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- (71) **Applicant (for all designated States except US):** SUMITOMO CHEMICAL COMPANY, LIMITED [JP/JP]; 27-1, Shinkawa 2-chome, Chuo-ku, Tokyo, 1048260 (JP).
- (72) **Inventors; and**
- (75) **Inventors/Applicants (for US only):** KAWABATA, Tomonori [JP/JP]; c/o SUMITOMO CHEMICAL COMPANY, LIMITED, 1-98, Kasugadenaka 3-chome, Kono-hana-ku, Osaka-shi, Osaka, 5548558 (JP). YAMAMICHI, Hideaki [JP/JP]; c/o SUMITOMO CHEMICAL COMPANY, LIMITED, 1-98, Kasugadenaka 3-chome, Kono-hana-ku, Osaka-shi, Osaka, 5548558 (JP).
- (74) **Agents:** HASEGAWA, Yoshiki et al.; SOEI PATENT AND LAW FIRM, Marunouchi MY PLAZA (Meiji Yas-

uda Life Bldg.) 9th fl., 1-1, Marunouchi 2-chome, Chiyo-da-ku, Tokyo, 1000005 (JP).

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(54) **Title:** METHOD FOR PRODUCING TITANOSILICATE-CONTAINING CATALYST

(57) **Abstract:** The present invention relates to a method for producing a titanosilicate-containing catalyst, including: a pulverizing step of pulverizing titanosilicate particles to obtain a pulverized product by a wet process until a d (0.90) value of the particles on a volume basis is 1 μm or less; and a forming step of adding a binder to the pulverized product and forming the obtained mixture into granules, wherein the particles have an X-ray diffraction pattern with peaks at the positions indicated by the lattice spacing(d/Å) of 12.4 ± 0.8 , 10.8 ± 0.5 , 9.0 ± 0.3 , 6.0 ± 0.3 , 3.9 ± 0.3 and 3.4 ± 0.1 .



DESCRIPTION

Title of Invention

METHOD FOR PRODUCING TITANOSILICATE-CONTAINING
CATALYST

5 Technical Field

[0001] The present invention relates to a method for producing a titanosilicate-containing catalyst and a method for producing an oxirane compound.

Background Art

10 [0002] In a method of producing an olefin oxide such as propylene oxide, a titanosilicate-containing catalyst is used. As such a catalyst, for example, Patent Literature 1 describes a titanosilicate obtained by subjecting a boron-containing compound, tetrabutyl orthotitanate, fumed silica and piperidine to hydrothermal synthesis at a temperature
15 of 170°C and bringing the obtained layered compound (also referred to as as-synthesized sample) into contact with an aqueous nitric acid solution under reflux conditions. Then, Patent Literature 1 also describes a method for producing propylene oxide from hydrogen peroxide and propylene using the titanosilicate as a catalyst.

20 Citation List

Patent Literature

[0003] [Patent Literature 1] JP 2005-262164 A (Examples)

Summary of Invention

Technical Problem

25 [0004] A problem to be solved by the present invention is to find a novel production method required for providing a

titanosilicate-containing catalyst with a high olefin oxide production activity.

Solution to Problem

[0005] Under such circumstances, the present inventors have intensively studied and, as a result, have accomplished the present invention as follows. That is, the present invention relates to the followings:

[1] A method for producing a titanosilicate-containing catalyst, including: a pulverizing step of pulverizing titanosilicate particles by a wet process so that a $d(0.90)$ value of the particles on a volume basis is 1 μm or less to obtain a pulverized product; and a forming step of adding a binder to the pulverized product and forming the obtained mixture into granules, wherein the particles have an X-ray diffraction pattern with peaks at the positions of 12.4 ± 0.8 , 10.8 ± 0.5 , 9.0 ± 0.3 , 6.0 ± 0.3 , 3.9 ± 0.3 and 3.4 ± 0.1 as shown by the lattice spacing($d/\text{\AA}$).

[2] The method according to [1], wherein the pulverized product is an aqueous suspension of the titanosilicate particles with a $d(0.90)$ value on a volume basis of 1 μm or less;

[3] The method according to [1] or [2], wherein the pulverizing step is a step comprising sending an aqueous suspension containing the titanosilicate particles into a generator made of a hard material with a fine passage formed therein at a high rate using a high-pressure pump to pulverize the titanosilicate particles by a shear force generated when the suspension passes through the generator;

[4] The method according to any of [1] to [3], wherein the granule forming step is a step of forming the mixture into granules using a spray

dry method;

[5] A method for producing an oxirane compound, including a step of epoxidizing an olefin with hydrogen peroxide by a catalytic reaction using a titanosilicate-containing catalyst obtained by the method according to any of [1] to [4] (hereinafter, also simply referred to as "the present titanosilicate-containing catalyst");

[6] The method according to [5], wherein the olefin is propylene;

[7] A method for producing an oxirane compound, including a step of reacting an olefin, hydrogen and oxygen in the presence of a composite catalyst including a noble metal supported on a titanosilicate-containing catalyst obtained by the method according to any of [1] to [4], or a composite catalyst including a titanosilicate-containing catalyst obtained by the method according to any of [1] to [4] and a noble metal supported on a carrier component which is a substance different from the titanosilicate-containing catalyst (hereinafter, also referred to as "the present titanosilicate-containing composite catalyst");

[8] The method according to [7], wherein the olefin is propylene; and

[9] The method according to [7] or [8], wherein the noble metal is palladium.

Advantageous Effects of Invention

[0006] The present invention can provide a novel production method required for providing a titanosilicate-containing catalyst with a high olefin oxide production activity.

Description of Embodiments

[0007] A method for producing a titanosilicate-containing catalyst the present invention includes:

(1) a step of pulverizing titanosilicate particles having an X-ray diffraction pattern with peaks at the following positions indicated by the lattice spacing (hereinafter, also referred to as "the present titanosilicate particles") by a wet process so that a d (0.90) value of the particles on a volume basis is 1 μm or less (hereinafter, also referred to as "pulverizing step by a wet process"), and

(2) a step of adding a binder to a pulverized product obtained by the pulverizing step (hereinafter, also simply referred to as "the present pulverized product") and forming the obtained mixture into granules (hereinafter, also referred to as "granule forming step").

[0008] <Peak positions indicated by lattice spacing in X-ray diffraction pattern (lattice spacing $d/\text{\AA}$)>

12.4 ± 0.8 , 10.8 ± 0.5 , 9.0 ± 0.3 , 6.0 ± 0.3 , 3.9 ± 0.3 and 3.4 ± 0.1 .

[0009] The "d (0.90) value of the particles on a volume basis" means a particle size of accumulation 90% from the fine particle size in the particle size distribution on a volume basis. Such a d (0.90) value of the particles on a volume basis may be measured in accordance with a method described in, for example, "Particle Size Distribution Measurement of Titanosilicate Particles" described later.

[0010] The present titanosilicate particles have the X-ray diffraction pattern with the values indicated above. Hereinafter, a method for measuring an X-ray diffraction pattern will be described.

[0011] An X-ray diffraction pattern may be measured with a commercially available general X-ray diffractometer using Cu K-alpha radiation as a radiation source. Specifically, for example, it may be determined using the present titanosilicate particles as a specimen with

an X-ray diffractometer such as RINT2500V manufactured by Rigaku Denki Co., Ltd. under the following conditions.

(Measurement Conditions)

- Output: 40 kV-300 mA
- Scanning range: $2\theta = 0.75^\circ$ to 20°
- Scanning Rate: $1^\circ/\text{minute}$

[0012] The present titanosilicate particles may be those with substantially 4-coordinate Ti. The present titanosilicate particles may be those where the maximum absorption peak for an ultraviolet and visible absorption spectrum in a wavelength region of 200 nm to 400 nm appears within a wavelength region of 210 nm to 230 nm (for example, see Chemical Communications 1026-1027 (2002) Figure 2 (d), (e)). The ultraviolet and visible absorption spectrum can be measured with an ultraviolet and visible spectrophotometer provided with a diffuse reflection apparatus based on a diffuse reflection method.

[0013] The content of titanium atoms in the present titanosilicate particles is in the range of, for example, 0.001 to 0.1 mol, and preferably in the range of 0.005 to 0.05 mol, based on 1 mol of a content of silicon atoms.

[0014] Specific examples of the present titanosilicate particles (showing the X-ray diffraction pattern with the values indicated above) may include a Ti-MWW precursor (for example, one described in JP 2005-262164 A), Ti-YNU-1 (for example, one described in Angewandte Chemie International Edition 43, 236-240, (2004)), a crystalline titanosilicate, Ti-MWW (for example, one described in JP 2003-327425 A) which is a crystalline titanosilicate having an MWW structure in the

structure code of IZA (International Zeolite Association), and Ti-MCM-68 (for example, one described in JP 2008-50186 A) which is a crystalline titanosilicate having an MSE structure in the same structure code of IZA. Preferable examples of the present titanosilicate particles include a Ti-MWW precursor.

[0015] The Ti-MWW precursor means a substance which is a titanosilicate having a layered structure (hereinafter, also referred to as layered compound) and forms Ti-MWW precursor through dehydration-condensation. Such dehydration-condensation is usually performed by heating the Ti-MWW precursor at a temperature of higher than 200°C and 1000°C or lower, preferably about 300°C to 650°C. The Ti-MWW precursor may be subjected to a structure-directing agent treatment, as described later, in its production process. Further, the Ti-MWW precursor thus obtained may be subjected to a structure-directing agent treatment, as described later, again. They are also referred to as "Ti-MWW precursor" in the present invention.

[0016] Hereinafter, a method for producing a Ti-MWW precursor will be described in detail. Examples of the method for producing a Ti-MWW precursor may include the following first method, second method, third method and fourth method. Preferable examples include the third method.

[0017] The first method includes a step of heating a mixture containing a structure-directing agent, a compound containing a Group 13 element of the element periodic table (hereinafter, referred to as "Group 13 element-containing compound"), a silicon-containing compound, a titanium-containing compound and water (hereinafter, referred to as

"step (1-1)"), and a step of mixing a layered compound obtained in step (1-1) with an acid (hereinafter, referred to as "step (1-2)").

[0018] A heating temperature in step (1-1) is in the range of, for example, 110°C to 200°C, and preferably in the range of 140°C to 180°C.

[0019] A heating time in step (1-1) is shorter as the heating temperature is higher, and the heating time is longer as the heating temperature is lower. The heating time is in the range of, for example, 60 hours to 360 hours in the case where the heating temperature is in the range of, for example, from 110°C to 140°C. On the other hand, the heating time is in the range of 30 hours to 240 hours in the case where the heating temperature is a range of 140°C to 200°C.

[0020] In step (1-1), a rate of temperature rise during heating the mixture is in the range of, for example, 0.1°C/minute to 2°C/minute.

The rate of temperature rise may be constant or may not be necessarily constant, and may be gradually lowered as the heating temperature comes close to an intended temperature.

[0021] In step (1-1), examples of a method for heating a mixture may include a heating method by heat transfer such as a method of heating a jacket of an autoclave, and a heating method by microwave irradiation.

[0022] In step (1-1), when the mixture is heated, the mixture may be heated while being stirred with a stirring blade or the like.

[0023] Examples of a shape of the stirring blade to be used for stirring may include an anchor blade, a paddle blade, a plate blade, an inclined paddle blade, a turbine paddle, a propeller blade, a hollow blade, a pfaudler blade and a double helical blade. These stirring blades may

be used in a combination of one type of a plurality of stirring blades, or may be used in a combination of two types of stirring blades such as a combination of a stirring blade for horizontally convecting the mixture and a stirring blade for vertically convecting the mixture. Specific examples may include a combination of a broad paddle blade with a ratio of a longitudinal length of the paddle blade to a lateral length thereof of 1/2 or more and an anchor blade where they blades are placed up and down across each other, a combination of a paddle blade and a propeller blade, and a combination of an anchor blade and an inclined paddle blade.

[0024] The stirring rate of the stirring blade to be used for stirring is in the range of, for example, 0.1 km/h to 40 km/h when being represented by a tip rate of the stirring blade. The stirring rate may be constant or may not be necessarily constant, and may be lowered to a range of 1/2 to 1/100 after a lapse of a constant time (specifically, for example, after the completion of temperature rise).

[0025] The reaction product obtained in step (1-1) (including a layered compound) may be solid-liquid separated into a solid component (including a layered compound) and a liquid component (including unreacted raw materials) by filtration under reduced pressure, filtration under pressure, centrifugation or the like, before being subjected to step (1-2) and after being cooled as required.

[0026] The lower limit temperature of such cooling to be performed as required may be for example 0°C or higher, and preferably 50°C or higher. The upper limit temperature of the cooling can be for example the heating temperature in step (1-1).

[0027] The solid component (including a layered compound) obtained by the solid-liquid separation may be dried by a drying method such as draught drying, drying under reduced pressure, or drying by heating after being washed with a wash liquid such as water, as required, until
5 no reduction in mass of the obtained solid is observed. The temperature for such drying is in the range of, for example, 0°C to 200°C.

[0028] Then, in step (1-2), examples of a method for mixing the layered compound obtained in step (1-1) with an acid may include (a) a method
10 of spraying an acid (or a solution including an acid) to the layered compound, (b) a method of applying an acid (or a solution including an acid) to the layered compound, (c) a method of flowing an acid (or a solution including an acid) and the layered compound into a heated vessel or tube, (d) a method of immersing the layered compound in an
15 acid (or a solution including an acid), and (e) a method of stirring an acid (or a solution including an acid) and the layered compound. Preferable examples include the method (d) and the method (e). The method (d) and the method (e) can be performed in a batch manner or can be performed in a continuous manner.

[0029] In the method (d), it is suitable to flow an acid (or a solution including an acid) by convection by heating, stirring or the like. The "convection by heating" herein may be performed by utilizing generation of gas by reflux, a temperature difference in liquid by heating, or the like. In the case of refluxing an acid (or a solution
20 including an acid), a difference between a temperature of an acid (or a solution including an acid) and a temperature of a heating medium such
25

as a jacket to be used for mixing with which a stirring chamber is equipped may be in the range of, for example, 1°C to 50°C.

[0030] The mixing temperature in step (1-2) is in the range of, for example, 0°C to 200°C, preferably in the range of 50°C to 150°C, and more preferably in the range of 60°C to 120°C. The mixing time in step (1-2) is in the range of, for example, 0.1 hours to 240 hours, and preferably in the range of 2 hours to 48 hours.

[0031] In step (1-2), a pressure during mixing the layered compound obtained in step (1-1) with an acid is in the range of, for example, 0.01 MPa to 1.1 MPa at an absolute pressure, and preferably, for example, atmosphere pressure.

[0032] In order to recover a Ti-MWW precursor as a solid from the mixture of the layered compound obtained in step (1-2) and an acid, it is sufficient to solid-liquid separate the mixture (one having a temperature of, for example, 0°C or higher, preferably a range of 20°C to 100°C) into a solid component (containing a Ti-MWW precursor) and a liquid component (structure-directing agent dissolved in an acid, containing an acid) by filtration under reduced pressure, filtration under pressure, centrifugation, or the like. In the case of performing such solid-liquid separation in several times, each operation of the solid-liquid separation may be performed in conjunction with a stirring operation for preventing the solid component from adhering.

[0033] The solid component (containing a Ti-MWW precursor) obtained by the solid-liquid separation may be dried by a drying method such as draught drying, drying under reduced pressure, or drying by heating until no reduction in mass of the obtained solid is observed,

after being washed with a wash liquid such as an aqueous solution containing a structure-directing agent and/or boric acid, water, or a 0.01% by mass to 10% by mass aqueous hydrogen peroxide solution, as required.

5 [0034] The temperature of the wash liquid for the washing may be in the range of 0°C to 110°C.

[0035] Further, a temperature for the drying is in the range of, for example, 50°C to 200°C, preferably in the range of 100°C to 200°C, and more preferably in the range of 150°C to 200°C.

10 [0036] In the case where the washing operation is performed in several times, it is suitably performed it until a pH of the wash liquid after the washing operation reaches a range of 4 to 8, and the temperature of the wash liquid may be different from each washing operation. Specific examples of a method therefor may include a method in which a wash
15 liquid at 30°C or lower is used in a first washing operation with relatively favorable filterability, and a wash liquid at 30°C or higher is used in second and subsequent washing operations if filterability is deteriorated.

[0037] The dried Ti-MWW precursor thus obtained may be stored in an
20 airtight container. The airtight container is suitably one which shields against light. The storage period is not particularly limited, and it is for example in the order of one day to one year.

[0038] The second method includes a step of heating a mixture containing a structure-directing agent, a Group 13 element-containing
25 compound, a silicon-containing compound and water (hereinafter, referred to as "step (2-1)"), and a step of mixing a layered compound

obtained in step (2-1), a titanium-containing compound and an acid (hereinafter, referred to as "step (2-2)").

[0039] Step (2-1) may be performed in the same operation as in step (1-1) of the first method, except for not using the titanium-containing compound.

[0040] Step (2-2) may also be performed in the same operation as in step (1-2) of the first method, except for using the layered compound obtained in step (2-1) in place of the layered compound obtained in step (1-1).

[0041] The third method includes a step of heating a mixture containing a structure-directing agent, a Group 13 element-containing compound, a silicon-containing compound, a titanium-containing compound and water (hereinafter, referred to as "step (3-1)"), and a step of mixing a layered compound obtained in step (3-1), a titanium-containing compound and an acid (hereinafter, referred to as "step (3-2)").

[0042] Step (3-1) may be performed in the same operation as in step (1-1) of the first method. Step (3-2) may be performed in the same operation as in step (2-2) of the second method, except for using the layered compound obtained in step (3-1) in place of the layered compound obtained in step (2-1).

[0043] The fourth method is a method including a step of heating a mixture containing a structure-directing agent, a Group 13 element-containing compound, a silicon-containing compound and water to obtain a layered borosilicate, firing the obtained layered borosilicate (preferably, after removing the structure-directing agent by contact with an acid) to obtain B-MWW, removing boron in the

obtained B-MWW by an acid or the like, then adding thereto a structure-directing agent, a titanium-containing compound and water and heating the obtained mixture to obtain a layered compound, and bringing this layered compound into contact with about 6M nitric acid (for example, see Chemical Communication 1026-1027, (2002)).

[0044] Examples of the "acid" to be used in the above various methods include inorganic acids such as nitric acid, hydrochloric acid, sulfuric acid, perchloric acid, boric acid and fluorosulfonic acid; organic acids such as formic acid, acetic acid, propionic acid and tartaric acid; and combinations of two or more thereof. Preferable examples include an acid containing at least one inorganic acid having a higher oxidation-reduction potential than tetravalent titanium. Examples of the "inorganic acid having a higher oxidation-reduction potential than tetravalent titanium" may include nitric acid, perchloric acid, fluorosulfonic acid, a combination of nitric acid and sulfuric acid, and a combination of nitric acid and boric acid.

[0045] The acid to be used in the above various methods is usually used in a state of a solution prepared by being dissolved in a solvent. Examples of the "solvent" may include water, an alcohol solvent, an ether solvent, an ester solvent, a ketone solvent and mixtures thereof. Preferable examples include water.

[0046] The concentration of the acid contained in the solution is in the range of, for example, 0.01 mol/l to 20 mol/l. In the case where an inorganic acid is used as the acid, it is preferable that a concentration of the inorganic acid be in the range of, for example, 1 mol/l to 5 mol/l.

[0047] Examples of the "Group 13 element of the element periodic

table" may include a boron-containing compound, an aluminum-containing compound and a gallium-containing compound. Preferable examples include a boron-containing compound.

[0048] Examples of the boron-containing compound may include boric acid, borate, boron oxide, boron halide, and a trialkylboron compound having an alkyl group with 1 to 4 carbon atoms. Preferable examples include boric acid.

[0049] Examples of the aluminum-containing compound may include sodium aluminate. Examples of the gallium-containing compound may include gallium oxide.

[0050] The amount of the Group 13 element-containing compound to be used is in the range of, for example, 0.01 mol to 10 mol and preferably in the range of 0.1 mol to 5 mol, based on 1 mol of silicon contained in the silicon-containing compound.

[0051] Examples of the "silicon-containing compound" may include silicic acid, silicate, silicon oxide, silicon halide, tetraalkyl orthosilicate and colloidal silica. Preferable examples include orthosilicic acid, metasilicic acid and metadisilicic acid.

[0052] Examples of the silicate include alkali metal silicates such as sodium silicate and potassium silicate, and alkali earth metal silicates such as calcium silicate and magnesium silicate.

[0053] Examples of the silicon oxide may include crystalline silica like quartz, and amorphous silica like fumed silica. Preferable examples include fumed silica. As the "fumed silica" herein, it is suitable to use those generally marketed, with a BET specific surface area of 50 m²/g to 380 m²/g. Among them, those with a BET specific surface area of 50

m²/g to 200 m²/g are suitable because of being easily handled. Those with a BET specific surface area of 100 m²/g to 380 m²/g are also suitable because of being easily dissolved in an aqueous solution.

[0054] Examples of the silicon halide may include silicon tetrachloride and silicon tetrafluoride.

[0055] Examples of the tetraalkyl orthosilicate may include tetramethyl orthosilicate and tetraethyl orthosilicate.

[0056] Examples of the "titanium-containing compound" may include titanium alkoxide, titanate, titanium oxide, titanium halide, an inorganic acid salt of titanium and an organic acid salt of titanium.

[0057] Examples of the titanium alkoxide may include titanium alkoxides having an alkoxy group with 1 to 4 carbon atoms, such as tetramethyl orthotitanate, tetraethyl orthotitanate, tetraisopropyl orthotitanate and tetra-n-butyl orthotitanate. Preferable examples include titanium alkoxide. More preferable examples may include tetra-n-butyl orthotitanate.

[0058] Examples of the organic acid salt of titanium may include titanium acetate.

[0059] Examples of the inorganic acid salt of titanium may include titanium nitrate, titanium sulfate, titanium phosphate and titanium perchlorate.

[0060] Examples of the titanium halide may include titanium tetrachloride.

[0061] Examples of the titanium oxide may include titanium dioxide.

[0062] The amount of the titanium-containing compound to be used in the method for producing a Ti-MWW precursor is for example 0.001

parts by weight to 1 part by weight and preferably in the range of 0.01 parts by weight to 0.5 parts by weight, based on 1 part by weight of the obtained layered compound, in terms of the weight of titanium atoms in the titanium-containing compound..

5 [0063] Examples of "water" to be used in the method for producing a Ti-MWW precursor may include purified water such as distilled water and ion-exchange water.

[0064] The amount of water to be used in the method for producing a Ti-MWW precursor is in the range of, for example, 5 mol to 20 mol and
10 preferably in the range of 10 mol to 50 mol, based on 1 mol of silicon contained in the silicon-containing compound.

[0065] Examples of the "structure-directing agent" (that is, structure-directing agent capable of forming zeolite having an MWW structure) may include organic amines such as piperidine and
15 hexamethyleneimine; and quaternary ammonium salts such as N,N,N-trimethyl-1-adamantane ammonium salts (for example, N,N,N-trimethyl-1-adamantane ammonium hydroxide and N,N,N-trimethyl-1-adamantane ammonium iodide) and octyltrimethyl
20 ammonium salts (for example, octyltrimethyl ammonium hydroxide and octyltrimethyl ammonium bromide)(for example, see Chemistry Letters 916-917 (2007)). Preferable examples include piperidine and hexamethyleneimine. More preferable examples may include piperidine. These compounds may be used alone, or two or more thereof may be mixed in any ratio and used.

25 [0066] The amount of the structure-directing agent to be used in the method for producing a Ti-MWW precursor (or structure-directing

agent treatment) is in the range of, for example, 0.1 mol to 5 mol and preferably in the range of 0.5 mol to 3 mol, based on 1 mol of silicon in the silicon-containing compound.

[0067] The "mixture" to be used in the first step of each of the above various methods (that is, step (1-1) in the first method, step (2-1) in the second method, step (3-1) in the third method, and a step for obtaining a layered borosilicate in the fourth method) can contain an additive such as a diol compound, an ammonium salt or a fluorine compound.

[0068] Examples of the "diol compound" as the additive may include ethylene glycol, propylene glycol, polyethylene glycol, polypropylene glycol, benzene-1,2-diol, benzene-1,3-diol and benzene-1,4-diol.

[0069] The amount of the diol compound to be used is in the range of, for example, 0.001 mol to 2 mol based on 1 mol of silicon in the silicon-containing compound contained in the mixture.

[0070] Examples of the "ammonium salt" as the additive may include ammonium phosphate, diammonium hydrogen phosphate, ammonium dihydrogen phosphate, ammonium pyrophosphate, ammonium bromide, ammonium iodide, ammonium chloride, ammonium fluoride, ammonium nitrate, ammonium sulfate, ammonium hydrogen sulfate, ammonium formate, ammonium acetate, ammonium carbonate, ammonium hydrogen carbonate, and mixtures thereof.

[0071] The ammonium salt may be added in a state of being dissolved in water or the like in advance or may be added in a state of a solid.

[0072] The amount of the ammonium salt to be used is in the range of, for example, 0.1 mol to 10 mol based on 1 mol of silicon in the silicon-containing compound contained in the mixture.

[0073] Examples of the "fluorine compound" as the additive may include hydrofluorides such as ammonium fluoride, calcium fluoride, sodium fluoride and potassium fluoride, and hydrofluoric acid.

[0074] The amount of the fluorine compound to be used is in the range of, for example, 0.1 mol to 10 mol based on 1 mol of silicon in the silicon-containing compound contained in the mixture.

[0075] In the "pulverizing step", the present titanosilicate particles are pulverized so that a particle size of at least 90% of the particles on a volume basis, determined by a laser diffraction scattering type particle size distribution measurement apparatus, is 1 μ m or less. That is, the present titanosilicate particles are pulverized by a wet process so that a d (0.90) value on a volume basis is 1 μ m or less.

[0076] One example of the thus obtained pulverized product (that is, the present pulverized product) may include an aqueous suspension of titanosilicate particles with a d (0.90) value on a volume basis, determined by a laser diffraction scattering type particle size distribution measurement apparatus, of 1 μ m or less. Hereinafter, a d (0.90) value on a volume basis, determined by a laser diffraction scattering type particle size distribution measurement apparatus, will be described.

[0077] The d (0.90) value on a volume basis, determined by a laser diffraction scattering type particle size distribution measurement apparatus, may be measured and calculated using a commercially available general laser diffraction scattering type particle size distribution measurement apparatus. Specifically, for example, it may be determined by measuring a particle size distribution using the pulverized product obtained by the "pulverizing step" (that is, the

present pulverized product (pulverized product containing titanosilicate fine particles)) as a specimen with a laser diffraction scattering type particle size distribution measurement apparatus such as LA-950V2 manufactured by HORIBA, Ltd. under the following conditions and calculating a d (0.90) value on a volume basis.

(Measurement Conditions)

- Pretreatment of specimen: particle dispersion treatment by internal ultrasonic irradiation (40 kHz) for 10 minutes

- Number of data intake (specimen, blank): 5000 times

- Refractive index: specimen (1.47), dispersion medium (water) (1.333)

[0078] Examples of the "pulverizing step" may include (1) a pulverizing step using a ball mill by a wet process, (2) a pulverizing step using a jet mill by a wet process, (3) a step of pulverizing titanosilicate particles by a shear force generated when sending an aqueous suspension containing the titanosilicate particles into a generator made of a hard material with a fine passage formed therein using a high-pressure pump at a high rate to allow the suspension to pass through the generator, and (4) a combination of these steps. Preferable examples include (3) the pulverizing step. One specific example of (3) the pulverizing step may include a pulverizing step by a nanomizer. It is herein important that the pulverizing step be not a pulverizing step by a dry process in accordance with a known gas-type technique but a pulverizing step by a wet process.

[0079] In the "granule forming step", to the pulverized product obtained in the "pulverizing step" (that is, the present pulverized product) is added a binder and the obtained mixture is formed into granules.

[0080] Examples of the "granule forming step" may include a step of forming the mixture into granules using a method such as (1) extruding, (2) compressing, (3) tableting, (4) flowing, (5) rolling or (6) spray drying. Preferable examples include a step of forming the mixture into granules using (6) the spray drying. A spray drying method may be carried out in accordance with a known method. Examples of a drying device to be used for such a spray drying method may include a spray dryer, a flush jet dryer (manufactured by SEISHIN ENTERPRISE Co., Ltd.) and a micro mist dryer (manufactured by fujisaki electric .co. ltd.).

[0081] Examples of an atomization system in the spray dryer may include a rotating disk system, a pressure nozzle system, a four-fluid nozzle system and a two-fluid nozzle system. Preferable examples include a four-fluid nozzle system.

[0082] Examples of the binder to be used in the "granule forming step" may include sols of oxides of metals such as silicon, aluminum, titanium and zirconium (hereinafter, sometimes also referred to as "metal oxide sol"). Preferable examples include a silicon oxide sol.

[0083] In order to add the binder to the present pulverized product, for example, it is sufficient to mix a solution of the metal oxide sol with the present pulverized product and stir them, as required.

[0084] In order to form the thus obtained mixture into granules, for example, it is sufficient to form the mixture (that is, the present pulverized product) into granules in which a median size of the particles on a volume basis (that is, corresponding to a $d(0.50)$ value on a volume basis) is in the range of 2 μm to 40 μm , using the spray drying method under proper conditions. Examples of controllable variables of

the spray drying for producing granules having a desired median size range on a volume basis may include a droplet size of the mixture to be fed, a feed rate to a drying unit, an air temperature for drying and an evaporation rate. The air temperature for drying is usually in the range of, for example, 80°C to 300°C and preferably in the range of 150°C to 280°C, while it differs depending on a concentration of a slurry solution, a liquid-sending rate, and the like. The "median size of the particles on a volume basis" herein means a particle size of accumulation 50% from the fine particle side in the particle size distribution on a volume basis. Such a d (0.50) value of the particles on a volume basis may be measured in accordance with a method described in, for example, "Particle Size Distribution Measurement of Titanosilicate Particles" described later.

[0085] The titanosilicate-containing catalyst obtained by the above production method (that is, the present titanosilicate-containing catalyst) may be further additionally dried and be used.

[0086] For example, the present titanosilicate-containing catalyst may be placed in a heating furnace such as an electric furnace, a temperature thereof is raised from 250°C to 1000°C, preferably from 300°C to 600°C over 1 hour to 24 hours, and the present titanosilicate-containing catalyst may be further kept warm at that temperature for 1 hour to 24 hours and then allowed to cool spontaneously in the heating furnace.

[0087] The heating furnace is preferably under an atmosphere of an inert gas such as nitrogen, argon, neon or helium, an oxidized gas such as air, oxygen or carbon dioxide, or a reducing gas such as hydrogen, carbon monoxide or propylene. They are also referred to as "the

present titanosilicate-containing catalyst" in the present invention.

[0088] The titanosilicate-containing catalyst obtained by the above production method (that is, the present titanosilicate-containing catalyst) may be further additionally subjected to the structure-directing agent treatment (again) as described above, and then used.

[0089] For example, the present titanosilicate-containing catalyst may be used after the following treatment: the present titanosilicate-containing catalyst is mixed with a structure-directing agent and water in an airtight pressure-resistant container such as a autoclave, followed by sealing the airtight pressure-resistant container, it is left to stand under heat and pressure or mixed with stirring to obtain a mixed liquid, and a solid product is separated from the obtained mixed liquid by a method such as filtration or centrifugation. The present titanosilicate-containing catalyst may also be used after the following treatment: the titanosilicate-containing catalyst is mixed with a structure-directing agent and water to obtain a mixed liquid under atmospheric pressure in a glass flask with or without stirring, and a solid product is separated from the obtained mixed liquid by a method such as filtration or centrifugation.

[0090] The present titanosilicate-containing catalyst treated as described above may be washed with water or the like. Such washing may be performed by appropriately controlling an amount of the wash liquid, a pH of a washing filtrate, and the like while observing them as required. Further, the obtained product washed with water may be dried in the range of, for example, 0°C to 200°C by draught drying, drying under reduced pressure, vacuum-freeze drying, or the like until

no reduction in weight is observed.

[0091] The amount of the structure-directing agent to be used is in the range of, for example, 0.01 mol to 10 mol and preferably in the range of 0.1 mol to 5 mol, based on 1 mol of silicon atom contained in the present titanosilicate-containing catalyst to be fed.. They are also referred to as "the present titanosilicate-containing catalyst" in the present invention.

[0092] The temperature to be used in the above mixing operation is, for example, 0°C to 250°C, preferably 20°C to 200°C, and more preferably 50°C to 180°C.

[0093] The mixing time to be used in the above mixing operation is, for example, 1 hour to 720 hours, preferably 2 hours to 720 hours, more preferably in the range of 4 hours to 720 hours, and particularly preferably in the range of 8 hours to 720 hours.

[0094] The pressure to be used in the above mixing operation is not particularly limited, but it is in the range of, for example, 0 MPa to 10 MPa in terms of gauge pressure.

[0095] The titanosilicate-containing catalyst obtained by the above production method (that is, the present titanosilicate-containing catalyst) has a high olefin oxide production activity. Then, the use of a catalytic reaction with the present titanosilicate-containing catalyst for epoxidizing an olefin such as propylene with hydrogen peroxide makes it possible to produce an oxirane compound (hereinafter, sometimes also referred to as "first epoxidizing reaction").

[0096] In the case where an olefin which is one of raw materials to be used for the first epoxidizing reaction is propylene, examples of such

propylene may include one produced by, for example, pyrolysis, heavy oil catalytic cracking, or methanol catalytic reforming.

[0097] The propylene may be purified propylene or may be crude propylene obtained without undergoing a purifying step. Preferable propylene may include propylene with purity of, for example, 90% by volume or more, preferably 95% by volume or more.

[0098] Examples of impurities contained in the propylene include propane, cyclopropane, methyl acetylene, propanediene, butadiene, butanes, butenes, ethylene, ethane, methane and hydrogen.

[0099] Examples of a form of the propylene may include a gas form and a liquid form. Examples of the "liquid form" herein may include (i) a liquid form of propylene alone and (ii) a mixed liquid in which propylene is dissolved in, for example, an organic solvent or a mixed solvent of an organic solvent and water. Examples of the "gas form" herein may include (i) a gas form of propylene alone and (ii) a mixed gas of gaseous propylene and other gas component such as nitrogen gas or hydrogen gas.

[0100] While an amount of an olefin differs depending on the type thereof and reaction conditions, it may be in the range of, for example, 0.01 parts by weight or more and more preferably 0.1 parts by weight or more, based on 100 parts by weight of a mixture of an acetonitrile-containing solvent, the present titanasilicate-containing catalyst and raw materials existing in a reaction system.

[0101] While an amount of the present titanasilicate-containing catalyst differs depending on the type thereof and reaction conditions, it is in the range of, for example, 0.01 parts by weight to 20 parts by weight based

on 100 parts by weight of a mixture of an acetonitrile-containing solvent, the present titanosilicate-containing catalyst and raw materials existing in a reaction system. It is preferably in the range of 0.1 parts by weight to 10 parts by weight, and more preferably in the range of 0.5 parts by weight to 8 parts by weight.

[0102] The "acetonitrile-containing solvent" means a solvent containing acetonitrile, and the acetonitrile-containing solvent may also contain a solvent other than acetonitrile. Examples of the solvent other than acetonitrile may include an organic solvent other than acetonitrile, and water. The proportion of acetonitrile contained in the acetonitrile-containing solvent in terms of weight is, for example, preferably 50% or more, and more preferably 60% to 100%.

[0103] The reaction temperature for the first epoxidizing reaction is in the range of, for example, 0°C to 200°C, and preferably in the range of 40°C to 150°C. In addition, a reaction pressure (gauge pressure) is, for example, 0.1 MPa or more, preferably 1 MPa or more, more preferably 10 MPa or more, and still more preferably 20 MPa or more.

[0104] For the first epoxidizing reaction, an ammonium salt, an alkyl ammonium salt, and an alkylaryl ammonium salt may also exist in the reaction system.

[0105] A buffering agent can exist in the reaction system because there are tendencies of preventing catalyst activity from being decreased, further increasing catalyst activity and enhancing use efficiency of hydrogen peroxide. The "buffering agent" herein means a compound such as a salt giving a buffering action on a hydrogen ion concentration in a solution.

[0106] The amount of the buffering agent may be an amount equal to or less than a solubility of the buffering agent in the mixture of the acetonitrile-containing solvent, the catalyst and the present raw material existing in the reaction system. It is preferably in the range of, for example, 0.001 mmol to 100 mmol based on 1 kg of the mixture.

[0107] Examples of the buffering agent may include a buffering agent including (1) an anion selected from the group consisting of a sulfate ion, a hydrogen sulfate ion, a carbonate ion, a hydrogen carbonate ion, a phosphate ion, a hydrogen phosphate ion, a dihydrogen phosphate ion, a hydrogen pyrophosphate ion, a pyrophosphate ion, a halogen ion, a nitrate ion, a hydroxide ion and a C1-C10 carboxylate ion, and (2) a cation selected from the group consisting of ammonium, a C1-C20 alkyl ammonium, a C7-C20 alkylaryl ammonium, an alkali metal cation and an alkali earth metal cation.

[0108] Specific examples of the "carboxylate ion with 1 to 10 carbon atoms" may include an acetate ion, a formate ion, a propionate ion, a butyrate ion, a valerate ion, a caproate ion, a caprylate ion, a caprate ion and a benzoate ion. Specific examples of the "alkyl ammonium" may include tetramethylammonium, tetraethylammonium, tetra-n-propylammonium, tetra-n-butylammonium and cetyltrimethylammonium. Specific examples of the "cation selected from the group consisting of an alkali metal cation and an alkali earth metal cation" may include a lithium cation, a sodium cation, a potassium cation, a rubidium cation, a cesium cation, a magnesium cation, a calcium cation, a strontium cation and a barium cation.

[0109] Specific examples of a preferable buffering agent may include

ammonium salts of an inorganic acid, such as ammonium sulfate, ammonium hydrogen sulfate, ammonium carbonate, ammonium hydrogen carbonate, diammonium hydrogen phosphate, ammonium dihydrogen phosphate, ammonium phosphate, ammonium hydrogen pyrophosphate, ammonium pyrophosphate, ammonium chloride and ammonium nitrate, and ammonium salts of a carboxylic acid with 1 to 10 carbon atoms, such as ammonium benzoate and ammonium acetate. Examples of a preferable ammonium salt include ammonium benzoate, ammonium dihydrogen phosphate and diammonium hydrogen phosphate.

[0110] In the case of the first epoxidizing reaction, it is preferable to continuously perform the reaction. For example, the first epoxidizing reaction is allowed to progress by continuously feeding raw materials into an epoxidizing reaction chamber in which the acetonitrile-containing solvent and the present titanasilicate-containing catalyst are accommodated.

[0111] As hydrogen peroxide which is one of raw materials to be used for the first epoxidizing reaction, a commercial product (that is, hydrogen peroxide water) may be used.

[0112] While a concentration of hydrogen peroxide differs depending on the type thereof and reaction conditions, it may be in the range of 0.0001% by weight to 100% by weight and more preferably in the range of 0.001% by weight to 5% by weight, as a concentration of hydrogen peroxide in hydrogen peroxide water.

[0113] While an amount of hydrogen peroxide differs depending on the type thereof and reaction conditions, it is in the range of, for example,

1000 : 1 to 1 : 1000 as an amount of hydrogen peroxide based on the amount of the olefin as a raw material existing in the reaction system (mol ratio), for example.

[0114] Hydrogen peroxide which is one of raw materials to be used for the first epoxidizing reaction may be fed in a state of being dissolved in a solvent such as water or acetonitrile, described later. In the case where hydrogen peroxide in a state of being dissolved in a solvent other than acetonitrile is used, a reaction mass including the solvent will be obtained.

[0115] Examples of the solvent other than acetonitrile for dissolving hydrogen peroxide may include an alcohol solvent, a ketone solvent, a nitrile solvent, an ether solvent, aliphatic hydrocarbon, aromatic hydrocarbon, a halogenated hydrocarbon, an ester solvent or mixtures thereof.

[0116] Examples of the alcohol solvent may include aliphatic alcohols having 1 to 8 carbon atoms, such as methanol, ethanol, isopropanol and tert-butanol, and glycols having 2 to 8 carbon atoms, such as ethylene glycol and propylene glycol. Preferable examples include a monovalent alcohol having 1 to 4 carbon atoms. More preferable examples include tert-butanol.

[0117] Examples of the aliphatic hydrocarbon may include aliphatic hydrocarbons having 5 to 10 carbon atoms, such as hexane and heptane.

[0118] Examples of the aromatic hydrocarbon may include aromatic hydrocarbons having 6 to 15 carbon atoms, such as benzene, toluene and xylene.

[0119] Examples of the nitrile solvent may include alkyl nitriles having

2 to 4 carbon atoms, such as propionitrile, isobutyronitrile and butyronitrile; and benzonitrile.

[0120] Examples of the acetonitrile for dissolving hydrogen peroxide may include purified acetonitrile, and crude acetonitrile as a by-product in a step of producing acrylonitrile. Examples of impurities contained in the crude acetonitrile, other than acetonitrile, may include water, acetone, acrylonitrile, oxazole, allyl alcohol, propionitrile, hydrocyanic acid, ammonia, copper and iron. The content of copper and iron is preferably 1% by weight or less in a trace amount.

[0121] The purity of the acetonitrile may be, for example, 95% by weight or more, preferably 99% by weight or more, and more preferably 99.9% by weight or more.

[0122] Furthermore, an oxirane compound can be produced (hereinafter, also referred to as "second epoxidizing reaction") even if an olefin such as propylene, hydrogen and oxygen are allowed to react in the presence of a composite catalyst including a noble metal, such as palladium, supported on a titanosilicate-containing catalyst obtained by the above production method or a composite catalyst including a titanosilicate-containing catalyst obtained by the above production method and a noble metal, such as palladium, supported on a carrier component which is a substance different from the titanosilicate-containing catalyst (that is, the present titanosilicate-containing composite catalyst).

[0123] In the case where an olefin which is one of raw materials to be used for the second epoxidizing reaction is propylene, such propylene may have, for example, the same raw materials, purity and form as

those in the first epoxidizing reaction.

[0124] The amount of the olefin such as propylene may be in the same range as in the first epoxidizing reaction.

[0125] The amount of the present titanasilicate-containing composite catalyst may be in the same range as in the first epoxidizing reaction.

[0126] The reaction temperature for the second epoxidizing reaction may be in the same range as in the first epoxidizing reaction.

[0127] For the second epoxidizing reaction, an ammonium salt, an alkyl ammonium salt, or an alkylaryl ammonium salt may also exist in the reaction system, as in the first epoxidizing reaction. By using such additives, there are tendencies of further increasing catalyst activity and enhancing use efficiency of oxygen and hydrogen. Amounts and types of the additives are also the same as in the first epoxidizing reaction.

[0128] Also in the case of the second epoxidizing reaction, it is preferable to continuously perform the reaction.

[0129] The content of the noble metal contained in the present titanasilicate-containing composite catalyst may be, for example, 0.00001 parts by weight or more, preferably 0.0001 parts by weight or more, more preferably 0.001 parts by weight or more, further preferably in the range of 0.01% by weight to 20% by weight, and particularly preferably in the range of 0.1% by weight to 5% by weight, based on 1 part by weight of the present titanasilicate-containing composite catalyst.

[0130] In the case where the present titanasilicate-containing composite catalyst is a composite catalyst including the present titanasilicate-containing catalyst, and a noble metal such as palladium

supported on a carrier component which is a substance different from the titanosilicate-containing catalyst, examples of the "carrier component which is a substance different from the titanosilicate-containing catalyst (the present titanosilicate-containing catalyst)" to be herein used may include carbon, alumina, titanium dioxide (TiO_2), zirconium oxide, and mixtures as combinations thereof. Herein, (1) the present titanosilicate-containing catalyst and (2) the noble metal supported on the carrier component which is a substance different from the titanosilicate-containing catalyst may function as a composite catalyst while existing in the reaction system with being separated from each other, or may function as a composite catalyst while existing in the reaction system with being integrated to each other.

[0131] Examples of the noble metal such as palladium, to be used when generating "hydrogen peroxide" from "oxygen and hydrogen" in the second epoxidizing reaction may include noble metals such as palladium, platinum, ruthenium, rhodium, iridium, osmium and gold, or alloys and mixtures of these noble metals. Examples of a preferable noble metal may include palladium, platinum and gold. Examples of a more preferable noble metal include palladium.

[0132] Palladium or a palladium compound described later may be also used in a form of, for example, colloid (for example, see JP 2002-294301 A, Example 1).

[0133] In the case where the noble metal is a noble metal compound and a main component of the noble metal is palladium, a noble metal other than palladium, such as platinum, rhodium, iridium, osmium or gold, can be further added to and mixed with the noble metal compound.

Examples of a preferable noble metal other than palladium may include platinum and gold.

[0134] Examples of the palladium compound may include tetravalent palladium compounds such as sodium hexachloro palladate (IV) tetrahydrate and potassium hexachloro palladate (IV); and divalent palladium compounds such as palladium (II) chloride, palladium (II) bromide, palladium (II) acetate, palladium (II) acetylacacetate, dichlorobis(benzonitrile)palladium (II), dichlorobis(acetonitrile)palladium (II), dichloro(bis(diphenylphosphino)ethane)palladium (II), dichlorobis(triphenylphosphine)palladium (II), dichlorotetraamminepalladium (II), dibromotetraamminepalladium (II), dichloro(cycloocta-1,5-diene)palladium (II) and palladium trifluoroacetate (II).

[0135] The noble metal such as palladium to be used when generating "hydrogen peroxide" from "oxygen and hydrogen" in the second epoxidizing reaction is the noble metal supported on the present titanasilicate-containing catalyst or the noble metal supported on a carrier component which is a substance different from the titanasilicate-containing catalyst.

[0136] In the second epoxidizing reaction, examples of a method for preparing the present titanasilicate-containing composite catalyst with the noble metal such as palladium to be used when generating "hydrogen peroxide" from "oxygen and hydrogen", supported on the present titanasilicate-containing catalyst, or the present titanasilicate-containing composite catalyst with the noble metal

supported on a carrier component which is a substance different from the titanosilicate-containing catalyst may include a common method such as an impregnation method. The present titanosilicate-containing composite catalyst obtained by the common method such as an impregnation method may be subjected to a reduction treatment using reducing gas. Examples of such reduction treatment may include a reduction treatment method by injecting reducing gas to a tube filled with the solid present titanosilicate-containing composite catalyst. Examples of the "reducing gas" herein may include hydrogen, carbon monoxide, methane, ethane, propane, butane, ethylene, propylene, butene, butadiene, or a mixed gas of two or more selected therefrom. Preferable reducing gas includes hydrogen. Further examples of the reducing gas may include nitrogen, helium, argon, steam, or a mixed gas thereof.

[0137] When generating "hydrogen peroxide" from "oxygen and hydrogen" by a noble metal such as palladium in the second epoxidizing reaction, a partial pressure ratio of oxygen and hydrogen in a mixed gas of oxygen and hydrogen to be fed to a reactor, oxygen : hydrogen, may be in the range of, for example, 1 : 50 to 50 : 1. The partial pressure ratio, oxygen : hydrogen, is preferably in the range of 1 : 10 to 10 : 1. In the case where the partial pressure ratio, oxygen : hydrogen, is higher than 1 : 50 in terms of oxygen partial pressure, such a case is preferable because there is a tendency that the production of a by-product with a carbon-carbon double bond of propylene being reduced by hydrogen atoms is decreased to enhance selectivity of propylene oxide, and in the case where the partial pressure ratio, oxygen : hydrogen, is lower than

50 : 1 in terms of oxygen partial pressure, such a case is preferable because there is a tendency that the production rate of propylene oxide is enhanced.

[0138] It is also preferable to handle the mixed gas of oxygen and hydrogen under the coexistence of a diluent gas. Examples of the "diluent gas" may include nitrogen, argon, carbon dioxide, methane, ethane and propane. Preferable examples include nitrogen and propane. More preferable examples may include nitrogen.

[0139] In the case where oxygen, hydrogen, propylene and a diluent gas are mixed to be handled, a mixing ratio thereof, as an example of the case where the diluent gas is nitrogen gas, is preferably as follows: a total concentration of hydrogen and propylene is 4.9% by volume or less, a concentration of oxygen is 9% by volume or less, and the balance is nitrogen gas; or a total concentration of hydrogen and propylene is 50% by volume or more, a concentration of oxygen is 50% by volume or less, and the balance is nitrogen gas.

[0140] As oxygen, air may be also used besides oxygen gas. Examples of such oxygen gas may include an inexpensive oxygen gas produced by a pressure swing method and a high purity oxygen gas produced by cryogenic separation.

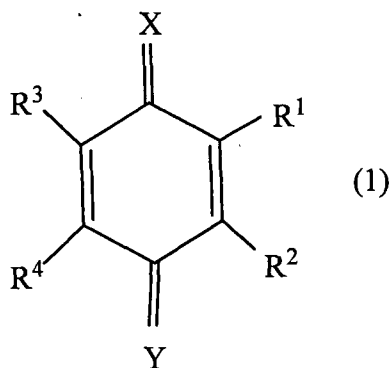
The amount of oxygen to be fed may be in the range of, for example, 0.005 to 10 mol and preferably in the range of 0.05 to 5 mol, based on 1 mol of propylene to be fed.

[0141] Examples of hydrogen may include one obtained by steam reforming hydrocarbon. The purity of hydrogen may be for example 80% by volume or more and preferably 90% by volume or more. The

amount of hydrogen to be fed may be in the range of, for example, 0.05 to 10 mol and preferably in the range of 0.05 to 5 mol, based on 1 mol of propylene to be fed.

[0142] When generating "hydrogen peroxide" from "oxygen and hydrogen" by a noble metal such as palladium in the second epoxidizing reaction, a quinoid compound preferably exists in the reaction system because there is a tendency of further increasing selectivity of an oxirane compound.

[0143] Examples of the quinoid compound may include a compound represented by formula (1):



wherein, R^1 , R^2 , R^3 and R^4 each independently represent a hydrogen atom, or R^1 and R^2 or R^3 and R^4 may be bonded to each other to form a benzene ring that may have a substituent or a naphthalene ring that may have a substituent, together with carbon atoms to which R^1 , R^2 , R^3 and R^4 each are bonded. X and Y each independently represent an oxygen atom or an NH group.

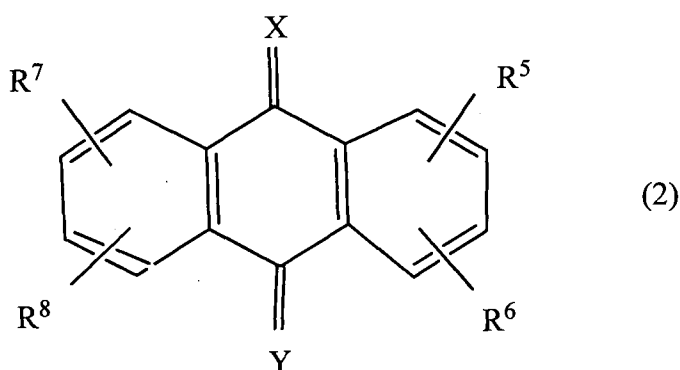
[0144] Examples of the compound represented by formula (1) may include:

1) a quinone compound (1A), wherein in formula (1), R^1 , R^2 , R^3 and R^4 are a hydrogen atom, and both X and Y are an oxygen atom;

2) a quinone-imine compound (1B), wherein in formula (1), R^1 , R^2 , R^3 and R^4 are a hydrogen atom, X is an oxygen atom, and Y is an NH group; and

3) a quinone-diimine compound (1C), wherein in formula (1), R^1 , R^2 , R^3 and R^4 are a hydrogen atom, and X and Y are an NH group.

[0145] Another examples of the compound represented by formula (1) may include an anthraquinone compound represented by formula (2):



wherein, X and Y are as defined in formula (1), R^5 , R^6 , R^7 and R^8 each independently represent a hydrogen atom, a hydroxyl group or an alkyl group (for example, an alkyl group having 1 to 5 carbon atoms, such as a methyl group, an ethyl group, a propyl group, a butyl group and a pentyl group).

[0146] In the compound represented by formula (1), X and Y may be preferably an oxygen atom.

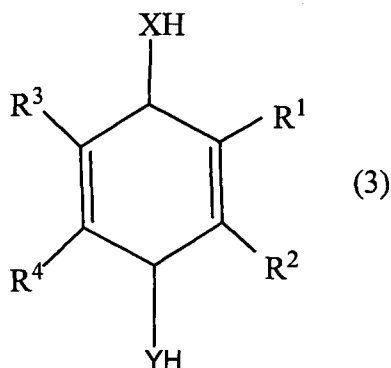
[0147] Examples of the compound represented by formula (1) may include quinone compounds such as benzoquinone and naphthoquinone; and anthraquinones; 2-alkylanthraquinone compounds such as 2-ethylanthraquinone, 2-t-butylanthraquinone, 2-amylanthraquinone, 2-methylanthraquinone, 2-butylanthraquinone, 2-t-amylanthraquinone, 2-isopropylanthraquinone, 2-s-butylanthraquinone and

2-s-amylnanthraquinone; polyalkylnanthraquinone compounds such as
1,3-diethylnanthraquinone, 2,3-dimethylnanthraquinone,
1,4-dimethylnanthraquinone and 2,7-dimethylnanthraquinone;
polyhydroxyanthraquinone compounds such as
5 2,6-dihydroxyanthraquinone; p-quinoid compounds such as
naphthoquinone and 1,4-phenanthraquinone; and o-quinoid compounds
such as 1,2-phenanthraquinone, 3,4-phenanthraquinone and
9,10-phenanthraquinone. Preferable examples include anthraquinone
and a 2-alkylnanthraquinone compound (in formula (2), X and Y
10 represent an oxygen atom, R⁵ represents an alkyl group, R⁶ represents
hydrogen, and R⁷ and R⁸ represent a hydrogen atom).

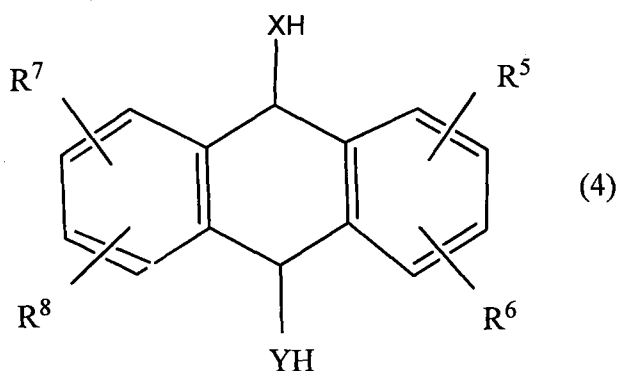
[0148] In the second epoxidizing reaction, an amount of such quinoid
compound to be used is in the range of, for example, 0.001 mmol to
500mmol and preferably in the range of 0.01 mmol to 50mmol, based
15 on 1 kg of a solvent.

[0149] The quinoid compound can also be prepared by oxidizing a
dihydro form of the quinoid compound using oxygen or the like in the
reaction system. For example, the quinoid compound may be
generated by adding a compound, where a quinoid compound such as
20 9,10-anthracenediol or hydroquinone is hydrogenated, to a liquid phase,
and oxidizing it with oxygen in the reaction system, and used.

[0150] Examples of the "dihydro form of the quinoid compound" may
include a compound represented by formula (3) which is a dihydro form
of the compound represented by formula (1) and a compound
25 represented by formula (4) which is a dihydro form of the compound
represented by formula (2).



wherein, R^1 , R^2 , R^3 , R^4 , X and Y represent the same meanings as in (1).



wherein, X, Y, R^5 , R^6 , R^7 and R^8 represent the same meanings as in (2).

5 Among the compound represented by formula (3) and the compound represented by formula (4), a preferable compound may include a dihydro form corresponding to a preferable quinoid compound. In addition, in the compound represented by formula (3) and the compound represented by formula (4), examples of preferable X and Y
10 may include an oxygen atom.

Examples

[0151] Hereinafter, the present invention will be described in more detail.

[0152] <Analytical Apparatuses to be used in Examples>

15 (Elemental Analysis Method)

Weights of Ti (titanium atoms) and Si (silicon atoms) contained

in the present titanosilicate-containing catalyst and the present titanosilicate-containing composite catalyst were determined by ICP emission spectrometry. That is, about 20 mg of a specimen was weighed in a platinum crucible, covered with sodium carbonate, and then subjected to a fusion operation by a gas burner. After the fusion, the content in the platinum crucible was dissolved in purified water and nitric acid by heating and then diluted to the constant volume with purified water, and thereafter the obtained measurement solution was analyzed in an ICP emission spectrometer (ICPS-8000, manufactured by Shimadzu Corporation) and each element was quantitatively determined.

[0153] N (nitrogen) of 10 to 20 mg of a sample weighed was measured by an oxygen circulating combustion/TCD detection system using a SUMIGRAPH NCH-22F model (manufactured by Sumika Chemical Analysis Service, Ltd.) (reaction temperature: 850°C, reduction temperature: 600°C). A column filled with porous polymer beads was used as a separation column, and acetanilide was used as a standard specimen.

[0154] (X-Ray Diffraction Method (XRD))

X-ray diffraction patterns of the granule-shaped present titanosilicate-containing catalyst and the granule-shaped present titanosilicate-containing composite catalyst were measured using the following apparatus under the following measurement conditions.

- Apparatus: RINT2500V manufactured by Rigaku Denki Co., Ltd.
- Radiation source: Cu K-alpha radiation
- Output: 40 kV-300 mA

- Scanning range: $2\theta = 0.75^\circ$ to 30°
- Scanning Rate: $1^\circ/\text{minute}$

[0155] (Ultraviolet and Visible Absorption Spectrum (UV-Vis))

5 The present titanosilicate-containing catalyst and the present titanosilicate-containing composite catalyst were pulverized by an agate mortar and further pelletized (7 mm ϕ) to prepare a sample for measurement. The ultraviolet and visible absorption spectrum of the obtained sample for measurement was measured using the following apparatus under the following conditions.

- 10
- Apparatus: diffuse reflection apparatus (Praying Mantis manufactured by HARRICK SCIENTIFIC PRODUCTS INC.)
 - Accessory: UV-VIS Spectrophotometer (V-7100, manufactured by JASCO)
 - Pressure: Atmospheric pressure
 - 15 • Measurement value: Reflectance
 - Data intake time: 0.1 second
 - Band width: 2 nm
 - Measurement wavelength: 200 to 900 nm
 - Slit height: Half open
 - 20 • Data intake interval: 1 nm
 - Baseline correction (reference): BaSO₄ pellet (7 mm ϕ)

[0156] (Particle Size Distribution Measurement of Titanosilicate Particles)

25 Particle size distribution of titanosilicate particles was measured using the following apparatus under the following conditions.

- Apparatus: LA-950V2 manufactured by HORIBA, Ltd.

- Pretreatment of specimen: particle dispersion treatment by internal ultrasonic wave irradiation (40 kHz) for 10 minutes
- Number of data intake (specimen, blank): 5000 times
- Refractive index: specimen (1.47), dispersion medium (water)(1.333)
- Calculation of d (0.90) value: on a volume basis

[0157] Example 1

Method for Producing Present Titanosilicate-Containing Catalyst (Catalyst A)(First Step: Preparation of Titanosilicate Powder)

In an autoclave, 899 g of piperidine (produced by Wako Pure Chemical Industries Ltd.), 2402 g of ion-exchange water, 46.4 g of TBOT (tetra-*n*-butyl orthotitanate, produced by Wako Pure Chemical Industries Ltd.), 565 g of boric acid (produced by Wako Pure Chemical Industries Ltd.) and 410 g of fumed silica (cab-o-sil M7D, produced by Cabot Corporation) were dissolved at 25°C with stirring to obtain a gel.

The obtained gel was further stirred for 1.5 hours, followed by sealing the autoclave. Then, a temperature of the gel was raised to 150°C over 8 hours while stirring the gel, and the gel was held at 150°C for 120 hours to thereby obtain a suspension. The obtained suspension was filtrated and then washed with water until a pH of the filtrate reached 10.3. The obtained solid content was dried at 50°C until no reduction in weight was observed, to obtain 524 g of a solid 1.

[0158] To 75 g of the solid 1 were added 3750 mL of 2M nitric acid and 9.5 g of TBOT (produced by Wako Pure Chemical Industries Ltd.), and then refluxed with heating for 20 hours. Then, the obtained solid product was filtrated and washed with water until a pH of the filtrate reached 5 or more, and subsequently the water-washed solid product

was dried in vacuum with heating at 150°C until no reduction in weight of the solid product was observed, to obtain 59 g of a white powder. This operation was repeated twice to obtain 118 g of a white powder in total (titanosilicate powder 1). It was confirmed that the X-ray diffraction pattern of the titanosilicate powder had peaks at 12.3 d/Å, 11.0 d/Å, 9.0 d/Å, 6.1 d/Å, 3.9 d/Å and 3.4 d/Å. It was further proved from the ultraviolet and visible absorption spectrum that the titanosilicate powder was a titanosilicate (Ti-MWW precursor).

[0159] Example 2

Method for Producing Present Titanosilicate-Containing Catalyst (Catalyst A)(Second Step: Pulverization of Titanosilicate Powder)

To 100 g of the titanosilicate powder 1 obtained in Example 1 was added 900 g of ion-exchange water and mixed well to obtain a slurry. Then, the obtained slurry was pretreated with an ultrasonic wave having an output of 1200 W for 5 minutes, and further treated with a nanomizer system (NM2-L200-D manufactured by yoshida kikai co., ltd.) to thereby obtain a slurry 1. The particle size distribution of the slurry 1 was measured, and as a result, it was confirmed that the d (0.90) value on a volume basis was 0.397 μm and was 1 μm or less.

[0160] Example 3

Method for Producing Present Titanosilicate-Containing Catalyst (Catalyst A) (Third Step: Production of formed article)

To 1000 g of the slurry 1 obtained in Example 2 was mixed 49.0 g of a binder with a content of SiO₂ of 20.4% (SNOWTEX N, produced by NISSAN CHEMICAL INDUSTRIES, LTD.), and spray-dried using a spray dryer (four-fluid nozzle system) to thereby produce a formed

article as granules (95 g: formed article 1). The median size $d(0.5)$ of the obtained formed article was 7.08 μm on a volume basis.

[0161] Example 4

Method for Producing Present Titanosilicate-Containing Catalyst
(Catalyst A) (Fourth Step: Heating and Structure-Directing Agent
Treatment)

Forty g of the formed article 1 obtained in the third step was heated at 530°C for 6 hours to obtain 36 g of a formed article 2. In an autoclave, 22.5 g of piperidine (produced by Wako Pure Chemical Industries Ltd.), 45 g of ion-exchange water and 7.5 g of the formed article 2 was dissolved at 25°C with stirring to obtain a gel. The gel was further stirred for 1.5 hours, followed by sealing the autoclave. Then, a temperature of the gel was raised to 160°C over 4 hours while stirring the gel, and the gel was held at 160°C for 16 hours to thereby obtain a suspension. The obtained suspension was filtrated and then washed with water until a pH of the filtrate reached 9.3. The obtained solid content was dried in vacuum with heating at 150°C until no reduction in weight was observed, to obtain 6.7 g of a white powder (catalyst A). It was confirmed that the X-ray diffraction pattern of the obtained catalyst A had peaks at 12.3 $d/\text{\AA}$, 11.1 $d/\text{\AA}$, 9.0 $d/\text{\AA}$, 6.1 $d/\text{\AA}$, 3.9 $d/\text{\AA}$ and 3.4 $d/\text{\AA}$. It was further proved from the ultraviolet and visible absorption spectrum that the catalyst A was a titanosilicate (Ti-MWW precursor). The titanium content by elemental analysis was 1.71% by weight. The median size $d(0.5)$ of the obtained formed article was 8.57 μm on a volume basis.

[0162] Example 5

Method for Producing Present Titanosilicate-Containing Catalyst
(catalyst B) (First Step: Preparation of Titanosilicate Powder)

In an autoclave, 265.2 g of piperidine (produced by Wako Pure Chemical Industries Ltd.), 666.9 g of ion-exchange water, 13.3 g of
5 TBOT (tetra-n-butyl orthotitanate, produced by Wako Pure Chemical Industries Ltd.), 156.6 g of boric acid (produced by Wako Pure Chemical Industries Ltd.), 146.2 g of ammonium fluoride (produced by Wako Pure Chemical Industries Ltd.) and 117.0 g of fumed silica (cab-o-sil M7D, produced by Cabot Corporation) were dissolved at
10 25°C with stirring to obtain a gel. The obtained gel was further stirred for 1.5 hours, followed by sealing the autoclave. Then, a temperature of the gel was raised to 165°C over 8 hours while stirring the gel, and the gel was held at 165°C for 168 hours to thereby obtain a suspension. The obtained suspension was filtrated and then washed with
15 ion-exchanged water until a pH of the filtrate reached 8.3. The obtained solid content was dried at 50°C until no reduction in weight was observed, to obtain 135.3 g of a solid 2.

[0163] To 15 g of the solid 2 were added 750 mL of 2M nitric acid and 1.9 g of TBOT (produced by Wako Pure Chemical Industries Ltd.), and
20 then refluxed with heating for 8 hours. Then, the obtained solid product was filtrated and washed with water until a pH of the filtrate reached 5 or more, and subsequently the water-washed solid product was dried in vacuum with being heated at 150°C until no reduction in weight of the solid product was observed, to obtain 11.5 g of a white
25 powder. This operation was repeated four times to obtain 46 g of a white powder in total (titanosilicate powder 2). It was confirmed that

the X-ray diffraction pattern of the titanosilicate powder had peaks at 12.3 d/Å, 11.1 d/Å, 8.9 d/Å, 6.2 d/Å, 3.9 d/Å and 3.4 d/Å. It was further proved from the ultraviolet and visible absorption spectrum that the titanosilicate powder was a titanosilicate (Ti-MWW precursor).

5 [0164] Example 6

Method for Producing Present Titanosilicate-Containing Catalyst (catalyst B) (Second Step: Pulverization of Titanosilicate Powder)

To 41.6 g of the titanosilicate powder 2 obtained in Example 5 was added 374.5 g of ion-exchange water and mixed well to obtain a slurry. Then, the obtained slurry was pretreated with an ultrasonic wave having an output of 1200 W for 5 minutes, and further treated with a nanomizer system (NM2-L200-D manufactured by yoshida kikai co., ltd.) to thereby obtain a slurry 2. The particle size distribution of the slurry 2 was measured, and as a result, it was confirmed that the d (0.90) value on a volume basis was 0.340 μm and was 1 μm or less.

15 [0165] Example 7

Method for Producing Present Titanosilicate-Containing Catalyst (catalyst B) (Third Step: Production of formed article)

To 416.1 g of the slurry 2 obtained in Example 6 was mixed 20.4 g of a binder with a content of SiO₂ of 20.4% (SNOWTEX N, produced by NISSAN CHEMICAL INDUSTRIES, LTD.), and spray-dried using a spray dryer (four-fluid nozzle system) to thereby produce a formed article as granules (44 g: formed article 2). The median size d (0.5) of the obtained formed article was 4.95 μm on a volume basis.

25 [0166] Example 8

Method for Producing Present Titanosilicate-Containing Catalyst
(catalyst B) (Fourth Step: Heating and Structure-Directing Agent
Treatment)

Forty g of the formed article 2 obtained in the third step was
heated at 530°C for 6 hours to obtain 36 g of a formed article 2. In an
autoclave, 22.5 g of piperidine (produced by Wako Pure Chemical
Industries Ltd.), 45 g of ion-exchange water and 7.5 g of the formed
article 2 was dissolved at 25°C with stirring to obtain a gel. The gel
was further stirred for 1.5 hours, followed by sealing the autoclave.
Then, a temperature of the gel was raised to 160°C over 4 hours while
stirring the gel, and the gel was held at 160°C for 16 hours to thereby
obtain a suspension. The obtained suspension was filtrated and then
washed with water until a pH of the filtrate reached 9.3. The obtained
solid content was dried in vacuum with heating at 150°C until no
reduction in weight was observed, to obtain 6.7 g of a white powder
(catalyst B). It was confirmed that the X-ray diffraction pattern of the
obtained catalyst B had peaks at 12.3 d/Å, 11.1 d/Å, 8.9 d/Å, 6.2 d/Å,
3.9 d/Å and 3.4 d/Å. It was further proved from the ultraviolet and
visible absorption spectrum that the catalyst B was a titanosilicate
(Ti-MWW precursor). The titanium content by elemental analysis was
1.78% by weight. The median size d (0.5) of the obtained formed
article was 4.85 µm on a volume basis.

[0167] Comparative Example 1

Method for Producing Titanosilicate-Containing Catalyst (catalyst C)

The white solid obtained in Example 1 was directly subjected to
the structure-directing agent treatment in Example 4 to obtain a catalyst

powder (catalyst C). It was confirmed that the X-ray diffraction pattern of the obtained catalyst C had peaks at 12.3 d/Å, 11.0 d/Å, 9.0 d/Å, 6.1 d/Å, 3.9 d/Å and 3.4 d/Å. It was further proved from the ultraviolet and visible absorption spectrum that the catalyst C was a
5 titanosilicate (Ti-MWW precursor). The titanium content by elemental analysis was 2.08% by weight.

[0168] Example 9

Production Example 1 of Propylene Oxide

A mixture of 0.1 g of the catalyst A, and 100 g of a solution
10 containing 0.1% by weight of hydrogen peroxide in water/acetonitrile (weight ratio = 1/4) was stirred under room temperature (about 20°C) for 1 hour. The obtained mixture was filtrated. The obtained cake was washed with 500 mL of water to thereby obtain a titanosilicate treated with hydrogen peroxide.

15 A solution containing 30% by weight of hydrogen peroxide in water (produced by Wako Pure Chemical Industries Ltd.), acetonitrile (produced by Nacalai Tesque Inc.) and ion-exchange water were mixed to thereby prepare a solution containing 0.5% by weight of hydrogen peroxide in a mixed solvent of acetonitrile/water (acetonitrile/water =
20 4/1 (weight ratio)). A 100 mL-stainless autoclave was filled with 60 g of the prepared solution and 0.010 g of the catalyst A. Then, the autoclave was transferred on an ice bath, and filled with 1.2 g of propylene. The pressure inside the autoclave was increased to 2 MPa (gauge pressure) with argon. The temperature thereof was raised to
25 60°C over 15 minutes while the mixed liquid in the autoclave being stirred, and the mixed liquid was stirred at 60°C for 1 hour. Then, the

stirring was stopped, and the autoclave was cooled with ice.

After cooling with ice, the obtained mixed liquid was analyzed by gas chromatography, and as a result, the propylene oxide production activity per unit weight of titanasilicate was $0.632 \text{ mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$.

5 [0169] Example 10

Production Example 2 of Propylene Oxide

The same operation as in Example 9 was performed except that the catalyst B obtained in Example 8 was used in place of the catalyst A. As a result, the propylene oxide production activity per unit weight of
10 titanasilicate was $1.646 \text{ mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$.

[0170] Comparative Example 2

Comparative Production Example 1 of Propylene Oxide

The same operation as in Example 9 was performed except that the catalyst C obtained in Comparative Example 1 was used in place of
15 the catalyst A. As a result, the propylene oxide production activity per unit weight of titanasilicate was $0.600 \text{ mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$.

[0171] As described above, in the epoxidizing reaction of propylene using hydrogen peroxide (that is, first epoxidizing reaction), the present titanasilicate-containing catalyst has a high production activity of an
20 olefin oxide.

[0172] Example 11

In order to produce the present titanasilicate-containing composite catalyst, palladium is added to the spray-dried present titanasilicate-containing catalyst.

25 [0173] Into a 1-L pear-shaped flask are added 6 g of the present titanasilicate-containing catalyst and 300 mL of water containing 0.18

mmol of Pd-tetraammine chloride, and the mixture is stirred at 20°C in air. After the mixture is stirred for 8 hours, the moisture thereof is removed using a rotary evaporator, and the mixture is dried in vacuum at 80°C for 6 hours and also fired under a nitrogen stream at 300°C for 6 hours to obtain a titanosilicate-containing composite catalyst. The theoretical amount of palladium is 0.317% by weight.

[0174] The present titanosilicate-containing composite catalyst thus obtained has a high production activity of an olefin oxide.

[0175] The present titanosilicate-containing composite catalyst produced as described above is used for catalyzing the production of propylene oxide in accordance with a known method.

[0176] Using an autoclave with a volume of 0.3 L as a reactor, to the reactor is charged 3.33 g of the titanosilicate-containing composite catalyst and then sealed. To the reactor, gas of oxygen/hydrogen/nitrogen in a volume ratio of 3.3/3.6/93.1, a solution containing 0.7 mmol/kg of anthraquinone and 3.0 mmol/kg of diammonium hydrogen phosphate in water/acetonitrile (weight ratio = 30/70), and propylene are fed at a rate of 281 L/hours, 90 g/hours, and 36 g/hours, respectively, and a continuous reaction is performed in which a solution containing a reaction product (liquid phase) and a product gas (gas phase) are withdrawn from the reaction mixture from the reactor through a filter (residence hours: 60 minutes). During this time, the temperature of the content in the reactor is 50°C and the pressure inside the reactor was 4.0 MPa (gauge pressure) to allow propylene oxide to generate.

Industrial Applicability

[0177] The present invention makes it possible to a novel production method required for providing a titanosilicate-containing catalyst with a high production activity of an olefin oxide.

CLAIMS

1. A method for producing a titanosilicate-containing catalyst, comprising:

5 a pulverizing step of pulverizing titanosilicate particles to obtain a pulverized product by a wet process until a $d(0.90)$ value of the particles on a volume basis is $1\ \mu\text{m}$ or less; and

a forming step of adding a binder to the pulverized product and forming the obtained mixture into granules,

10 wherein the particles have an X-ray diffraction pattern with peaks at the positions indicated by the lattice spacing($d/\text{\AA}$) of 12.4 ± 0.8 , 10.8 ± 0.5 , 9.0 ± 0.3 , 6.0 ± 0.3 , 3.9 ± 0.3 and 3.4 ± 0.1 .

2. The method according to claim 1, wherein the pulverized product is an aqueous suspension of the titanosilicate particles with a $d(0.90)$ value on a volume basis of $1\ \mu\text{m}$ or less.

15 3. The method according to claim 1 or 2, wherein the pulverizing step is a step comprising sending an aqueous suspension containing the titanosilicate particles into a generator made of a hard material with a fine passage formed therein at a high rate using a high-pressure pump to pulverize the titanosilicate particles by a shear force generated when the suspension passes through the generator.

20 4. The method according to any one of claims 1 to 3, wherein the forming step is a step of forming the mixture into granules using a spray dry method.

25 5. A method for producing an oxirane compound, comprising a step of epoxidizing an olefin with hydrogen peroxide by a catalytic reaction using a titanosilicate-containing catalyst obtained by the

method according to any one of claims 1 to 4.

6. The method according to claim 5, wherein the olefin is propylene.

7. A method for producing an oxirane compound, comprising:

5 a step of reacting an olefin, hydrogen and oxygen in the presence of a composite catalyst comprising a noble metal supported on a titanosilicate-containing catalyst obtained by the method according to any one of claims 1 to 4, or a composite catalyst comprising a titanosilicate-containing catalyst obtained by the method according to
10 any one of claims 1 to 4 and a noble metal supported on a carrier component which is a substance different from the titanosilicate-containing catalyst.

8. The method according to claim 7, wherein the olefin is propylene.

15 9. The method according to claim 7 or 8, wherein the noble metal is palladium.

INTERNATIONAL SEARCH REPORT

International application No

PCT/JP2012/061801

A. CLASSIFICATION OF SUBJECT MATTER

INV. B01J37/06 C07D301/12 C01B37/00
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C07D C01B B01J

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

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

EPO-Internal, WPI Data, CHEM ABS Data, BEILSTEIN Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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A	EP 1 731 515 A1 (SUMITOMO CHEMICAL CO [JP]) 13 December 2006 (2006-12-13) page 4; example 1 page 5, paragraph 39; example 2 -----	1-9
A	WO 2010/067855 A1 (SUMITOMO CHEMICAL CO [JP]; KAWABATA TOMONORI [JP]; YAKO MAKOTO [JP]) 17 June 2010 (2010-06-17) page 30; example 5 -----	1-9
A	WO 2009/128356 A1 (SUMITOMO CHEMICAL CO [JP]; KAWABATA TOMONORI [JP]; ABEKAWA HIROAKI [JP]) 22 October 2009 (2009-10-22) page 18 - page 19 -----	1-9



Further documents are listed in the continuation of Box C.



See patent family annex.

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Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Jeanjean, Fabien

INTERNATIONAL SEARCH REPORT

Information on patent family members

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