. If the through hole density of the cross section of the honeycomb unit perpendicular to the longitudinal direction is less than 31 pcs/cm^2, the zeolite does not easily contact with exhaust gas so that the NOx purifying performance decreases. If the through hole density of the cross section of the honeycomb unit perpendicular to the longitudinal direction is more than 155 pcs/cm^2, the honeycomb catalyst has a higher pressure loss.

[0068] In the honeycomb catalyst of the embodiment of the present invention, the partitions in the honeycomb unit have a thickness of preferably 0.1 to 0.4 mm, and more preferably 0.1 to 0.3 mm. If the partitions in the honeycomb unit have a thickness of less than 0.1 mm, the honeycomb unit has a lower strength. If the partitions in the honeycomb unit have a thickness of more than 0.4 mm, exhaust gas does not easily permeate into the partitions of the honeycomb unit. Thus, the zeolite is not effectively utilized for NOx purification.

[0069] In the case where an outer periphery coat layer is formed on the honeycomb unit in the honeycomb catalyst of the embodiment of the present invention, the outer periphery coat layer preferably has a thickness of 0.1 to 2.0 mm. The outer periphery coat layer having a thickness of less than 0.1 mm does not produce a sufficient effect of increasing the strength of the honeycomb catalyst. The outer periphery coat layer having a thickness of more than 2.0 mm reduces the zeolite content per unit volume of the honeycomb catalyst so that the NOx purifying performance decreases.

[0070] The shape of the honeycomb catalyst of the embodiment of the present invention is not limited to cylindrical but may be a polygonal prism, an elliptical prism, an oval prism, a round-chamfered polygonal prism (e.g., round-chamfered triangular pillar), or the like.

[0071] In the honeycomb catalyst of the embodiment of the present invention, the shape of the through hole is not limited to a quadrangular prism but may be a triangular prism, a hexagonal prism, or the like.

[0072] The following will describe one example of a method for manufacturing the honeycomb catalyst **10** shown in FIG. **1**.

[0073] First, a material paste that includes a zeolite, inorganic particles, an inorganic binder, and further optionally at least one selected from the group consisting of an inorganic fiber, a scaly material, a tetrapod-shaped material, and a three-dimensional needle-shaped material is extrusion molded to manufacture a round pillar-shaped honeycomb molded body with a plurality of through holes that are arranged in parallel in a longitudinal direction and partitions that are provided between the through holes.

[0074] The material paste may contain any inorganic binder. Examples of the inorganic binder include alumina sol, silica sol, titania sol, soluble glass, sepiolite, attapulgite, and boehmite; two or more kinds of these may be used in combination.

[0075] The material paste may further optionally contain additives such as an organic binder, a dispersing medium, or a molding aid.

[0076] The organic binder is not particularly limited. Examples thereof include methyl cellulose, carboxyl methyl cellulose, hydroxy ethyl cellulose, polyethylene glycol, phenolic resin, and epoxy resin; two or more kinds of these may be used in combination. The amount of the organic binder to be added is preferably 1 to 10% of a total mass of the zeolite, inorganic particles, inorganic binder, inorganic fiber, scaly material, tetrapod-shaped material, and three-dimensional needle-shaped material.

[0077] The dispersing medium is not particularly limited. Examples thereof include organic solvents (e.g., water, benzene) and alcohols (e.g., methanol); two or more kinds of these may be used in combination.

[0078] The molding aid is not particularly limited. Examples thereof include ethylene glycol, dextrin, fatty acids, fatty acid soaps, and poly alcohols; two or more kinds of these may be used in combination.

[0079] The material paste may further optionally contain a pore-forming material.

[0080] The pore-forming material is not particularly limited. Examples thereof include polystyrene particles, acrylic particles, and starch; two or more kinds of these may be used in combination. In particular, polystyrene particles are preferred.

[0081] The pore size distribution of the partitions can be adjusted within a predetermined range by controlling the particle sizes of the CHA and the pore-forming material.

[0082] For example, in the case of the CHA having an average particle size of 0.1 μm, a pore-forming material having an average particle size of 0.1 to 3 μm is added in an amount of 10 to 30 vol % of the amount of the CHA to allow the partitions to have an average pore size of 0.05 to 0.2 μm. In the case of the CHA having an average particle size of 1.2 μm, a pore-forming material is not necessarily added.

[0083] The pore size distribution of the partitions can be adjusted within a predetermined range by controlling the particle sizes of the CHA and the inorganic particles even without adding the pore-forming material.

[0084] The material paste may be preferably prepared by mixing with a mixer, an attritor, or the like, or by kneading with a kneader, or the like.

[0085] Next, the honeycomb molded body is dried using a drier, such as a microwave drier, a hot air drier, a dielectric drier, a reduced pressure drier, a vacuum drier, or a freeze drier, to thereby manufacture a honeycomb dried body.

[0086] The honeycomb dried body is degreased to manufacture a honeycomb degreased body. The condition for the degreasing may be appropriately determined depending on the kinds and amounts of organic substances in the honeycomb dried body but is preferably under a temperature of 200 to 500° C. for a period of 2 to 6 hours.

[0087] Next, the honeycomb degreased body is fired to manufacture a round pillar-shaped honeycomb unit **11**. The firing temperature is preferably 600 to 1000° C., and more preferably 600 to 800° C. A firing temperature of lower than 600° C. fails to proceed the sintering to decrease the strength of the honeycomb unit **11**. A firing temperature of higher than 1000° C. leads to excessive sintering to reduce reaction sites of the zeolite.

[0088] Thereafter, a paste for forming an outer periphery coat layer is applied to the outer peripheral face, except for both end faces, of the round pillar-shaped honeycomb unit **11**.

[0089] The paste for forming an outer periphery coat layer is not particularly limited. Examples thereof include mixtures of an inorganic binder and inorganic particles, mixtures of an inorganic binder and an inorganic fiber, and mixtures of an inorganic binder, inorganic particles, and an inorganic fiber.

[0090] The paste for forming an outer periphery coat layer may contain any inorganic binder. The inorganic binder is added as silica sol, alumina sol, or the like but is preferably added as silica sol. Two or more kinds of the inorganic binders may be used in combination.

[0091] The paste for forming an outer periphery coat layer may contain any inorganic particles. Examples of the inorganic particles include particles of an oxide such as zeolite, eucryptite, alumina, and silica; particles of a carbide such as silicon carbide; and particles of a nitride such as silicon nitride and boron nitride. Two or more kinds of the inorganic particles may be used in combination. As eucryptite has a similar coefficient of thermal expansion to that of the honeycomb unit, particles of eucryptite are preferred.

[0092] The paste for forming an outer periphery coat layer may contain any inorganic fiber. Examples of the inorganic fiber include silica alumina fiber, mullite fiber, alumina fiber, and silica fiber; two or more kinds of these may be used in combination. In particular, alumina fiber is preferred.

[0093] The paste for forming an outer periphery coat layer may further contain an organic binder.

[0094] The paste for forming an outer periphery coat layer may contain any organic binder. Examples of the organic binder include polyvinyl alcohol, methyl cellulose, ethyl cellulose, and carboxyl methyl cellulose; two or more kinds of these may be used in combination.

[0095] The paste for forming an outer periphery coat layer may further contain balloons (i.e. fine hollow spheres) of oxide-based ceramic, a pore-forming material, or the like.

[0096] The paste for forming an outer periphery coat layer may contain any balloon. Examples of the balloon include an alumina balloon, a glass micro balloon, a shirasu balloon, a fly ash balloon, and a mullite balloon; two or more kinds of these may be used in combination. In particular, an alumina balloon is preferred.

[0097] The paste for forming an outer periphery coat layer may contain any pore-forming material. Examples of the pore-forming material include spherical acrylic particles and graphite; two or more kinds of these may be used in combination.

[0098] Next, the honeycomb unit **11** with the paste for forming an outer periphery coat layer applied thereto is dried to solidify the paste to thereby manufacture a round pillar-shaped honeycomb catalyst **10**. In the case where the paste for forming an outer periphery coat layer contains an organic binder, degreasing is preferably performed. The condition for the degreasing may be appropriately determined depending on the kinds and amounts of the organic substances but is preferably under a temperature of 500° C. for a period of one hour.

[0099] The honeycomb unit **11** or the honeycomb catalyst **10** may be immersed in an aqueous solution containing a copper ion so that the zeolite is ion-exchanged with a copper ion. Alternatively, the material paste containing a zeolite that is ion-exchanged with a copper ion may be used.

[0100] FIG. **2** shows one example of the exhaust gas purifying apparatus of the embodiment of the present invention. An exhaust gas purifying apparatus **100** shown in FIG. **2** can be manufactured by canning the honeycomb catalyst **10** in a metal container (shell) **30**, the honeycomb catalyst **10** having a holding sealing material **20** on the outer periphery thereof. The exhaust gas purifying apparatus **100** includes an injector (not illustrated), such as injection nozzle, inside a pipe (not illustrated) on an upstream of the honeycomb catalyst **10** with respect to the direction in which exhaust gas flows (in FIG. **2**, G indicates exhaust gas, and arrows indicate flows of exhaust gas). The injector injects ammonia or a compound that generates ammonia when decomposed. The injector supplies ammonia into exhaust gas flowing through the pipe. Thus, NOx contained in exhaust gas is reduced by the zeolite included in the honeycomb unit **11**.

[0101] The compound that generates ammonia when decomposed may be any compound that can generate ammonia when it is hydrolyzed inside the pipe. Preferably, the compound is urea water as it has excellent storage stability.

[0102] Urea water heated by exhaust gas inside the pipe is hydrolyzed to generate ammonia.

[0103] FIG. **3** shows another example of the honeycomb catalyst of the embodiment of the present invention. A honeycomb catalyst **10'** in FIG. **3** has the same structure as that of the honeycomb catalyst **10**, except that it includes a plurality of honeycomb units **11'** that are combined with one another with adhesive layers **13** provided between the honeycomb units **11'**. Each honeycomb unit **11'** is provided with a plurality of through holes **11***a* that are arranged in parallel in the longitudinal direction and partitions **11***b* that are provided between the through holes **11***a* (see FIG. **4**).

[0104] The cross section of each honeycomb unit **11'** perpendicular to the longitudinal direction has a cross-sectional area of preferably 10 to 200 cm^2. If the cross-sectional area is less than 10 cm^2, the honeycomb catalyst **10'** has a higher pressure loss. If the cross-sectional area is more than 200 cm^2, the honeycomb units **11'** are hardly combined with one another.

[0105] The honeycomb unit **11'** has the same structure as that of the honeycomb unit **11**, except for the cross sectional area of the cross section perpendicular to the longitudinal direction.

[0106] The adhesive layers **13** preferably have a thickness of 0.1 to 3.0 mm. If the adhesive layers **13** have a thickness of less than 0.1 mm, the bonding strength between the honeycomb units **11'** becomes insufficient. If the adhesive layers **13** have a thickness of more than 3.0 mm, the honeycomb catalyst **10'** has a higher pressure loss, or cracks occur in the adhesive layers.

[0107] The following will describe one example of a method for manufacturing the honeycomb catalyst **10'** shown in FIG. **3**.

[0108] First, honeycomb units **11'** having sectorial prism shapes are manufactured in the same manner as the method for manufacturing the honeycomb unit **11** that forms the honeycomb catalyst **10**. The adhesive layer paste is applied to the outer peripheral faces of the honeycomb units **11'** except for the arc faces. Then, the honeycomb units **11'** are bonded to each other and dried to solidify the paste to thereby manufacture an aggregate of the honeycomb units **11'**.

[0109] The adhesive layer paste is not particularly limited. Examples of the adhesive layer paste include mixtures of an inorganic binder and inorganic particles, mixtures of an inorganic binder and an inorganic fiber, and mixtures of an inorganic binder, inorganic particles, and an inorganic fiber.

[0110] The adhesive layer paste may contain any inorganic binder. The inorganic binder is added as silica sol, alumina sol, or the like but is preferably added as silica sol. Two or more kinds of the inorganic binders may be used in combination.

[0111] The adhesive layer paste may contain any inorganic particles. Examples of the inorganic particles include particles of an oxide such as zeolite, eucryptite, alumina, and silica; particles of a carbide such as silicon carbide; and particles of a nitride such as silicon nitride and boron nitride. Two or more kinds of the inorganic particles may be used in combination. As eucryptite has a similar coefficient of thermal expansion to that of the honeycomb unit, particles of eucryptite are preferred.

[0112] The adhesive layer paste may contain any inorganic fiber. Examples of the inorganic fiber include silica alumina fiber, mullite fiber, alumina fiber, and silica fiber; two or more kinds of these may be used in combination. In particular, alumina fiber is preferred.

[0113] The adhesive layer paste may further contain an organic binder.

[0114] The adhesive layer paste may contain any organic binder. Examples of the organic binder include polyvinyl alcohol, methyl cellulose, ethyl cellulose, and carboxyl methyl cellulose; two or more kinds of these may be used in combination.

[0115] The adhesive layer paste may further contain balloons (i.e. fine hollow spheres) of oxide-based ceramic, a pore-forming material, or the like.

[0116] The adhesive layer paste may contain any balloon. Examples of the balloon include an alumina balloon, a glass micro balloon, a shirasu balloon, a fly ash balloon, and a mullite balloon; two or more kinds of these may be used in combination. In particular, an alumina balloon is preferred.

[0117] The adhesive layer paste may contain any pore-forming material. Examples of the pore-forming material include spherical acrylic particles and graphite; two or more kinds of these may be used in combination.

[0118] In order to improve the roundness, the aggregate of the honeycomb units **11'** is optionally machined and ground into a round pillar-shaped aggregate of the honeycomb units **11'**.

[0119] Thereafter, a paste for forming an outer periphery coat layer is applied to the outer peripheral face, except for both end faces, of the round pillar-shaped aggregate of the honeycomb units **11'**.

[0120] The paste for forming an outer periphery coat layer may be the same as or different from the adhesive layer paste.

[0121] Next, the round pillar-shaped aggregate of the honeycomb units **11'** with the paste for forming an outer periphery coat layer applied thereto is dried to solidify the paste to thereby manufacture a round pillar-shaped honeycomb catalyst **10'**. In the case where the adhesive layer paste and/or the paste for forming an outer periphery coat layer contain an organic binder, preferably degreasing is performed. The condition for the degreasing may be appropriately determined depending on the kinds and the amounts of the organic substances but is preferably under a temperature of 500° C. for a period of one hour.

[0122] The honeycomb catalyst **10'** is formed of four pieces of the honeycomb units **11'** which are bonded to one another with the adhesive layers **13** provided between the honeycomb units **11'**. The number of the honeycomb units forming the honeycomb catalyst is not particularly limited. For example, a round pillar-shaped honeycomb catalyst may be formed of 16 pieces of quadrangular prism-shaped honeycomb units which are bonded to one another with the adhesive layers provided between the honeycomb units.

[0123] The honeycomb catalysts **10** and **10'** may not have the outer periphery coat layer **12**.

[0124] As mentioned earlier, in the honeycomb catalyst of the embodiment of the present invention, a honeycomb unit manufactured using a CHA as zeolite enables to improve the NOx purifying performance. Too large an amount of the CHA causes thermal stress so that the honeycomb unit tends to be damaged. The coefficient of thermal expansion of the entire honeycomb unit can be normalized by allowing the honeycomb unit to include an oxide having a positive coefficient of thermal expansion. Thus, the honeycomb catalyst of the embodiment of the present invention is excellent in NOx purifying performance and is capable of suppressing damage of the honeycomb unit during use of the exhaust gas purifying apparatus.

[0125] In the honeycomb catalyst of the embodiment of the present invention, the honeycomb unit has a coefficient of thermal expansion of preferably -4.5×10^{-6} to 4.5×10^{-6}/K, and more preferably -3.0×10^{-6} to 3.0×10^{-6}/K for suppressing damage of the honeycomb unit.

EXAMPLES

[0126] The embodiment of the present invention is illustrated by, but not limited to, examples which specifically describe the embodiment of the present invention.

Example 1

[0127] A material paste **1** was prepared by mixing a CHA (29% by mass) having an average particle size of 0.1 μm as a zeolite, an alumina (6% by mass) having an average particle size of 3.0 μm as inorganic particles, boehmite (5% by mass) as an inorganic binder, a glass fiber (8% by mass) having an average fiber diameter of 6.5 μm and an average fiber length of 100 μm, polystyrene particles (6% by mass) having an average particle size of 0.8 μm as a pore-forming material, methyl cellulose (5% by mass), a fatty acid soap (4% by mass) as a molding aid, and ion exchange water (37% by mass). The zeolite used was a copper ion-exchanged CHA having a specific gravity of 2.02, a ratio of Si/Al of 32, and a specific surface area of 600 m^2/g.

[0128] The volume ratio of the zeolite to the inorganic particles (CHA:alumina) was 90:10 in Example 1.

[0129] Then, the material paste **1** was extrusion molded with an extruder into a square prism-shaped honeycomb molded body. The honeycomb molded body was dried with a vacuum microwave dryer at a power output of 4.5 kW for 7 minutes under a reduced pressure of 6.7 kPa, followed by degreasing and firing at 700° C. for 2 hours, so that a honeycomb fired body (honeycomb unit **11'**) was manufactured. The honeycomb unit **11'** is in a square prism shape having a length of a side of 38 mm and a length in the longitudinal direction of 150 mm. The honeycomb unit **11'** is provided with through holes **11***a* at a density of 124 pcs/cm^2 and partitions **11***b* each having a thickness of 0.20 mm.

[0130] Moreover, the honeycomb unit **11'** includes the zeolite in an amount of 217 g and a copper ion in an amount of 7.1 g per liter of an apparent volume of the honeycomb unit **11'**.

Examples 2 to 5

[0131] Honeycomb units **11'** were manufactured in the same manner as in Example 1, except that the volume ratio of the zeolite to the inorganic particles (CHA:alumina) was changed to 80:20 in Example 2, 70:30 in Example 3, 64:40 in Example 4, and 50:50 in Example 5.

Comparative Example 1

[0132] A honeycomb unit **11'** was manufactured in the same manner as in Example 1, except that the volume ratio of the zeolite to the inorganic particles (CHA:alumina) was changed to 100:0. In other words, no inorganic particles (alumina) were used in Comparative Example 1.

Comparative Examples 2 and 3

[0133] Honeycomb units **11'** were manufactured in the same manner as in Example 1, except that the volume ratio of the zeolite to the inorganic particles (CHA:alumina) was changed to 40:60 in Comparative Example 2, and 20:80 in Comparative Example 3.

Comparative Example 4

[0134] A honeycomb unit **11'** was manufactured in the same manner as in Example 1, except that the volume ratio of the zeolite to the inorganic particles (CHA:alumina) was changed to 0:100. In other words, no zeolite (CHA) was used in Comparative Example 4.

Example 6

[0135] A material paste **1** was prepared by mixing a CHA (26% by mass) having an average particle size of 0.1 μm as a zeolite, a titania (13% by mass) having an average particle size of 0.2 μm as inorganic particles, boehmite (7% by mass) as an inorganic binder, a glass fiber (7% by mass) having an average fiber diameter of 6.5 μm and an average fiber length of 100 μm, polystyrene particles (5% by mass) having an average particle size of 0.8 μm as a pore-forming material, methyl cellulose (5% by mass), a fatty acid soap (4% by mass) as a molding aid, and ion exchange water (33% by mass). The zeolite used was a copper ion-exchanged CHA having a specific gravity of 2.02, a ratio of Si/Al of 32, and a specific surface area of 600 m^2/g.

[0136] The volume ratio of the zeolite to the inorganic particles (zeolite:titania) was 80:20.

[0137] Except for the above, a honeycomb unit **11'** was manufactured in the same manner as in Example 1.

Examples 7 and 8

[0138] Honeycomb units **11'** were manufactured in the same manner as in Example 6, except that the volume ratio of the zeolite to the inorganic particles (CHA:titania) was changed to 70:30 in Example 7, and 60:40 in Example 8.

Comparative Example 5

[0139] A honeycomb unit **11'** was manufactured in the same manner as in Example 6, except that the volume ratio of the zeolite to the inorganic particles (CHA:titania) was changed to 100:0. In other words, no inorganic particles (titania) were used in Comparative Example 5.

Comparative Examples 6 and 7

[0140] Honeycomb units **11'** were manufactured in the same manner as in Example 6, except that the volume ratio of the zeolite to the inorganic particles (CHA:titania) was changed to 40:60 in Comparative Example 6, and 20:80 in Comparative Example 7.

Comparative Example 8

[0141] A honeycomb unit **11'** was manufactured in the same manner as in Example 6, except that the volume ratio of the zeolite to the inorganic particles (CHA:titania) was changed to 0:100. In other words, no zeolite (CHA) was used in Comparative Example 8.

Example 9

[0142] A material paste **1** was prepared by mixing a CHA (31% by mass) having an average particle size of 0.1 μm as a zeolite, a zirconia (10% by mass) having an average particle size of 0.4 μm as inorganic particles, boehmite (5% by mass) as an inorganic binder, a glass fiber (8% by mass) having an average fiber diameter of 6.5 μm and an average fiber length of 100 μm, polystyrene particles (6% by mass) having an average particle size of 0.8 μm as a pore-forming material, methyl cellulose (6% by mass), a fatty acid soap (4% by mass) as a molding aid, and ion exchange water (30% by mass). The zeolite used was a copper ion-exchanged CHA having a specific gravity of 2.02, a ratio of Si/Al of 32, and a specific surface area of 600 m^2/g.

[0143] The volume ratio of the zeolite to the inorganic particles (zeolite:zirconia) was 90:10.

[0144] Except for the above, a honeycomb unit **11'** was manufactured in the same manner as in Example 1.

Examples 10 and 11

[0145] Honeycomb units **11'** were manufactured in the same manner as in Example 9, except that the volume ratio of the zeolite to the inorganic particles (CHA:zirconia) was changed to 80:20 in Example 10, and 70:30 in Example 11.

Comparative Example 9

[0146] A honeycomb unit **11'** was manufactured in the same manner as in Example 9, except that the volume ratio of the zeolite to the inorganic particles (CHA:zirconia) was changed to 100:0. In other words, no inorganic particles (zirconia) were used in Comparative Example 9.

Comparative Example 10

[0147] A honeycomb unit **11'** was manufactured in the same manner as in Example 9, except that the volume ratio of the zeolite to the inorganic particles (CHA:zirconia) was changed to 0:100. In other words, no zeolite (CHA) was used in Comparative Example 10.

[Measurement of Coefficient of Thermal Expansion of Honeycomb Unit]

[0148] The honeycomb units manufactured in Examples 1 to 11 and Comparative Examples 1 to 10 were measured for the coefficient of thermal expansion (CTE) by the following method.

[0149] A 5 mm×5 mm×25 mm piece was cut out of each honeycomb unit with a diamond cutter to prepare a measurement sample. The sample was dried at 200° C. for 2 hours and weighed. Then, the sample was allowed to stand in a steam atmosphere until it had a water absorption of 10%.

[0150] Next, the measurement sample and a standard alumina sample (5 mm×5 mm×25 mm) were placed next to each other in a sealable container in a manner that the longitudinal directions of the samples were in parallel with the horizontal direction. Each sample was provided with a detection rod which contacted a center portion of the upper face (i.e., the 5 mm×25 mm upper face).

[0151] The measurement sample and the standard sample were allowed to stand under argon atmosphere while the temperature was raised from room temperature to 50° C., maintained for 10 hours, and further raised to 700° C. at a rate of 10° C./min, and then lowered to room temperature at a rate of 10° C./min. The measurement was performed in helium (He) flowing at a rate of 100 mL/min. The detection rod detects the change derived from thermal expansion of the measurement sample and the standard sample and displacement in the water absorption of the measurement sample. The coefficient of thermal expansion of the measurement sample (honeycomb unit) can be determined based on the difference between the change of the standard sample and the change of the measurement sample.

[0152] A thermal expansion meter (NETZSCH DIL402C, manufactured by Bruker Japan Co., Ltd.) was used for the measurement.

[0153] FIG. **5** shows relationships between the amounts of the inorganic particles and the coefficients of thermal expansion of the honeycomb units.

[0154] In FIG. **5**, the horizontal axis shows the relative amount (vol %) of the inorganic particles to a total amount of the zeolite and the inorganic particles.

[0155] FIG. **5** indicates that the coefficient of thermal expansion of the honeycomb units can be controlled within a range of -4.5×10^{-6} to 2.0×10^{-6}/K when the amount of the inorganic particles is 10 to 50 vol %, that is, when the volume ratio of the zeolite to the inorganic particles is from 50:50 to 90:10.

[Measurement of NOx Purification Rate]

[0156] A cylindrical test sample having a diameter of 1 inch and a length of 3 inches was cut out of each of the honeycomb units manufactured in Examples 1 to 4, 6 to 8, 10, and 11, and Comparative Examples 1, 3, 5, 6, and 9 with a diamond cutter. In a state where an imitation gas of 200° C. or 525° C. was allowed to flow into each test sample at a space velocity (SV) of 40000/hr (200° C.) or 100000/hr (525° C.), the amount of NOx flowing out of the test sample was measured with a catalyst evaluation apparatus (SIGU-2000/MEXA-6000FT, manufactured by Horiba Ltd.). The NOx purification rate (%) that is expressed by the following formula: (Inflow of NOx−Outflow of NOx)/(Inflow of NOx)×100 was calculated. Tables 1 to 3 show the result. The imitation gas of 200° C. contains the following components: nitric oxide (260 ppm), nitrogen dioxide (90 ppm), ammonia (350 ppm), oxygen (10%), carbon dioxide (5%), water (5%), and nitrogen (balance); and the imitation gas of 525° C. contains the following components: nitric oxide (315 ppm), nitrogen dioxide (35 ppm), ammonia (385 ppm), oxygen (10%), carbon dioxide (5%), water (5%), and nitrogen (balance).

TABLE 1

	Zeolite	Inorganic particles	CHA:Alumina (Volume ratio)	NO*x* purification rate [%] 200° C.	NO*x* purification rate [%] 525° C.
Comparative Example 1	CHA	Alumina	100:0	94	80
Example 1			90:10	95	83
Example 2			80:20	93	84
Example 3			70:30	93	83
Example 4			60:40	86	84
Comparative Example 3			20:80	16.1	54

TABLE 2

	Zeolite	Inorganic particles	CHA:Titania (Volume ratio)	NO*x* purification rate [%] 200° C.	NO*x* purification rate [%] 525° C.
Comparative Example 5	CHA	Titania	100:0	94	80
Example 6			80:20	92	83
Example 7			70:30	90	83

TABLE 2-continued

	Zeolite	Inorganic particles	CHA:Titania (Volume ratio)	NOx purification rate [%] 200° C.	NOx purification rate [%] 525° C.
Example 8			60:40	84	84
Comparative Example 6			40:60	63	85

TABLE 3

	Zeolite	Inorganic particles	CHA:Zirconia (Volume ratio)	NOx purification rate [%] 200° C.	NOx purification rate [%] 525° C.
Comparative Example 9	CHA	Zirconia	100:0	94	80
Example 10			80:20	91	86
Example 11			70:30	93	87

[0157] Tables 1 to 3 revealed that, when the volume ratio of the zeolite to the inorganic particles is 50:50 to 100:0, the rates of purifying the NOx of 200° C. and the NOx of 525° C. are as high as approximately 80% or more. In contrast, when the relative amount of the inorganic particles to a total amount of the zeolite and the inorganic particles exceeds 50 vol %, the NOx purification rates decrease.

[0158] When the volume ratio of the zeolite to the inorganic particles is 100:0, the NOx purification rate is high. However, the honeycomb units have a large negative coefficient of thermal expansion of -5.0×10^{-6}/K as shown in FIG. **5**.

[0159] Hence, the honeycomb catalyst of the embodiment of the present invention is considered to have excellent NOx purifying performance and to be capable of suppressing damage of the honeycomb unit during use of the exhaust gas purifying apparatus.

[0160] The essential feature of the honeycomb catalyst of the embodiment of the present invention is to include a honeycomb unit with a plurality of through holes that are arranged in parallel in a longitudinal direction and partitions that are provided between the through holes, wherein the honeycomb unit includes a zeolite, inorganic particles, and an inorganic binder; the zeolite is a CHA-structured aluminosilicate having a Si/Al ratio of 15 to 50; the inorganic particles include an oxide that has a positive coefficient of thermal expansion; and the volume ratio of the zeolite to the inorganic particles (zeolite:inorganic particles) is 50:50 to 90:10.

[0161] Desired effects can be obtained by appropriately combining the essential feature with the various structures (for example, the structure of the zeolite, the structure of the inorganic particles, the structure of the inorganic binder, the structure of the honeycomb unit, the conditions for manufacturing the honeycomb catalyst, the structure of the exhaust gas purifying apparatus, or the like) mentioned in detail in the above description of the embodiment of the present invention.

[0162] Obviously, numerous modifications and variations of the present invention are possible in light of the above teachings. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described herein.

1. A honeycomb catalyst comprising:
a honeycomb unit having a plurality of through holes that are arranged in parallel in a longitudinal direction and partitions that are provided between the plurality of through holes, the honeycomb unit comprising:
a zeolite comprising a CHA-structured aluminosilicate having a Si/Al ratio of about 15 to about 50;
inorganic particles comprising an oxide that has a positive coefficient of thermal expansion, a volume ratio of the zeolite to the inorganic particles being about 50:about 50 to about 90:about 10; and
an inorganic binder.

2. The honeycomb catalyst according to claim **1**,
wherein the volume ratio of the zeolite to the inorganic particles is about 60:about 40 to about 80:about 20.

3. The honeycomb catalyst according to claim **1**,
wherein the inorganic particles comprise at least one of alumina, titania, and zirconia.

4. The honeycomb catalyst according to claim **1**,
wherein the zeolite has an average particle size of about 0.1 to about 2.0 μm, and
the inorganic particles have an average particle size of about 0.1 to about 5.0 μm.

5. The honeycomb catalyst according to claim **4**,
wherein an average particle size of the inorganic particles is about ⅕ to about 50 times an average particle size of the zeolite.

6. The honeycomb catalyst according to claim **4**,
wherein an average particle size of the inorganic particles is larger than an average particle size of the zeolite but is not larger than four times the average particle size of the zeolite.

7. The honeycomb catalyst according to claim **1**,
wherein the zeolite is ion-exchanged with a copper ion.

8. The honeycomb catalyst according to claim **7**,
wherein the honeycomb unit contains the copper ion in an amount of about 5.5 to about 7.5 g per liter of an apparent volume of the honeycomb unit.

9. The honeycomb catalyst according to claim **1**,
wherein the honeycomb unit comprises the zeolite in an amount of about 150 to about 250 g per liter of an apparent volume of the honeycomb unit.

10. The honeycomb catalyst according to claim **1**,
wherein the honeycomb unit further comprises at least one of an inorganic fiber, a scaly material, a tetrapod-shaped material, and a three-dimensional needle-shaped material.

11. An exhaust gas purifying apparatus comprising a honeycomb catalyst comprising:
a honeycomb unit having a plurality of through holes that are arranged in parallel in a longitudinal direction and partitions that are provided between the plurality of through holes, the honeycomb unit comprising:
a zeolite comprising a CHA-structured aluminosilicate having a Si/Al ratio of about 15 to about 50;
inorganic particles comprising an oxide that has a positive coefficient of thermal expansion, a volume ratio of the zeolite to the inorganic particles being about 50:about 50 to about 90:about 10; and
an inorganic binder.

12. The honeycomb catalyst according to claim **2**,
wherein the inorganic particles comprise at least one of alumina, titania, and zirconia.

13. The honeycomb catalyst according to claim **2**,
wherein the zeolite has an average particle size of about 0.1 to about 2.0 μm, and
the inorganic particles have an average particle size of about 0.1 to about 5.0 μm.

14. The honeycomb catalyst according to claim **3**,
wherein the zeolite has an average particle size of about 0.1 to about 2.0 μm, and
the inorganic particles have an average particle size of about 0.1 to about 5.0 μm.

15. The honeycomb catalyst according to claim **5**,
wherein the average particle size of the inorganic particles is larger than the average particle size of the zeolite but is not larger than four times the average particle size of the zeolite.

16. The honeycomb catalyst according to claim **2**,
wherein the zeolite is ion-exchanged with a copper ion.

17. The honeycomb catalyst according to claim **3**,
wherein the zeolite is ion-exchanged with a copper ion.

18. The honeycomb catalyst according to claim **4**,
wherein the zeolite is ion-exchanged with a copper ion.

19. The honeycomb catalyst according to claim **5**,
wherein the zeolite is ion-exchanged with a copper ion.

20. The honeycomb catalyst according to claim **6**,
wherein the zeolite is ion-exchanged with a copper ion.

* * * * *