FLUE GAS DENITRATION CATALYST AND PREPARATION PROCESS THEREOF

Inventors: Shigeru Nojima, Hiroshima (JP); Kozo Iida, Hiroshima (JP); Yoshiaki Obayashi, Hiroshima (JP); Katsumi Nochi, Hiroshima (JP); Masashi Kiyosawa, Nagasaki-ken (JP)

Correspondence Address:
MYERS BIGELE SIBLEY & SAJOVEC
PO BOX 37428
RALEIGH, NC 27627 (US)

Appl. No.: 10/705,365
Filed: Nov. 10, 2003

Prior Publication Data
Correction of US 2004/0180783 A1 Sep. 16, 2004
See Filing Date.

Foreign Application Priority Data

Publication Classification
Int. Cl. ............................... B01J 23/30
U.S. Cl. ............................... 502/309

ABSTRACT

Provided are a flue gas denitrification catalyst having high denitrification activity and capable of suppressing a side reaction, that is, oxidation of SO₂ and a preparation process of the catalyst. The flue gas denitrification catalyst comprises TiO₂, WO₃, and V₂O₅. In the surface layer of the catalyst within 200 μm from the surface thereof, V₂O₅ is supported on a carrier containing TiO₂ and WO₃. The supported amounts of V₂O₅ range from 0.4 to 5 wt. % based on the weight of the surface layer and range from 0.1 to 0.9 wt. % based on the total weight of the catalyst. The V₂O₅ thus supported has a crystallite size of less than 10 nm as measured by X-ray diffraction. The catalyst can be available by preparing a mixture containing TiO₂ and WO₃ and having V₂O₅ supported on the surface of an extruded product of the prepared mixture by a vapor phase method. The catalyst can be also available by having V₂O₅ supported on a powder of the prepared mixture by a vapor phase method and having the resulting powder supported on the surface of a formed product.
FLUE GAS DENITRATION CATALYST AND PREPARATION PROCESS THEREOF

RELATED APPLICATION


BACKGROUND OF THE INVENTION

[0002] The present invention relates to a flue gas denitrification catalyst for the removal of nitrogen oxides from a flue gas of a combustion furnace such as a large-sized boiler for electricity generation; and a preparation process of the catalyst.

[0003] A flue gas from a boiler usually contains nitrogen oxides and sulfur oxides. One denitrification method for such a flue gas is to add ammonia to the flue gas which passes over a catalyst composed mainly of titanium (Ti), tungsten (W), and vanadium (V) where nitrogen oxides are treated in accordance with the following reaction formula:

\[ 4\text{NO} + 4\text{NH}_3 + 4\text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} \]

[0004] A flue gas denitrification catalyst can Ordinarily be prepared by forming, into a monolithic honeycomb shape, a powdery catalyst obtained by supporting tungsten trioxide (WO₃) and vanadium pentoxide (V₂O₅) on a carrier of titanium dioxide (TiO₂) by impregnation. This preparation process however involves such a problem that an increase in the amount of V₂O₅, which is a main active component of the catalyst, improves denitrification activity but it simultaneously enhances oxidation of sulfur dioxide which is a reaction as shown in the below-described reaction formula:

\[ \text{SO}_3 + \text{O}_2 \rightarrow \text{SO}_2 \]

[0005] There is therefore proposed a preparation process comprising forming a TiO₂ powder into a honeycomb carrier, supporting WO₃ on the resulting honeycomb carrier by an impregnation method and then supporting V₂O₅ on the result carrier by a vapor phase method (refer to Japanese Examined Patent Publication No. 6-40957). Compared with the conventional catalyst which is obtained by impregnation and whose V₂O₅ concentration is uniform even inside the bulk, the catalyst obtained by the above-described process can contain V₂O₅ thinly and uniformly along the surface of the catalyst at a high concentration so that it is possible to promote the denitrification reaction which proceeds sufficiently in the surface layer of the catalyst alone and to prevent the oxidation of SO₂ occurring even inside the bulk.

[0006] Emission standards of nitrogen oxides are becoming more stringent, and flue gas denitrification catalysts have to have higher denitrification performance. In addition, in the denitrification method employed particularly for the exhaust gas from a coal-fired boiler among various exhaust gases, catalysts capable of suppressing oxidation of SO₂ which is a side reaction and having high denitrification activity are required. Moreover, in the method as described in the above patent publication, it is difficult to form TiO₂ into a monolithic honeycomb, because upon its formation, even if various binders are added to TiO₂, they fail to give sufficient strength to the TiO₂ carrier.

SUMMARY OF THE INVENTION

[0007] In light of above-described problems, an object of the present invention is therefore to provide a flue gas denitrification catalyst which has high denitrification activity and is capable of suppressing the oxidation of SO₂ which is a side reaction; and a preparation process of such a catalyst.

[0008] For satisfying the above-described object, a preparation process of a flue gas denitrification catalyst according to the present invention comprises preparing a mixture containing titanium dioxide and tungsten trioxide, and having vanadium pentoxide supported on the surface of an extruded catalyst body or on a powder of the prepared mixture using a vapor phase method.

[0009] Extrusion of the mixture obtained by adding WO₃ to TiO₂ increases adhesion, thereby improving the denitrification activity. By adopting a vapor phase approach, V₂O₅ can be supported on the surface of the extruded catalyst body thinly and uniformly at a high concentration so that the oxidation of SO₂ can be suppressed. Moreover, the addition of WO₃ improves lubrication upon extrusion of the mixture and also compression strength of the extruded catalyst body.

[0010] Alternatively, with V₂O₅ being supported on the powder of a TiO₂ and WO₃ mixture, adhesion between TiO₂ and WO₃ is increased, making it possible to improve the denitrification activity of the catalyst. Further, by having the resulting powder supported on the surface of a formed product, V₂O₅ exists only on the surface and the oxidation of SO₂ can be suppressed. In such systems, a boiling bed type (ebullient bed type) or a moving bed type (fluidized bed type) is preferably employed for the vapor phase method.

[0011] In the preparation process of a flue gas denitrification catalyst according to the present invention, titanium dioxide and tungsten trioxide in the mixture preferably exist as a complex oxide thereof. The vanadium source in the vapor phase method is preferably at least one compound selected from vanadium oxytrichloride, vanadium oxytribromide, vanadium pentachloride and vanadium dichloride. The above-described mixture further preferably contains silicon dioxide. Titanium dioxide, tungsten trioxide and silicon dioxide in the above-described mixture preferably exist as a complex oxide thereof.

[0012] In another aspect of the present invention, there is also provided a flue gas denitrification catalyst available by preparing a mixture containing titanium dioxide and tungsten trioxide, and having vanadium pentoxide supported on the surface of an extruded catalyst body or on a powder of the prepared mixture using a vapor phase method. In addition, there is also provided a flue gas denitrification catalyst available by further having the resulting powder supported on the surface of a formed product. The formed product preferably contains titanium dioxide, tungsten trioxide and vanadium pentoxide.

[0013] In the flue gas denitrification catalyst of the present invention, titanium dioxide and tungsten trioxide in the above-described mixture preferably exist as a complex compound thereof. The amounts of vanadium pentoxide range preferably from 0.4 to 5 wt. % based on the surface layer of the denitrification catalyst which has a thickness of 200 μm from its surface, and range from 0.1 to 0.9 wt. % based on the total weight of the catalyst. The crystallite size of the vanadium pentoxide supported by the vapor phase method is preferably less than 10 nm as measured by X-ray diffraction. The extruded catalyst body and the formed product have preferably a honeycomb shape. The above-described mix-
ture preferably contains silicon dioxide. Titanium dioxide, tungsten trioxide and silicon dioxide in the above-described mixture preferably exist as a complex oxide thereof.

[0014] In a still further aspect of the present invention, there is also provided a flue gas denitrization catalyst comprising titanium dioxide, tungsten trioxide and vanadium pentoxide, wherein the vanadium pentoxide is supported on a carrier containing titanium dioxide and tungsten trioxide in the surface layer of the catalyst which has a thickness of 200 μm from its surface; wherein the amounts of vanadium pentoxide range from 0.4 to 5 wt. % based on the weight of the surface layer, and range from 0.1 to 0.9 wt. % based on the total weight of the catalyst; and wherein the vanadium pentoxide on the carrier has a crystallite size of less than 10 nm as measured by X-ray diffraction.

BRIEF DESCRIPTION OF THE DRAWING

[0015] FIG. 1 is a schematic view illustrating the measuring method of crushing strength.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

[0016] The embodiments of the present invention will next be described.

First Embodiment

[0017] A preparation process of a flue gas denitrization catalyst according to a first embodiment of the present invention comprises extruding a mixture containing TiO₂ and WO₃, and having V₂O₅ supported on the surface of the extruded catalyst body using a vapor phase method.

[0018] As the mixture containing TiO₂ and WO₃, a kneaded mixture of TiO₂ and WO₃, or a complex oxide of TiO₂ and WO₃ may be used. Use of a complex oxide of TiO₂ and WO₃ is particularly preferred, because it promotes denitrization reactions, suppresses oxidation of SO₂ and facilitates extrusion into a honeycomb catalyst. The TiO₂:WO₃ ratio by weight preferably ranges from 100:5 to 100:20, more preferably from 100:6 to 100:18. Adjustment to such a ratio not only suppresses the oxidation of SO₂ but also improves an extrusion property into a monolithic honeycomb catalyst.

[0019] The further addition of SiO₂ to the mixture is preferred. Addition of SiO₂ increases the amount of a solid acid in the catalyst. An increase in the amount of a solid acid not only improves an adsorption rate of NH₃ but also makes it possible to suppress adsorption of SO₂, so as to suppress the oxidation of SO₂ which is a side reaction. When SiO₂ is added, it is preferably added in the form of a complex oxide of TiO₂, SiO₂ and WO₃, because if so, the denitrization is promoted, the oxidation of SO₂ is suppressed and the extrusion property into a honeycomb catalyst can be improved. The TiO₂:SiO₂ ratio by weight preferably ranges from 100:1 to 100:15, more preferably from 100:3 to 100:10. By adjusting to a ratio within the above-described range, the resulting catalyst is capable of exhibiting the above-described properties. Various binders can be added to the mixture in order to facilitate extrusion.

[0020] No particular limitation is imposed on how the mixture is extruded and known extruders can be used. The extruded catalyst body thus obtained preferably has a monolithic honeycomb shape. The term “honeycomb shape” as used herein means not only regular hexagons in its cross-section but also squares. By forming the catalyst into a honeycomb shape, a specific surface area of the extruded catalyst body increases, leading to an improvement in the denitrization performance.

[0021] As a method for having V₂O₅ supported on the surface of the extruded catalyst body by the vapor phase method, a fixed bed system is preferred. For example, usable is a method of blowing a vanadium source, together with a carrier gas, into a reaction furnace set at high temperatures and feeding the surface of the extruded catalyst body with a vanadium vapor. As the vanadium source, vanadium oxytrichloride (VOCl₃), vanadium oxytribromide (VOBr₃), vanadium pentachloride (VCl₅) and vanadium dichloride (VCl₂) are preferred. Such vanadium sources are in the liquid or solid form at normal temperatures, but by converting them into the vapor phase, a vanadium component can be supported on the surface of the extruded catalyst body.

[0022] When VOCl₃ is employed as the vanadium source, it reacts with the hydroxyl group (—OH) on the surface of TiO₂ to form —VO(OH)₂ thereon. Then, the Cl is removed therefrom by calcination or hydrolysis, and —OVO(OH)₃ is formed. When the —OVO(OH)₃ formed in the surface of the catalyst is calcined, a monomolecular layer of V₂O₅ can be formed uniformly. Thus, V₂O₅ can be uniformly supported mainly on the surface of the extruded catalyst body by the vapor phase method.

[0023] The flue gas denitrization catalyst thus obtained has V₂O₅ mainly on the surface layer of the extruded catalyst body at a high concentration, and has little V₂O₅ inside the bulk of the extruded catalyst body. It is therefore possible to promote the denitrization reaction which proceeds sufficiently only in the surface layer of the extruded catalyst body and at the same time, to suppress the oxidation of SO₂ which occurs also inside the bulk of the extruded catalyst body.

[0024] The amounts of V₂O₅ preferably range from 0.4 to 5 wt. % based on the weight of the surface layer of the flue gas denitrization catalyst which has a thickness of 200 μm from its surface and range from 0.1 to 0.9 wt. % based on the total weight of the catalyst. Since the amount of V₂O₅ is 0.4 wt. % or greater based on the surface layer, the catalyst is capable of exhibiting high denitrization activity. Since the amount is 5 wt. % or less, the oxidation of SO₂ in the surface layer can be suppressed completely. The amount of V₂O₅ based on the total weight of the catalyst is 0.1 wt. % or greater so that predetermined denitrization performance is exhibited even if the supported amount of vanadium in the surface layer is not uniform. The amount is 0.9 wt. % or less so that the oxidation of SO₂ inside the bulk can be suppressed completely. The supported amounts of V₂O₅ more preferably range from 0.4 to 3 wt. % based on the weight of the surface layer and range from 0.1 to 0.3 wt. % based on the total weight of the catalyst.

[0025] The V₂O₅ supported by the vapor phase method is finely pulverized so that it has high denitrization activity compared with V₂O₅ supported by conventional impregnation. The V₂O₅ preferably has a crystallite size of less than 10 nm as measured by X-ray diffraction. Adjustment of the crystallite size of V₂O₅ to less than 10 nm enables a drastic improvement in its denitrization activity. The crystallite size of V₂O₅ is more preferably 8 nm or less as measured by X-ray diffraction.
Second Embodiment

A preparation process of a flue gas denitration catalyst according to the second embodiment of the present invention comprises having V$_2$O$_5$ supported on a powder mixture containing TiO$_2$ and WO$_3$, by a vapor phase method, and having the resulting powder supported on the surface of a formed product.

As the powder mixture containing TiO$_2$ and WO$_3$, a mixture of TiO$_2$ powder and WO$_3$ powder or a complex oxide powder of TiO$_2$ and WO$_3$ is usable. The complex oxide powder of TiO$_2$ and WO$_3$ is particularly preferred. Addition of SiO$_2$ to the powder mixture is also preferred as in the first embodiment, of which use of a complex oxide powder of TiO$_2$, SiO$_2$, and SO$_3$ is more preferred. A weight ratio of powders constituting the mixture is similar to that used in the first embodiment. Although no particular limitation is imposed on the average particle size of the powder, a range of from 0.1 μm to 30 μm is preferred.

In a similar manner to that employed in the first embodiment, V$_2$O$_5$ can be supported on the powder by a vapor phase method. As well as the fixed bed system, a boiling bed system or a moving bed system can be adopted. Use of the boiling bed system or moving bed system enables continuous supporting of V$_2$O$_5$, so that V$_2$O$_5$ can be supported efficiently to a large amount of powders.

The V$_2$O$_5$ supported powder is supported on the surface of a formed product, for example, by converting the powder into a slurry, applying the slurry to the surface of the formed product and then drying. Although no particular limitation is imposed on the formed product insofar as it permits stable supporting of the V$_2$O$_5$ supported powder on a carrier made of TiO$_2$ and WO$_3$, for a long period of time, the formed product composed mainly of TiO$_2$ is preferred, of which the formed product composed of TiO$_2$ and WO$_3$ and optionally V$_2$O$_5$ is more preferred, with the formed product having WO$_3$ and V$_2$O$_5$ supported thereon by impregnation being still more preferred. The formed product is preferably obtained in the monolithic honeycomb form by extrusion.

The flue gas denitration catalyst thus obtained has V$_2$O$_5$ on the surface of the formed product at a high concentration, but has little V$_2$O$_5$ inside the bulk of the formed product so that the denitration reaction which proceeds sufficiently only in the surface layer of the catalyst can be accelerated and at the same time, the oxidation of SO$_2$ inside the bulk of the catalyst can be suppressed.

Similar to the flue gas denitration catalyst available according to the first embodiment, the catalyst of the second embodiment preferably has V$_2$O$_5$ supported thereon in an amount of from 0.4 to 5 wt. % based on the surface layer of the catalyst which has a thickness of 200 μm from its surface and in an amount of from 0.1 to 9 wt. % based on the total weight of the catalyst, of which amounts of from 0.4 to 3 wt. % based on the surface layer and from 0.1 to 0.3 wt. % based on the whole catalyst are more preferred, respectively. The V$_2$O$_5$ supported in accordance with the vapor phase method is in the finely pulverized form as in the first embodiment.

The crystallite size of V$_2$O$_5$ is preferably less than 10 nm as measured by X-ray diffraction, with 8 nm or less being more preferred.

EXAMPLES

An aqueous TiOSO$_4$ solution (1500 g) having a concentration of 15% in terms of TiO$_2$ was cooled to 20° C. or less. Then, the resulting solution was neutralized to pH 8 by adding 15% aqueous ammonia in portions. The titanium hydroxide precipitate thus obtained was washed with water and collected by filtration, whereby titanium hydroxide in the paste form was obtained. Ammonium para-tungstate was added to the resulting titanium hydroxide paste (at a TiO$_2$:WO$_3$ ratio by weight of 10:1), followed by sufficient kneading and mixing. The kneaded mass was dried, and calcined at 500° C. for 5 hours, whereby a TiO$_2$:WO$_3$ complex oxide was obtained.

To 95 parts by weight of the complex oxide were added 5 parts by weight of glass fibers and 10 parts by weight of an organic binder (cellulose acetate). After the addition of water and sufficient mixing in a kneader, the reaction mixture was adjusted to have an adequate water concentration. The holes of a honeycomb extruder were adjusted to squares and the mixture was extruded into a honeycomb shape having an opening of 6.0 mm and a wall thickness of 1.0 mm. The extruded product was dried, and calcined at 500° C. for 3 hours.

The resulting calcined honeycomb was placed in a reaction furnace having a constant temperature of 400° C., followed by blowing therein VOCI$_3$, a compound which takes a liquid form at normal temperature, at 40 ml/min. while using N$_2$ as a carrier gas. The calcined honeycomb was then fed for 20 minutes with the VOCI$_3$ vapor generated by a fixed bed system. After the resulting calcined product was taken out from the reaction furnace, it was calcined for 3 hours in the air, whereby a honeycomb catalyst (Example 1) was obtained.

The V$_2$O$_5$ distribution of this honeycomb catalyst was analyzed by an X-ray microanalyzer. The supported amounts of V$_2$O$_5$ were 0.90 wt. % based on the surface layer within 200 μm from the surface of the honeycomb catalyst and 0.28 wt. % based on the total weight of the catalyst including also the inside of the bulk.

In a similar manner to that employed in Example 1 except the use of VOBr$_3$, VCl$_3$, and VCl$_4$, instead of VOCI$_3$ as the vanadium source, honeycomb catalysts (Examples 2 to 4) were obtained, respectively. As a result, in Examples 2 to 4, the supported amounts of V$_2$O$_5$ were 0.84 wt. %, 0.92 wt. % and 0.83% based on the surface layer of the honeycomb catalyst; and 0.22%, 0.19 wt. % and 0.18 wt. % based on the whole catalyst, respectively.

After a TiO$_2$:WO$_3$ complex oxide was obtained as in Example 1, it was pulverized into a powdery complex oxide. The resulting powder (200 g) was filled in a boiling
bed reactor (80 mm in diameter quartz cylindrical tube) and was confirmed to be boiled uniformly by an upflow. VOCl₃ was added to an N₂ gas heated to 400°C and the resulting mixture was supplied to the filled layer from the downstream toward the upstream at 100 cc/min for 20 minutes. The resulting vanadium-supported powder was calcined in the air at 500°C for 3 hours. The resulting powder was found to have 0.65 wt. % of V₂O₅ uniformly. The powder thus obtained was designated as “powder catalyst (a).”

A preparation process of honeycomb catalyst (c) to be used as a base material will next be described.

First, titanium hydroxide in the paste form was obtained in a similar manner to that employed in Example 1. It was then dried and calcined at 500°C for 5 hours, and a TiO₂ powder was prepared. The TiO₂ powder thus obtained was extruded in a similar manner to that employed in Example 1, whereby a honeycomb TiO₂ having an opening of 6.0 mm and a wall thickness of 1.0 mm was obtained. The resulting honeycomb TiO₂ was impregnated with an aqueous solution of ammonium paratungstate, followed by drying and subsequent calcination at 500°C for 3 hours. The resulting honeycomb of WO₃-supporting TiO₂ was impregnated with an aqueous solution of ammonium metavanadate, followed by drying and subsequent calcination at 500°C for 3 hours, and denitration catalyst (c) in the honeycomb form was obtained. Denitration catalyst (c) was composed of TiO₂, WO₃ and V₂O₅ at a ratio by weight of 91:8:9:0.1.

Powder catalyst (a) was supported on the honeycomb denitration catalyst (c) serving as a base material in the following manner. Water was added to powder catalyst (a) and the mixture was converted in a slurry in a wet ball mill. Powder catalyst (a) was applied to the surface of denitration catalyst (c) to give 100 g/cm² per surface area of denitration catalyst (c). After drying the catalyst thus applied, it was calcined at 500°C for 3 hours, whereby a honeycomb catalyst (Example 5) was obtained.

A moving bed reactor (a cylindrical tube of 60 mm in diameter, moved while rotating at 10 cm/min) was filled with 200 g of a powdery complex oxide obtained in a similar manner to that employed in Example 5. VOCl₃ was added to an N₂ gas heated to 400°C and the mixture was fed to a reactor for 20 minutes. The vanadium-supporting powder thus obtained was calcined at 500°C for 3 hours. It was found that on the resulting powder, 0.69 wt. % of V₂O₅ was supported uniformly. The V₂O₅-supporting powder thus obtained was designated as powder catalyst (b). Powder catalyst (b) was applied to denitration catalyst (c) in a similar manner to that employed in Example 5. After drying, the catalyst thus applied was calcined at 500°C for 3 hours, whereby a honeycomb catalyst (Example 6) was obtained.

Examples 7 and 8

In a similar manner to Example 1 except that the VOCl₃ vapor was fed for 15 minutes and 30 minutes instead of 20 minutes, honeycomb catalysts (Examples 7 and 8) were obtained, respectively. In Examples 7 and 8, the supported amounts of V₂O₅ were 0.75 wt. % and 0.98 wt. % based on the surface layer of the honeycomb catalysts; and 0.23 wt. % and 0.32 wt. % based on the whole catalysts, respectively.

Example 9

In a similar manner to Example 1 except that instead of preparation of a TiO₂—WO₃ complex oxide, a TiO₂—SiO₂—WO₃ complex oxide was prepared by adding silica sol (“Snowtex O”, trade name) to a titanium hydroxide paste at a T:Si ratio by weight of 10:1, a honeycomb catalyst (Example 9) was obtained. The supported amounts of V₂O₅ were 0.80 wt. % based on the surface layer of the honeycomb catalyst and 0.24 wt. % based on the whole catalyst, respectively.

Example 10

In a similar manner to Example 1, titanium hydroxide was obtained in the paste form. The resulting titanium hydroxide paste was dried, and then calcined at 500°C for 5 hours, and a TiO₂ powder was prepared. In a similar manner to Example 1, the resulting TiO₂ was extruded into a honeycomb shape. After measuring the saturated water content of the resulting honeycomb TiO₂, it was impregnated with an aqueous solution of ammonium paratungstate to support ammonium paratungstate on the honeycomb TiO₂ to give a TiO₂—WO₃ ratio by weight of 10:1. The impregnation was followed by drying and calcining at 500°C for 3 hours, whereby WO₃ was supported. The honeycomb WO₃-supporting TiO₂ thus obtained was then impregnated with an aqueous solution of ammonium metavanadate. After drying, the resulting product was calcined at 500°C for 3 hours. As a result of the analysis of the distribution condition of V₂O₅ in the resulting honeycomb catalyst (Example 10), it was found that V₂O₅ was supported uniformly in the catalyst from the surface to the inside of the bulk. The supported amounts of V₂O₅ based on the surface layer and the whole catalyst were both 0.29 wt. %.

Denitration Performance Test

The honeycomb catalysts obtained in Examples 1 to 10 were subjected to a denitration performance test under the below-described conditions. The test results (denitration ratio, SO₂ oxidation ratio) after treatment of a gas with these catalysts for 50 hours are shown in Table 1.

Shape of catalyst: honeycomb shape (volume: 2.5 L) of 5 cm×5 cm×100 cm

Gas flow rate: 25 Nm³/h (GHSV 10,000 h⁻¹)

Temperature: 350°C, 420°C C.

molar ratio NH₃/NO: 1

Gas composition: NO: 200 ppm, NH₃: 200 ppm, SO₂:800 ppm, O₂: 4%, CO₂: 12%, H₂O: 10%, N₂: balance

Measurement of Crystallite Size of V₂O₅

The crystallite size of V₂O₅ supported on each of the honeycomb catalysts obtained in Examples 1 to 10 was determined in accordance with the Scherrer equation based on data obtained by the X-ray diffraction method. The results of the measurement are also shown in Table 1.

Measurement of Crushing Strength of Honeycomb Catalysts

Crushing strength was measured in accordance with the below-described method in order to find the strength of the honeycomb shape of each of the honeycomb catalysts obtained in Examples 1 to 10. The results are also
shown in Table 1. For the measurement, a tensile/compression tester ("THK-TK18", trade name; product of Tokyokoki Seizosho Ltd.) was employed.

(0058) (1) As illustrated in FIG. 1, a honeycomb catalyst 10 including the outside wall 12 was cut into a cube (5 cm x 5 cm x 5 cm).

(0059) (2) The honeycomb 10 was covered at upper and lower surfaces thereof with two walls 20 (1 cm thick) a little wider than the surface of the honeycomb catalyst 10 and then packed in a vinyl bag.

(0060) (3) A primary crush value (kg) was measured by a tensile/compression tester.

(0061) (4) Crushing strength (kg/cm²) per unit area was calculated.

TABLE 1

<table>
<thead>
<tr>
<th>Active component (V₂O₅)</th>
<th>Supported component</th>
<th>Supporting method (system)</th>
<th>Support amount [wt. %]</th>
<th>Denitrification [%]</th>
<th>SO₂ oxidation [%]</th>
<th>Crushing strength [kg/cm²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carrier</td>
<td>Surface layer</td>
<td>Whole catalyst</td>
<td>Crystallite size [nm]</td>
<td>350°C</td>
<td>420°C</td>
<td>550°C</td>
</tr>
<tr>
<td>Example 1</td>
<td>TiO₂</td>
<td>Vapor phase (fixed bed)</td>
<td>0.90</td>
<td>0.28</td>
<td>3</td>
<td>85</td>
</tr>
<tr>
<td>Example 2</td>
<td>TiO₂</td>
<td>Vapor phase (fixed bed)</td>
<td>0.84</td>
<td>0.22</td>
<td>4</td>
<td>85</td>
</tr>
<tr>
<td>Example 3</td>
<td>TiO₂</td>
<td>Vapor phase (fixed bed)</td>
<td>0.92</td>
<td>0.19</td>
<td>4</td>
<td>82</td>
</tr>
<tr>
<td>Example 4</td>
<td>TiO₂</td>
<td>Vapor phase (fixed bed)</td>
<td>0.83</td>
<td>0.18</td>
<td>3</td>
<td>81</td>
</tr>
<tr>
<td>Example 5</td>
<td>TiO₂</td>
<td>Vapor phase (moving bed)</td>
<td>0.65</td>
<td>0.10</td>
<td>4</td>
<td>83</td>
</tr>
<tr>
<td>Example 6</td>
<td>TiO₂</td>
<td>Vapor phase (moving bed)</td>
<td>0.69</td>
<td>0.10</td>
<td>3</td>
<td>84</td>
</tr>
<tr>
<td>Example 7</td>
<td>TiO₂</td>
<td>Vapor phase (fixed bed)</td>
<td>0.75</td>
<td>0.23</td>
<td>3</td>
<td>86</td>
</tr>
<tr>
<td>Example 8</td>
<td>TiO₂</td>
<td>Vapor phase (fixed bed)</td>
<td>0.98</td>
<td>0.32</td>
<td>3</td>
<td>87</td>
</tr>
<tr>
<td>Example 9</td>
<td>TiO₂</td>
<td>Vapor phase (fixed bed)</td>
<td>0.80</td>
<td>0.24</td>
<td>4</td>
<td>86</td>
</tr>
<tr>
<td>Example 10</td>
<td>TiO₂</td>
<td>Impregnation</td>
<td>0.29</td>
<td>0.29</td>
<td>10</td>
<td>78</td>
</tr>
</tbody>
</table>

(0062) As illustrated in Table 1, the honeycomb catalysts obtained in Examples 1 to 9 in which the supported amount of (V₂O₅) based on the surface layer of each catalyst within 200 nm from its surface was as high as about 0.6 to 1.0 wt. % and V₂O₅ was finely pulverized with a crystallite size of 4 nm or less exhibited a denitration ratio as high as about 80 to 95%. The supported amount of V₂O₅ based on the whole catalyst including the inside of the bulk was as low as about 0.1 to 0.35 wt. %, making it possible to suppress an SO₂ oxidation ratio to as low as 0.3 to 0.8%. The honeycomb catalyst obtained in Example 10 in which the supported amounts of V₂O₅ based on the surface layer and based on the whole catalyst were both 0.29% and had a crystallite size as large as 10 nm exhibited a denitration ratio of less than 80% and an SO₂ oxidation ratio of 1.0% or greater. Thus, the desired performance was not attained by Example 10.

(0063) As illustrated in Table 1, the honeycomb catalysts of Examples 1 to 4 and 7 to 9 obtained by extruding a mixture of TiO₂ and WO₃, and optionally SiO₂ into a honeycomb shape exhibited excellent crushing strength of from 5.5 to 7.5 kg/cm². The honeycomb catalyst of Example 10 obtained by extrusion of only TiO₂ exhibited crushing strength of 3.5 kg/cm² and the desired crushing strength was not attained.

What is claimed is:

1. A process for preparing a flue gas denitrification catalyst, which comprises preparing a mixture containing titanium dioxide and tungsten trioxide; and having vanadium pentoxide supported on the surface of an extruded catalyst body or on a powder of the prepared mixture using a vapor phase method.

2. A process of claim 1, which further comprises having the resulting powder supported on the surface of a formed product.
9. A flue gas denitration catalyst of claim 8, which is obtained by further having the resulting powder supported on the surface of a formed product.

10. A flue gas denitration catalyst of claim 8, wherein titanium dioxide and tungsten trioxide in the mixture exists in the form of a complex oxide thereof.

11. A flue gas denitration catalyst of claim 8, wherein the supported amounts of vanadium pentoxide range from 0.4 to 5 wt. % based on the surface layer of the catalyst which has a thickness of 200 μm from its surface and range from 0.1 to 0.9 wt. % based on the total weight of the catalyst.

12. A flue gas denitration catalyst of claim 8, wherein vanadium pentoxide supported by the vapor phase method has a crystallite size of less than 10 nm as measured by X-ray diffraction.

13. A flue gas denitration catalyst of claim 8, wherein the catalyst body has a honeycomb shape.

14. A flue gas denitration catalyst of claim 9, wherein the formed product has a honeycomb shape.

15. A flue gas denitration catalyst of claim 8, wherein the mixture further contains silicon dioxide.

16. A flue gas denitration catalyst of claim 15, wherein titanium dioxide, tungsten trioxide and silicon dioxide in the mixture exists in the form of a complex oxide thereof.

17. A flue gas denitration catalyst of claim 9, wherein the formed product contains titanium dioxide, tungsten trioxide and vanadium pentoxide.

18. A flue gas denitration catalyst comprising titanium dioxide, tungsten trioxide and vanadium pentoxide, wherein vanadium pentoxide is supported on a carrier containing titanium dioxide and tungsten trioxide in the surface layer of the catalyst which has a thickness of 200 μm from its surface; wherein the supported amounts of vanadium pentoxide range from 0.4 to 5 wt. % based on the surface layer and range from 0.1 to 0.9 wt. % based on the total weight of the catalyst; and wherein vanadium pentoxide thus supported has a crystallite size of less than 10 nm as measured by X-ray diffraction.

* * * * *