

Description

TITLE OF THE INVENTION:

CATALYST FOR PRODUCING METHACRYLIC ACID, METHOD FOR
5 PRODUCING SAME, AND METHOD FOR PRODUCING METHACRYLIC ACID AND
METHACRYLIC ACID ESTER

TECHNICAL FIELD

[0001]

10 The present invention relates to a catalyst for producing methacrylic acid and a method for
producing the same, and a method for producing methacrylic acid and methacrylic acid ester.

BACKGROUND ART

[0002]

15 A metal oxide catalyst has been put into practical use in an oxidation reaction of an
oxygen-containing organic substance such as a hydrocarbon or a carbonyl compound or an
alcohol, an ammoxidation, an oxidation dehydration, a hydrogenation of CO or an unsaturated
compound, a dehydrogenation catalyst, a solid acid/base catalyst, and the like (Non-Patent
Document 1).

20 [0003]

As the metal oxide catalyst, an oxide catalyst containing molybdenum and vanadium
(hereinafter, also referred to as "Mo-V based oxide catalyst") is known. Mo-V based oxide
catalyst has been industrialized as a catalyst used for the selective oxidation of lower alkanes
typified by ethane and propane and ammoxidation, and a catalyst for selectively oxidizing
25 acrolein to produce acrylic acid and the like. Since Mo-V based oxide catalyst has excellent heat
resistance as compared with the molybdenum-containing heteropolyacid-based catalyst, it is
expected that the catalyst lifetime is superior.

[0004]

30 Examples of applying Mo-V based oxide catalyst to selective oxidation of unsaturated
aldehydes include: when Mo-V based oxide catalyst was applied to the selective oxidation of
acrolein and methacrolein, it exhibited "acrolein conversion of 100%, acrylic acid selectivity of
97%," "methacrolein conversion of 57%, and methacrylic acid selectivity of 19%," respectively
(Non-Patent Document 2). When Mo-V based oxide catalyst containing tungsten was applied to
the selective oxidation of acrolein and methacrolein, it exhibited "acrolein conversion of 95%,

acrylic acid selectivity of 90%," "methacrolein conversion of 40%, and methacrylic acid selectivity of 35%," respectively (Non-Patent Document 3). Thus, Mo-V based oxide was suitable for acrolein selective oxidation, whereas it was unsuitable for methacrolein selective oxidation.

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PRIOR-ART DOCUMENT

NON-PATENT DOCUMENT

[0005]

[Non-Patent Document 1] Yoshihiko Morooka, Catalyst, 1984, Vol. 26, No. 2, p.76

10 [Non-Patent Document 2] Makoto Misono, Applied Catalysis, 1990, Vol. 64, p.1-30

[Non-Patent Document 3] A. Drocher, D. Ohlig, S. Knoche, N. Gora, M. Heid, N. Menning, T. Petzold, H. Vogel, Topics in Catalysis, 2016, Vol. 59, p.1518-1532

SUMMARY OF THE INVENTION

15 TECHNICAL PROBLEMS

[0006]

As described above, Mo-V based oxide catalyst has excellent heat resistance compared with the molybdenum-containing heteropolyacid-based catalyst, while the methacrylic acid yield is insufficient.

20 [0007]

It is an object of the present invention to provide a molybdenum-containing oxide catalyst for producing methacrylic acid in a higher yield than in the prior art and a method for producing the same, and a method for producing methacrylic acid using the catalyst, and a method for producing methacrylic acid ester.

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MEANS FOR SOLVING THE PROBLEMS

[0008]

In view of the above problems, the present inventors have intensively studied the molybdenum-containing oxide catalyst which can be suitably used for oxidation of methacrolein, and as a result, have found that methacrylic acid can be produced in a yield higher than that of a conventional one by using a catalyst containing a metal oxide including a specific cyclic structure, thereby completing the present invention.

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That is, the present invention is [1]-[40] and [1']-[21'] below.

[0009]

[1] A catalyst used in producing methacrylic acid by oxidation of methacrolein, wherein the catalyst for producing methacrylic acid is characterized in that the catalyst comprises a metal oxide containing molybdenum, and the metal oxide has a cyclic structure satisfying the following conditions (a) and (b).

5 (a) The cyclic structure satisfying the following formula (I).

$$(\text{sum of number of moles of Mo, V, and X}) : (\text{number of moles of O}) = 7:35 \quad (\text{I})$$

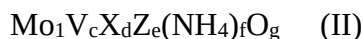
(In the formula (I), Mo, V, and O represent molybdenum, vanadium, and oxygen, respectively. X represents at least one element selected from the group consisting of niobium, tantalum, tungsten, titanium, aluminum, zirconium, chromium, manganese, iron, copper, cobalt, rhodium,
10 nickel, palladium, platinum, phosphorus, arsenic, antimony, tellurium, bismuth, boron, indium, zinc, magnesium, and cerium.)

(b) The cyclic structure in which each of the seven metal-oxygen octahedrons (octahedral structures) is bonded by sharing oxygen at adjacent vertices.

[0010]

15 [2] The catalyst for producing methacrylic acid according to [1], wherein the metal oxide satisfies the following condition (c).

(c) The metal oxide having a composition represented by the following formula (II).



(In the formula (II), Mo, V, NH_4 , and O represent molybdenum, vanadium, an ammonium species, and oxygen, respectively. X represents at least one element selected from the group consisting of niobium, tantalum, tungsten, titanium, aluminum, zirconium, chromium, manganese, iron, copper, cobalt, rhodium, nickel, palladium, platinum, phosphorus, arsenic, antimony, tellurium, bismuth, boron, indium, zinc, magnesium, and cerium. Z represents at least one element selected from the group consisting of lithium, sodium, potassium, rubidium, cesium,
20 and calcium. c to g represent the molar ratio of each component, $0 \leq c < 0.5$, $0 \leq d < 0.5$, $0 \leq e \leq 0.1$, and $0 \leq f \leq 0.1$, and g is the molar ratio of oxygen required to satisfy the valence of each component.)

[0011]

30 [3] The catalyst for producing methacrylic acid according to [2], wherein $0 < c < 0.5$ in the formula (II).

[0012]

[4] The catalyst for producing methacrylic acid according to any one of [1] to [3], wherein the metal oxide satisfies the following condition (d).

(d) The metal oxide satisfying the following formula (III), where M1 is the mass of the

metal oxide and M2 is the mass of inert ingredients contained in the metal oxide.

$$0 \leq M2/M1 < 0.05 \quad (\text{III})$$

[0013]

[5] The catalyst for producing methacrylic acid according to any one of [1] to [4], wherein the metal oxide satisfies the following condition (e).

(e) The metal oxide having absorption peaks at $1557 \pm 10\text{cm}^{-1}$, $1456 \pm 10\text{cm}^{-1}$, and $1374 \pm 10\text{cm}^{-1}$ in a difference spectrum between an infrared absorption spectrum obtained by FT-IR measurement of the metal oxide and an infrared absorption spectrum obtained by FT-IR measurement after holding the metal oxide under a methacrolein atmosphere of 2.0% by volume or more for 60 minutes.

[0014]

[6] The catalyst for producing methacrylic acid according to any one of [1] to [5], wherein the metal oxide satisfies the following condition (f).

(f) The metal oxide having a BET-specific surface area S of 1.5 to $60\text{ m}^2/\text{g}$, calculated by nitrogen-adsorption.

[0015]

[7] The catalyst for producing methacrylic acid according to any one of [1] to [6], wherein the metal oxide satisfies the following condition (g).

(g) The metal oxide showing diffraction peaks at $2\theta = 22.1^\circ \pm 0.3^\circ$ and $45.2^\circ \pm 0.3^\circ$ in X-ray diffraction pattern (using Cu-K α ray).

[0016]

[8] The catalyst for producing methacrylic acid according to [7], wherein the metal oxide satisfies the following condition (g1).

(g1) The metal oxide showing diffraction peaks only at $2\theta = 22.1^\circ \pm 0.3^\circ$ and $45.2^\circ \pm 0.3^\circ$ in X-ray diffraction pattern (using Cu-K α ray).

[0017]

[9] The catalyst for producing methacrylic acid according to [7], further showing diffraction peaks at $2\theta = 6.6^\circ \pm 0.3^\circ$, $7.9^\circ \pm 0.3^\circ$, $9.0^\circ \pm 0.3^\circ$, $26.4^\circ \pm 0.3^\circ$, $26.9^\circ \pm 0.3^\circ$, $27.2^\circ \pm 0.3^\circ$, and $27.4^\circ \pm 0.3^\circ$ under the condition (g).

[0018]

[10] The catalyst for producing methacrylic acid according to [7], further showing diffraction peaks at $2\theta = 4.7^\circ \pm 0.3^\circ$, $8.3^\circ \pm 0.3^\circ$, $25.3^\circ \pm 0.3^\circ$, $25.7^\circ \pm 0.3^\circ$, $27.0^\circ \pm 0.3^\circ$, $27.9^\circ \pm 0.3^\circ$, and $28.3^\circ \pm 0.3^\circ$ under the condition (g).

[0019]

[11] A method for producing the catalyst for producing methacrylic acid according to any one of [1] to [10], wherein the method for producing the catalyst for producing methacrylic acid comprising:

- (1) A step of heating an aqueous solution or slurry containing at least molybdenum at 80 to 300 °C for 3 to 200 hours to produce a solid content,
- (2) A step of calcining the solid content to obtain the metal oxide.

[0020]

[12] A method for producing the catalyst for producing methacrylic acid according to [9] or [10], wherein the method for producing the catalyst for producing methacrylic acid comprising:

- (1) A step of heating an aqueous solution or slurry containing at least molybdenum at 80 to 300 °C for 3 to 200 hours to produce a solid content,
 - (1b) A step of dispersing the solid content in an aqueous oxalic acid solution, hydrochloric acid, ethylene glycol, or hydrogen peroxide solution to obtain the solid content,
 - (2b) A step of calcining the solid content obtained in (1b) to obtain the metal oxide,
- and wherein the solid content is dispersed in an aqueous oxalic acid solution, hydrochloric acid, ethylene glycol, or hydrogen peroxide solution.

[0021]

[13] The method for producing a catalyst for producing methacrylic acid according to [11] or [12], wherein the solid content satisfies the following conditions (h) and (i).

- (h) The solid content having an average length of crystals of 2 to 50 μm observed by an electron microscope.
- (i) The solid content having an average aspect ratio of crystals of 2 to 30 observed by an electron microscope.

(Note that average aspect ratio = (average length of crystals)/(average diameter of crystals))

[0022]

[14] A method for producing methacrylic acid, comprising: producing methacrylic acid by oxidation of methacrolein using the catalyst for producing methacrylic acid according to any one of [1] to [10].

[0023]

[15] A method for producing methacrylic acid, comprising: producing the catalyst for producing methacrylic acid by the method according to any one of [11] to [13], and producing methacrylic acid by oxidation of methacrolein using the catalyst for producing methacrylic acid.

[0024]

[16] The method for producing methacrylic acid according to [14] or [15], wherein a gas having a composition represented by the following formula (IV) is supplied as a raw material gas.



(In the formula (IV), A represents nitrogen or helium. k to n represent the molar ratio of each gas, and when $k + l + m + n = 100$, $0.5 < k < 8.0$, $2.0 < l < 20.0$, and $0 \leq m < 45$.)

[0025]

[17] The method for producing methacrylic acid according to any one of [14] to [16], wherein the reaction temperature is 180 to 500 °C, and a raw material gas containing methacrolein is supplied so as to satisfy the following formula (V).

$$15 < W/F < 550 \quad (\text{V})$$

(In the formula (V), W represents the mass (g) of the metal oxide charged in a reactor, and F represents the feed amount (mol/h) of methacrolein per unit time.)

[0026]

[18] The method for producing methacrylic acid according to any one of [14] to [17], wherein the reaction temperature is 180 to 500 °C, and a raw material gas containing methacrolein is supplied so as to satisfy the following formula (VI).

$$0.00002 < F/(S \times W) < 0.008 \quad (\text{VI})$$

(In the formula (VI), S represents the BET-specific surface area (m²/g) of the metal oxide calculated by nitrogen-adsorption, W represents the mass (g) of the metal oxide charged in a reactor, and F represents the feed amount (mol/h) of methacrolein per unit time.)

[0027]

[19] A method for producing methacrylic acid ester, comprising: esterifying methacrylic acid produced by the method according to any one of [14] to [18].

[0028]

[20] A method for producing methacrylic acid ester, comprising: producing methacrylic acid by the method according to any one of [14] to [18], and esterifying the methacrylic acid.

[0029]

[21] A catalyst used in producing methacrylic acid by oxidation of methacrolein, wherein the catalyst for producing methacrylic acid comprises a metal oxide satisfying the following conditions (b') and (c).

(b') The metal oxide including a cyclic structure in which each of the seven metal-oxygen octahedrons (octahedral structures) is bonded.

(c) The metal oxide having a composition represented by the following formula (II).



(In the formula (II), Mo, V, NH₄, and O represent molybdenum, vanadium, an ammonium species, and oxygen, respectively. X represents at least one element selected from the group consisting of niobium, tantalum, tungsten, titanium, aluminum, zirconium, chromium, manganese, iron, copper, cobalt, rhodium, nickel, palladium, platinum, phosphorus, arsenic, antimony, tellurium, bismuth, boron, indium, zinc, magnesium, and cerium. Z represents at least one element selected from the group consisting of lithium, sodium, potassium, rubidium, cesium, and calcium. c to g represent the molar ratio of each component, $0 \leq c < 0.5$, $0 \leq d < 0.5$, $0 \leq e \leq 0.1$, and $0 \leq f \leq 0.1$, and g is the molar ratio of oxygen required to satisfy the valence of each component.)

10 [0030]

[22] The catalyst for producing methacrylic acid according to [21], wherein $0 < c < 0.5$ in the formula (II).

[0031]

15 [23] The catalyst for producing methacrylic acid according to [21] or [22], wherein the metal oxide satisfies the following condition (d).

(d) The metal oxide satisfying the following formula (III), where M1 is the mass of the metal oxide and M2 is the mass of inert ingredients contained in the metal oxide.

$$0 \leq M2/M1 < 0.05 \quad (\text{III})$$

[0032]

20 [24] The catalyst for producing methacrylic acid according to any one of [21] to [23], wherein the metal oxide satisfies the following condition (e).

(e) The metal oxide having absorption peaks at $1557 \pm 10\text{cm}^{-1}$, $1456 \pm 10\text{cm}^{-1}$, and $1374 \pm 10\text{cm}^{-1}$ in a difference spectrum between an infrared absorption spectrum obtained by FT-IR measurement of the metal oxide and an infrared absorption spectrum obtained by FT-IR measurement after holding the metal oxide under a methacrolein atmosphere of 2.0% by volume or more for 60 minutes.

[0033]

[25] The catalyst for producing methacrylic acid according to any one of [21] to [24], wherein the metal oxide satisfies the following condition (f).

30 (f) The metal oxide having a BET-specific surface area S of 1.5 to 60 m²/g, calculated by nitrogen-adsorption.

[0034]

[26] The catalyst for producing methacrylic acid according to any one of [21] to [25], wherein the metal oxide satisfies the following condition (g).

(g) The metal oxide showing diffraction peaks at $2\theta = 22.1^\circ \pm 0.3^\circ$ and $45.2^\circ \pm 0.3^\circ$ in X-ray diffraction pattern (using Cu-K α ray).

[0035]

[27] The catalyst for producing methacrylic acid according to [26], wherein the metal oxide satisfies the following condition (g1).

(g1) The metal oxide showing diffraction peaks only at $2\theta = 22.1^\circ \pm 0.3^\circ$ and $45.2^\circ \pm 0.3^\circ$ in X-ray diffraction pattern (using Cu-K α ray).

[0036]

[28] The catalyst for producing methacrylic acid according to [26], further showing diffraction peaks at $2\theta = 6.6^\circ \pm 0.3^\circ$, $7.9^\circ \pm 0.3^\circ$, $9.0^\circ \pm 0.3^\circ$, $26.4^\circ \pm 0.3^\circ$, $26.9^\circ \pm 0.3^\circ$, $27.2^\circ \pm 0.3^\circ$, and $27.4^\circ \pm 0.3^\circ$ under the condition (g).

[0037]

[29] The catalyst for producing methacrylic acid according to [26], further showing diffraction peaks at $2\theta = 4.7^\circ \pm 0.3^\circ$, $8.3^\circ \pm 0.3^\circ$, $25.3^\circ \pm 0.3^\circ$, $25.7^\circ \pm 0.3^\circ$, $27.0^\circ \pm 0.3^\circ$, $27.9^\circ \pm 0.3^\circ$, and $28.3^\circ \pm 0.3^\circ$ under the condition (g).

[0038]

[30] A catalyst used in producing methacrylic acid by oxidation of methacrolein, wherein the catalyst for producing methacrylic acid comprises a metal oxide satisfying the following conditions (c) and (g1).

(c) The metal oxide having a composition represented by the following formula (II).



(In the formula (II), Mo, V, NH₄, and O represent molybdenum, vanadium, an ammonium species, and oxygen, respectively. X represents at least one element selected from the group consisting of niobium, tantalum, tungsten, titanium, aluminum, zirconium, chromium, manganese, iron, copper, cobalt, rhodium, nickel, palladium, platinum, phosphorus, arsenic, antimony, tellurium, bismuth, boron, indium, zinc, magnesium, and cerium. Z represents at least one element selected from the group consisting of lithium, sodium, potassium, rubidium, cesium, and calcium. c to g represent the molar ratio of each component, $0 \leq c < 0.5$, $0 \leq d < 0.5$, $0 \leq e \leq 0.1$, and $0 \leq f \leq 0.1$, and g is the molar ratio of oxygen required to satisfy the valence of each component.)

(g1) The metal oxide showing diffraction peaks only at $2\theta = 22.1^\circ \pm 0.3^\circ$ and $45.2^\circ \pm 0.3^\circ$ in X-ray diffraction pattern (using Cu-K α ray).

[0039]

[31] A method for producing the catalyst for producing methacrylic acid according to any one of

[21] to [30], wherein the method for producing the catalyst for producing methacrylic acid comprising:

(1) A step of heating an aqueous solution or slurry containing at least molybdenum at 80 to 300 °C for 3 to 200 hours to produce a solid content,

5 (2) A step of calcining the solid content to obtain the metal oxide.

[0040]

[32] A method for producing the catalyst for producing methacrylic acid according to [28] or [29], wherein the method for producing the catalyst for producing methacrylic acid comprising:

10 (1) A step of heating an aqueous solution or slurry containing at least molybdenum at 80 to 300 °C for 3 to 200 hours to produce a solid content,

(1b) A step of dispersing the solid content in an aqueous oxalic acid solution, hydrochloric acid, ethylene glycol, or hydrogen peroxide solution to obtain the solid content,

(2b) A step of calcining the solid content obtained in (1b) to obtain the metal oxide.

[0041]

15 [33] The method for producing the catalyst for producing methacrylic acid according to [31] or [32], wherein the solid content satisfies the following conditions (h) and (i).

(h) The solid content having an average length of crystals of 2 to 50 μm observed by an electron microscope.

20 (i) The solid content having an average aspect ratio of crystals of 2 to 30 observed by an electron microscope.

(Note that average aspect ratio = (average length of crystals)/(average diameter of crystals))

[0042]

25 [34] A method for producing methacrylic acid, comprising: producing methacrylic acid by oxidation of methacrolein using the catalyst for producing methacrylic acid according to any one of [21] to [30].

[0043]

30 [35] A method for producing methacrylic acid, comprising: producing the catalyst for producing methacrylic acid by the method according to any one of [31] to [33], and producing methacrylic acid by oxidation of methacrolein using the catalyst for producing methacrylic acid.

[0044]

[36] The method for producing methacrylic acid according to [34] or [35], wherein a gas having a composition represented by the following formula (IV) is supplied as a raw material gas.

Methacrolein:Oxygen:Water vapor:A = k:l:m:n (IV)

(In the formula (IV), A represents nitrogen or helium. k to n represent the molar ratio of each gas, and when $k + l + m + n = 100$, $0.5 < k < 8.0$, $2.0 < l < 20.0$, and $0 \leq m < 45$.)

[0045]

[37] The method for producing methacrylic acid according to any one of [34] to [36], wherein the reaction temperature is 180 to 500 °C, and a raw material gas containing methacrolein is supplied so as to satisfy the following formula (V).

$$15 < W/F < 550 \quad (V)$$

(In the formula (V), W represents the mass (g) of the metal oxide charged in a reactor, and F represents the feed amount (mol/h) of methacrolein per unit time.)

[0046]

[38] The method for producing methacrylic acid according to any one of [34] to [37], wherein the reaction temperature is 180 to 500 °C, and a raw material gas containing methacrolein is supplied so as to satisfy the following formula (VI).

$$0.00002 < F/(S \times W) < 0.008 \quad (VI)$$

(In the formula (VI), S represents the BET-specific surface area (m²/g) of the metal oxide calculated by nitrogen-adsorption, W represents the mass (g) of the metal oxide charged in a reactor, and F represents the feed amount (mol/h) of methacrolein per unit time.)

[0047]

[39] A method for producing methacrylic acid ester, comprising: esterifying methacrylic acid produced by the method according to any one of [34] to [38].

[0048]

[40] A method for producing methacrylic acid ester, comprising: producing methacrylic acid by the method according to any one of [34] to [38], and esterifying the methacrylic acid.

[1'] A catalyst used in producing methacrylic acid by a gas phase catalytic oxidation reaction of methacrolein, wherein the catalyst for producing methacrylic acid comprises a metal oxide satisfying the following condition (a').

(a') The metal oxide containing at least molybdenum and including a cyclic structure having a molar ratio represented by the following formula (I), in which metal-oxygen octahedrons (octahedral structures) having a metal coordination number of 6 are annularly bonded.

$$(\text{sum of number of moles of Mo, V, and X}) : (\text{number of moles of O}) = 7:35 \quad (I)$$

(In the formula (I), Mo, V, and O represent molybdenum, vanadium, and oxygen, respectively. X represents at least one element selected from the group consisting of niobium, tantalum, tungsten, titanium, aluminum, zirconium, chromium, manganese, iron, copper, cobalt, rhodium,

nickel, palladium, platinum, phosphorus, arsenic, antimony, tellurium, bismuth, boron, indium, zinc, magnesium, and cerium.)

[0049]

[2'] The catalyst for producing methacrylic acid according to [1'], wherein the metal oxide satisfies the following condition (c).

(c) The metal oxide having a composition represented by the following formula (II).



(In the formula (II), Mo, V, NH_4 , and O represent molybdenum, vanadium, an ammonium species, and oxygen, respectively. X represents at least one element selected from the group consisting of niobium, tantalum, tungsten, titanium, aluminum, zirconium, chromium, manganese, iron, copper, cobalt, rhodium, nickel, palladium, platinum, phosphorus, arsenic, antimony, tellurium, bismuth, boron, indium, zinc, magnesium, and cerium. Z represents at least one element selected from the group consisting of lithium, sodium, potassium, rubidium, cesium, and calcium. c to g represent the molar ratio of each component, $0 \leq c < 0.5$, $0 \leq d < 0.5$, $0 \leq e \leq 0.1$, and $0 \leq f \leq 0.1$, and g is the molar ratio of oxygen required to satisfy the valence of each component.)

[0050]

[3'] The catalyst for producing methacrylic acid according to [2'], wherein $0 < c < 0.5$ in the formula (II).

[0051]

[4'] The catalyst for producing methacrylic acid according to any one of [1'] to [3'], wherein the metal oxide satisfies the following condition (d).

(d) The metal oxide satisfying the following formula (III), where M1 is the mass of the metal oxide and M2 is the mass of inert ingredients contained in the metal oxide.

$$0 \leq \text{M2/M1} < 0.05 \quad (\text{III})$$

[0052]

[5'] The catalyst for producing methacrylic acid according to any one of [1'] to [4'], wherein the metal oxide satisfies the following condition (e).

(e) The metal oxide having absorption peaks at $1557 \pm 10\text{cm}^{-1}$, $1456 \pm 10\text{cm}^{-1}$, and $1374 \pm 10\text{cm}^{-1}$ in a difference spectrum between an infrared absorption spectrum obtained by FT-IR measurement of the metal oxide and an infrared absorption spectrum obtained by FT-IR measurement after holding the metal oxide under a methacrolein atmosphere of 2.0% by volume or more for 60 minutes.

[0053]

[6'] The catalyst for producing methacrylic acid according to any one of [1'] to [5'], wherein the metal oxide satisfies the following condition (f).

(f) The metal oxide having a BET-specific surface area S of 1.5 to 60 m²/g, calculated by nitrogen-adsorption.

5 [0054]

[7'] The catalyst for producing methacrylic acid according to any one of [1'] to [6'], wherein the metal oxide satisfies the following condition (g).

(g) The metal oxide showing diffraction peaks at $2\theta = 22.1^\circ \pm 0.3^\circ$ and $45.2^\circ \pm 0.3^\circ$ in X-ray diffraction pattern (using Cu-K α ray).

10 [0055]

[8'] The catalyst for producing methacrylic acid according to [7'], showing diffraction peaks only at $2\theta = 22.1^\circ \pm 0.3^\circ$ and $45.2^\circ \pm 0.3^\circ$ under the condition (g).

[0056]

15 [9'] The catalyst for producing methacrylic acid according to [7'], further showing diffraction peaks at $2\theta = 6.6^\circ \pm 0.3^\circ$, $7.9^\circ \pm 0.3^\circ$, $9.0^\circ \pm 0.3^\circ$, $26.4^\circ \pm 0.3^\circ$, $26.9^\circ \pm 0.3^\circ$, $27.2^\circ \pm 0.3^\circ$, and $27.4^\circ \pm 0.3^\circ$ under the condition (g).

[0057]

20 [10'] The catalyst for producing methacrylic acid according to [7'], further showing diffraction peaks at $2\theta = 4.7^\circ \pm 0.3^\circ$, $8.3^\circ \pm 0.3^\circ$, $25.3^\circ \pm 0.3^\circ$, $25.7^\circ \pm 0.3^\circ$, $27.0^\circ \pm 0.3^\circ$, $27.9^\circ \pm 0.3^\circ$, and $28.3^\circ \pm 0.3^\circ$ under the condition (g).

[0058]

[11'] A method for producing the catalyst for producing methacrylic acid according to any one of [1'] to [7'], [9'], and [10'], comprising the following steps (1) and (2):

25 (1) A step of heating an aqueous solution or slurry containing at least molybdenum at 80 to 300 °C for 3 to 200 hours to obtain a solid content.

(2) A step of calcining the solid content to obtain the metal oxide.

[0059]

[12'] A method for producing the catalyst for producing methacrylic acid according to [8'], comprising the following steps (1) and (2):

30 (1) A step of heating an aqueous solution or slurry containing at least molybdenum at 80 to 300 °C for 3 to 200 hours to obtain a solid content.

(2) A step of calcining the solid content to obtain the metal oxide.

[0060]

[13'] The method for producing the catalyst for producing methacrylic acid according to [11'],

comprising: a dispersion treatment step of subjecting the solid content to the dispersion treatment in an aqueous oxalic acid solution, hydrochloric acid, ethylene glycol, or hydrogen peroxide solution after obtaining the solid content in the step (1) and before calcining the solid content in the step (2).

5 [0061]

[14'] The method for producing the catalyst for producing methacrylic acid according to any one of [11'] to [13'], wherein in the step (2), the solid content or the solid content after the dispersion treatment obtained in the dispersion treatment step satisfies the following conditions (h) and (i).

10 (h) The solid content having an average length of crystals of 2 to 50 μm observed by an electron microscope.

(i) The solid content having an average aspect ratio of crystals of 2 to 30 observed by an electron microscope.

(Note that average aspect ratio = (average length of crystals)/(average diameter of crystal))

[0062]

15 [15'] A method for producing methacrylic acid, comprising: producing methacrylic acid by a vapor phase catalytic oxidation reaction of methacrolein using the catalyst for producing methacrylic acid according to any one of [1'] to [10'].

[0063]

20 [16'] A method for producing methacrylic acid, comprising: producing the catalyst for producing methacrylic acid by the method according to any one of [11'] to [14'], and producing methacrylic acid by a gas phase catalytic oxidation reaction of methacrolein using the catalyst for producing methacrylic acid.

[0064]

25 [17'] The method for producing methacrylic acid according to [15'] or [16'], wherein the reaction temperature is 180 to 500 $^{\circ}\text{C}$, and a raw material gas containing methacrolein is supplied so as to satisfy the following formula (V).

$$15 < W/F < 550 \quad (\text{V})$$

(In the formula (V), W represents the mass (g) of the metal oxide charged in a reactor, and F represents the feed amount (mol/h) of methacrolein per unit time.)

30 [0065]

[18'] The method for producing methacrylic acid according to any one of [15'] to [17'], wherein the reaction temperature is 180 to 500 $^{\circ}\text{C}$, and a raw material gas containing methacrolein is supplied so as to satisfy the following formula (VI).

$$0.00002 < F/(S \times W) < 0.008 \quad (\text{VI})$$

(In the formula (VI), S represents the BET-specific surface area (m^2/g) of the metal oxide calculated by nitrogen-adsorption, W represents the mass (g) of the metal oxide charged in a reactor, and F represents the feed amount (mol/h) of methacrolein per unit time.)

[19'] The method for producing methacrylic acid according to any one of [15'] to [18'], wherein a gas having a composition represented by the following formula (IV') is supplied as a raw material gas.



(In the formula (IV'), A represents nitrogen or helium. k to n represent the molar ratio of each gas, and when $k + l + m + n = 100$, $0.5 < k < 8.0$, $2.0 < l < 20.0$, and $4.5 < m < 45$.)

[0067]

[20'] A method for producing methacrylic acid ester, comprising: esterifying methacrylic acid produced by the method according to any one of [15'] to [19'].

[0068]

[21'] A method for producing a methacrylic acid ester, comprising: producing methacrylic acid by the method according to any one of [15'] to [19'], and esterifying the methacrylic acid.

EFFECT OF THE INVENTION

[0069]

According to the present invention, it is possible to provide a molybdenum-containing oxide catalyst having a high methacrylic acid yield, which is used for oxidation of methacrolein, and a method for producing the same, and a method for producing methacrylic acid using the catalyst, and a method for producing methacrylic acid ester.

BRIEF DESCRIPTION OF DRAWINGS

[0070]

[Fig. 1] Fig. 1 is a diagram showing the molecular structure of the metal-oxygen octahedron (octahedral structure).

[Fig. 2] Fig. 2 is a diagram showing the molecular structure when each of the seven octahedral structures shares the oxygen at adjacent vertices to form the cyclic structure.

[Fig. 3] Fig. 3 is a diagram showing an example of the molecular structure in an ab plane of the metal oxide when the plane in which the octahedral structures are bonded in a circle is defined as the ab plane.

DETAILED DESCRIPTION OF THE PRESENT INVENTION

[0071]

Hereinafter, the present invention will be described in detail.

[Catalyst for producing methacrylic acid]

[0072]

5 One aspect of the catalyst for producing methacrylic acid according to the present invention includes a metal oxide containing molybdenum, and the metal oxide has a cyclic structure satisfying the following conditions (a) and (b).

(a) The cyclic structure satisfying the following formula (I).

(sum of number of moles of Mo, V, and X):(number of moles of O) = 7:35 (I)

10 (In the formula (I), Mo, V, and O represent molybdenum, vanadium, and oxygen, respectively. X represents at least one element selected from the group consisting of niobium, tantalum, tungsten, titanium, aluminum, zirconium, chromium, manganese, iron, copper, cobalt, rhodium, nickel, palladium, platinum, phosphorus, arsenic, antimony, tellurium, bismuth, boron, indium, zinc, magnesium, and cerium.)

15 (b) The cyclic structure in which each of the seven metal-oxygen octahedrons (octahedral structures) is bonded by sharing oxygen at adjacent vertices.

[0073]

Further, another aspect of the catalyst for producing methacrylic acid according to the present invention includes a metal oxide satisfying the following conditions (b') and (c).

20 (b') The metal oxide including a cyclic structure in which each of the seven metal-oxygen octahedrons (octahedral structures) is bonded (a cyclic structure in which seven octahedral structures are annularly bonded).

(c) The metal oxide having a composition represented by the following formula (II).

$\text{Mo}_1\text{V}_c\text{X}_d\text{Z}_e(\text{NH}_4)_f\text{O}_g$ (II)

25 (In the formula (II), Mo, V, NH_4 , and O represent molybdenum, vanadium, an ammonium species, and oxygen, respectively. X represents at least one element selected from the group consisting of niobium, tantalum, tungsten, titanium, aluminum, zirconium, chromium, manganese, iron, copper, cobalt, rhodium, nickel, palladium, platinum, phosphorus, arsenic, antimony, tellurium, bismuth, boron, indium, zinc, magnesium, and cerium. Z represents at least one element selected from the group consisting of lithium, sodium, potassium, rubidium, cesium, and calcium. c to g represent the molar ratio of each component, $0 \leq c < 0.5$, $0 \leq d < 0.5$, $0 \leq e \leq 0.1$, and $0 \leq f \leq 0.1$, and g is the molar ratio of oxygen required to satisfy the valence of each component.)

[0074]

Further, another aspect of the catalyst for producing methacrylic acid according to the present invention includes a metal oxide satisfying the condition (c) and the following condition (g1).

(g1) The metal oxide showing diffraction peaks only at $2\theta = 22.1^\circ \pm 0.3^\circ$ and $45.2^\circ \pm 0.3^\circ$ in X-ray diffraction pattern (using Cu-K α ray).

Details of each condition will be described below.

[0075]

<Condition (a)>

The fact that the metal oxide has the cyclic structure satisfying the condition (a) can be confirmed by, for example, a high-angle annular dark field (HAADF) measurement using a scanning transmission electron microscope (STEM) (hereinafter, also referred to as "HAADF-STEM measurement") and an element species contained in the metal oxide.

The presence of the cyclic structure can be confirmed as an image by observing the powder of the metal oxide using HAADF-STEM measurement.

The metal element species contained in the metal oxide can be specified, for example, by dissolving the metal oxide in ammonia water or an aqueous solution of hydrofluoric acid and analyzing it by ICP atomic emission spectroscopy.

The fact that the cyclic structure confirmed in HAADF-STEM image satisfies the formula (I) can be confirmed by specifying the element shown in HAADF-STEM image from the contrast of HAADF-STEM image and the metal element species contained in the metal oxide, and calculating the ratios of each metal element in the cyclic structure.

[0076]

It is noted that, when the metal oxide is composed of only the components contained in the formula (I), if the presence of a cyclic structure is confirmed, it can be determined that the cyclic structure satisfies the formula (I). In this case, the presence of the cyclic structure can be confirmed not only by HAADF-STEM measurement of the metal oxide as described above, but also by the molecular probe method in the gas adsorption method.

When the molecular probe method in the gas adsorption method is used, the adsorption isotherm is created by filling the metal oxide into a closed vacuum system, pretreating at 200 to 400 °C, and then introducing several kinds of gas molecules with different molecular diameters into the vacuum system as a probe, and the pore diameter is calculated using the DA method (M.M. Dubinin, V. A. Astakhov, "Advances in Chemistry", 1971, Vol. 102, p.69). If the calculated pore diameter is 0.35 to 0.5nm, it can be determined that the cyclic structure exists.

[0077]

In the formula (I), from the viewpoint of methacrylic acid selectivity, X is preferably at least one element selected from the group consisting of niobium, tantalum, tungsten, manganese, iron, copper, cobalt, phosphorus, arsenic, antimony, tellurium, bismuth, boron, indium, zinc, magnesium, and cerium, and more preferably at least one element selected from the group consisting of tungsten, iron, copper, antimony and bismuth.

[0078]

Further, in the formula (I), from the viewpoint of methacrylic acid yield, Mo, V, and X preferably have a molar ratio represented by the following formula (I').

$$(\text{number of moles of Mo}):(\text{number of moles of V}):(\text{number of moles of X}) = (7 - a - b):a:b$$

(I')

(In the formula (I'), a and b are integers representing the molar ratios of vanadium and X, respectively, a = 0 to 3, more preferably a = 1 to 3, b = 0 to 3.)

The values of a and b can be specified by performing Rietvelt analysis on the X-ray diffractive pattern of the metal oxide measured by, for example, X-ray structural analysis.

[0079]

<Conditions (b) and (b')>

The molecular structure of the metal-oxygen octahedron (octahedral structure) is shown in Fig. 1. In Fig. 1, a metal element (Mo, V or X) having a coordination number of 6 is located at the center of the octahedral structure, and oxygen is located at all vertices of the octahedron. In addition, Fig. 2 shows the molecular structure when each of the seven octahedral structures, shown in Fig. 1, shares the oxygen at adjacent vertices to form the cyclic structure.

[0080]

In the oxidation of methacrolein, the cyclic structure shown in Fig. 2 has high catalytic activity. It is speculated that this is because the presence of the cyclic structure forms an adsorption site capable of producing methacrylic acid from methacrolein with a high selectivity. Further, the catalytic performance can be controlled by controlling the type, combination and amount of metal elements contained in the cyclic structure. In addition, a structure containing Mo, V or X may be arranged in the pores formed by the cyclic structure.

The cyclic structure shown in Fig. 2 corresponds to a part of the structure of the metal oxide. Fig. 3 shows an example of the molecular structure in an ab plane of the metal oxide when the plane in which the octahedral structures are bonded in a circle is defined as the ab plane in Fig. 2. In Fig. 3, the cyclic structure shown in Fig. 2 is bonded to other cyclic structure by sharing oxygen at the vertex. In addition, the cyclic structure in which the octahedral structures are annularly bonded is arranged so as to share one octahedral structure with other adjacent

cyclic structures. Note that the metal oxide may have the cyclic structure in which 6 or less octahedral structures are bonded by sharing oxygen at adjacent vertices.

[0081]

The fact that the metal oxide has the cyclic structure satisfying the condition (b) can be confirmed by, for example, HAADF-STEM measurement or a molecular probe method in the gas adsorption method.

[0082]

When HAADF-STEM measurement is used, it is possible to confirm the presence of the cyclic structure satisfying the condition (b) as an image by observing the powder of the metal oxide.

[0083]

When the molecular probe method in the gas adsorption method is used, the adsorption isotherm is created by filling the metal oxide into a closed vacuum system, pretreating at 200 to 400 °C, and then introducing CO₂, CH₄ or C₂H₆, which is the probe capable of adsorbing to pores of 0.40 to 0.43nm in diameter, into the vacuum system, and the pore diameter is calculated using the DA (Dubinin-Astakhov) method (M.M. Dubinin, V. A. Astakhov, "Advances in Chemistry", 1971, Vol. 102, p.69). If the calculated pore diameter is 0.40 to 0.43nm, it can be determined that the cyclic structure satisfying the condition (b) exists.

Further, the fact that the metal oxide has the cyclic structure satisfying the condition (b) indicates that the metal oxide satisfies the condition (b').

[0084]

<Condition (c)>

The molar ratio of each element in the metal oxide can be calculated by completely dissolving the metal oxide in ammonia water, nitric acid, hydrochloric acid, sulfuric acid, aqua regia or hydrofluoric acid and analyzing it by ICP atomic emission spectroscopy.

Further, the molar ratio of the ammonium species can be calculated by analyzing the metal oxide by a Kjeldahl method. It is noted that, in the present application, "ammonium species" means a generic term for ammonia (NH₃) which can be ammonium ion (NH₄⁺) and ammonium contained in ammonium-containing compounds such as ammonium salt.

[0085]

In the formula (II), from the viewpoint of methacrylic acid selectivity, the molar ratio of vanadium is preferably $0 < c < 0.5$.

[0086]

In addition, in the formula (II), from the viewpoint of methacrylic acid selectivity, X is

preferably at least one element selected from the group consisting of niobium, tantalum, tungsten, manganese, iron, copper, cobalt, phosphorus, arsenic, antimony, tellurium, bismuth, boron, indium, zinc, magnesium, and cerium, and more preferably at least one element selected from the group consisting of tungsten, iron, copper, antimony, and bismuth.

5 [0087]

When the metal oxide has the cyclic structure satisfying the conditions (a) and (b), and when the metal oxide satisfies the conditions (b') and (c), it is preferable that the metal oxide further satisfies the following condition (g).

10 (g) The metal oxide showing diffraction peaks at $2\theta = 22.1^\circ \pm 0.3^\circ$ and $45.2^\circ \pm 0.3^\circ$ in X-ray diffraction pattern (using Cu-K α ray).

[0088]

<Conditions (g) and (g1)>

In the X-ray diffraction pattern (using Cu-K α ray), the diffraction peak appearing at $2\theta = 22.1^\circ \pm 0.3^\circ$ is derived from the (001) plane of the crystal structure of the metal oxide, and the
15 diffraction peak appearing at $2\theta = 45.2^\circ \pm 0.3^\circ$ is derived from the (002) plane. When the axis perpendicular to the ab plane is defined as the c-axis, the presence of these diffraction peaks indicates that the metal oxide has a structure in which the crystals are regularly laminated in the c-axis direction. When the metal oxide satisfies the condition (g), it indicates that the ab planes are laminated at an interval of 0.396 to 0.410nm in the metal oxide. It is noted that, the
20 diffraction peak has a height of 5/100 or more with respect to the peak of the maximum intensity appearing in the range of $2\theta = 2$ to 60° .

In addition, in the condition (g), when further satisfying the following condition (g1), it can be specified that the metal oxide has an amorphous structure.

(g1) The metal compound showing diffraction peaks only at $2\theta = 22.1^\circ \pm 0.3^\circ$ and $45.2^\circ \pm 0.3^\circ$ in X-ray diffraction pattern (using Cu-K α ray).

25 [0089]

Further, in the condition (g), when diffraction peaks are further shown at $2\theta = 6.6^\circ \pm 0.3^\circ$, $7.9^\circ \pm 0.3^\circ$, $9.0^\circ \pm 0.3^\circ$, $26.4^\circ \pm 0.3^\circ$, $26.9^\circ \pm 0.3^\circ$, $27.2^\circ \pm 0.3^\circ$, and $27.4^\circ \pm 0.3^\circ$ other than $2\theta = 22.1^\circ \pm 0.3^\circ$ and $45.2^\circ \pm 0.3^\circ$, it can be specified that the metal oxide has an orthorhombic crystal
30 structure. In addition, when diffraction peaks are further shown at $2\theta = 4.7^\circ \pm 0.3^\circ$, $8.3^\circ \pm 0.3^\circ$, $25.3^\circ \pm 0.3^\circ$, $25.7^\circ \pm 0.3^\circ$, $27.0^\circ \pm 0.3^\circ$, $27.9^\circ \pm 0.3^\circ$, and $28.3^\circ \pm 0.3^\circ$ other than $2\theta = 22.1^\circ \pm 0.3^\circ$ and $45.2^\circ \pm 0.3^\circ$, it can be specified that the metal oxide has a trigonal crystal structure. From the viewpoint of methacrylic acid yield, it is preferable that the metal oxide has the amorphous structure, the orthorhombic crystal structure, or the trigonal crystal structure.

[0090]

Further, from the viewpoint of methacrylic acid yield, it is preferable that the metal oxide further satisfies at least one selected from the following conditions (d) to (f), and more preferably satisfies all of the following conditions (d) to (f).

- 5 (d) The metal oxide satisfying the following formula (III), where M1 is the mass of the metal oxide and M2 is the mass of inert ingredients contained in the metal oxide.

$$0 \leq M2/M1 < 0.05 \quad (\text{III})$$

- (e) The metal oxide having absorption peaks at $1557 \pm 10\text{cm}^{-1}$, $1456 \pm 10\text{cm}^{-1}$, and $1374 \pm 10\text{cm}^{-1}$ in a difference spectrum between an infrared absorption spectrum obtained by FT-IR measurement of the metal oxide and an infrared absorption spectrum obtained by FT-IR measurement after holding the metal oxide under a methacrolein atmosphere of 2.0% by volume or more for 60 minutes.
- 10

(f) The metal oxide having a BET-specific surface area S of 1.5 to 60 m²/g, calculated by nitrogen-adsorption.

- 15 Details of each condition will be described below.

[0091]

<Condition (d)>

- In the formula (III), M2/M1 indicates the mass ratio of inert ingredients contained in the metal oxide. An inert ingredient is a compound that does not exhibit catalytic activity or has extremely low catalytic activity when oxidizing methacrolein at a reaction temperature of 180 to 500 °C. Examples of inert ingredients include compound such as Al₂O₃, SiO₂, TiO₂, zeolites, and other catalytic support compounds.
- 20

[0092]

- When M2/M1 satisfies the formula (III), since the ratio of the active ingredient per unit volume in the metal oxide is sufficiently high, it is easy to achieve the desired methacrolein conversion and continuous operation time in the production of methacrylic acid.
- 25

[0093]

<Condition (e)>

- The device used for FT-IR measurement is not particularly limited, and it is sufficient that it can measure at least in the range of 1200 to 2000 cm⁻¹. Further, the measurement method may be any of a transmission method and a diffuse reflection method, and the metal oxide may be diluted with a diluent for measurement. As the diluent, a material that does not exhibit infrared absorption at least in the range of 1200 to 2000 cm⁻¹ can be used. Examples of the diluent include KBr. FT-IR measurement of the metal oxide is carried out by installing of the metal
- 30

oxide in the device, pretreating it at 300 °C or higher for 10 minutes or more under the flow of nitrogen or helium, and then cooling it to the measurement temperature. Next, the metal oxide is held under a water vapor atmosphere of 15 to 25% by volume for 5 to 60 seconds, and further held under a methacrolein atmosphere of 2.0% by volume or more for 60 minutes, followed by FT-IR measurement, and the difference spectrum is obtained from the difference between them. Methacrylic acid can be produced with higher methacrylic acid selectivity when it has absorption peaks at $1557 \pm 10 \text{ cm}^{-1}$, $1456 \pm 10 \text{ cm}^{-1}$, and $1374 \pm 10 \text{ cm}^{-1}$ in the difference spectrum. Note that the absorption peak is defined as a value whose peak area is 0.1 or more when the horizontal axis is defined as a wavelength and the vertical axis is defined as an absorbance detected by FT-IR measurement.

[0094]

<Condition (f)>

The BET-specific surface area S can be calculated by the nitrogen-adsorption measurement using nitrogen as a probe in the gas adsorption method. In the nitrogen-adsorption measurement, the metal oxide is filled in a closed vacuum system, and pretreated at 200 to 400 °C, and then nitrogen is adsorbed on the metal oxide at a liquid nitrogen temperature to draw an adsorption isotherm, and the specific surface area is calculated by a BET method. Since the BET-specific surface area S of the metal oxide is $1.5 \text{ m}^2/\text{g}$ or more, the methacrolein conversion is improved in the production of methacrylic acid. In addition, since the BET-specific surface area S is $60 \text{ m}^2/\text{g}$ or less, the calorific value in the production of methacrylic acid can be suppressed, and the operation can be stably continued.

[0095]

[Method for producing catalyst for producing methacrylic acid]

One aspect of the method for producing the catalyst for producing methacrylic acid according to the present invention includes the following steps (1) and (2).

(1) A step of heating an aqueous solution or slurry containing at least molybdenum at 80 to 300 °C for 3 to 200 hours to obtain a solid content.

(2) A step of calcining the solid content to obtain the metal oxide.

[0096]

Further, another aspect of the method for producing the catalyst for producing methacrylic acid according to the present invention includes the following steps (1), (1b), and (2b).

(1) A step of heating an aqueous solution or slurry containing at least molybdenum at 80 to 300 °C for 3 to 200 hours to obtain a solid content.

(1b) A step of dispersing the solid content in an aqueous oxalic acid solution, hydrochloric

acid, ethylene glycol, or hydrogen peroxide solution to obtain the solid content.

(2b) A step of calcining the solid content obtained in (1b) to obtain the metal oxide.

Details of each step will be described below.

[0097]

5 (Step (1))

In step (1), a portion or all of the catalyst raw material containing at least molybdenum is mixed with a solvent to prepare a solution or slurry, and the solution or slurry is heated at 80 to 300 °C for 3 to 200 hours to produce the solid content. When a portion of the catalyst raw material is mixed with a solvent to prepare the solution or slurry, the remaining catalyst raw material can be mixed after preparation of the solution or slurry.

[0098]

<Catalyst raw material>

The catalyst raw material is not particularly limited, and nitrates, carbonates, acetates, ammonium salts, oxides, halides, and the like of each element contained in the composition of the target metal oxide can be used in combination. Examples of the molybdenum raw material include ammonium heptamolybdate, molybdenum trioxide, molybdic acid, and molybdenum chloride, and a molybdenum-based polyoxometalate or the like can also be used. As the molybdenum-based polyoxometalate, a heteropolyacid, an isopolyacid and a raw material obtained by modifying a heteropolyacid and an isopolyacid with an alkylammonium ion, or the like can be used. As the raw material obtained by modifying an isopolyacid with an alkylammonium ion, $(\text{CH}_3\text{NH}_3)_6\text{Mo}_7\text{O}_{24}$, $(\text{C}_2\text{H}_5\text{NH}_3)\text{Mo}_3\text{O}_{10}$, and the like can be used.

[0099]

The catalyst raw material preferably contains vanadium, and examples of the vanadium raw material include vanadyl sulfate, vanadium sulfate, vanadium pentoxide, ammonium metavanadate, vanadium chloride, and the like. Further, a surfactant may be added as the catalyst raw material. Examples of the surfactant include an anionic surfactant or a cationic surfactant, and examples of the cationic surfactant include sodium dodecyl sulfate and the like.

[0100]

<Solvent>

As the solvent, water or an organic solvent can be used, but it is preferable to use water in view of ease of handling and safety. The mass of the solvent is preferably set to 500 to 5000 parts by mass with respect to 100 parts by mass of the total of the catalyst raw materials used for preparing the solution or slurry.

[0101]

<Preparation of solution or slurry>

The solution or slurry is prepared by mixing the catalyst raw material in the solvent. Although there is no particular limitation on the mixing method, a method in which the catalyst raw material is added to the solvent and stirred and mixed is preferred. There is no particular limitation on the order of addition, and can be appropriately set.

[0102]

In step (2) described later, from the viewpoint of forming the metal oxide having the cyclic structure satisfying the condition (a), it is preferable that the solution or slurry is prepared using the component contained in the formula (I).

In addition, a trace amount of the metal oxide having the composition represented by the formula (II) may be added to the solution or slurry. By adding the metal oxide in advance, the methacrylic acid yield of the finally obtained catalyst is improved.

[0103]

In step (2) described later, from the viewpoint of forming the metal oxide having the cyclic structure satisfying the condition (b), it is preferable that the pH of the solution or slurry is set to 1.7 to 3.5 and nitrogen, hydrogen, or helium is bubbled. The pH of the solution or slurry can be adjusted, for example, by using ammonia water or sulfuric acid as the catalyst raw material. Note that the pH of the solution or slurry can be measured by a portable pH meter D-72 (product name) manufactured by HORIBA or the like.

[0104]

< Production of solid content>

Subsequently, the solution or slurry is heated to produce the solid content. The heating temperature of the solution or slurry is preferably 80 to 300 °C. When the heating temperature is 80 °C or higher, in step (2) described later, the metal oxide having the cyclic structure satisfying the condition (b) can be advantageously formed. Further, when the heating temperature is 300 °C or less, the methacrylic acid yield of the finally obtained catalyst is improved. The lower limit of the heating temperature is more preferably 120 °C or more, further preferably 175 °C or more. The upper limit of the heating temperature is more preferably 260 °C or less, further preferably 230 °C or less.

[0105]

The heating time of the solution or slurry is preferably 3 to 200 hours from the viewpoint of methacrylic acid yield. More preferably, the lower limit of the heating time is 10 hours or more and the upper limit is 72 hours or less.

In the solution or slurry, a sheet made of Teflon (registered trademark), a glass plate, or the

like may be placed in advance and heated. Since the orthorhombic and the trigonal crystal structures tend to form on the surface of Teflon, the formation of these crystal structures is promoted by inserting the sheet made of Teflon or the glass plate.

[0106]

5 <Production of solid content by hydrothermal method>

From the viewpoint of methacrylic acid yield of the obtained catalyst, it is preferable to produce the solid content using a hydrothermal method capable of suppressing evaporation of water. The hydrothermal method is a method of performing synthesis or the like of compounds in the presence of hot water at high temperature and high pressure, and the raw material and
10 water are reacted by heating and pressurizing in a closed container called an autoclave. For the hydrothermal method, a pressure vessel such as the autoclave can be used. The container may be allowed to stand or rotate, or may be irradiated with electromagnetic waves from the outside of the container.

When the hydrothermal method is used, the structure of the solid content produced can be
15 controlled by the concentration of the molybdenum raw material used and the pH of the solution or slurry. For example, when ammonium heptamolybdate is used as the molybdenum raw material, the formation of the orthorhombic structure tends to be promoted by setting the concentration of ammonium heptamolybdate to 0.02 to 0.04 mol/l with respect to the solvent and setting the pH of the solution or slurry to 2.3 to 3.5, and the formation of the trigonal structure
20 tends to be promoted by setting the concentration of ammonium heptamolybdate to 0.02 to 0.04 mol/l with respect to the solvent and setting the pH to 1.7 to 2.3. In addition, the formation of the amorphous structure tends to be promoted by setting the concentration of ammonium heptamolybdate to 0.05 to 0.30 mol/l with respect to the solvent and setting the pH of the solution or slurry to 1.7 to 3.5.

25 [0107]

<Drying of solution or slurry>

After the solid content is produced, the solution or slurry is dried using suction filtration, centrifugation, a drum dryer, a spray dryer, or the like to obtain the solid content. When suction filtration or centrifugation is used, it is preferable to further remove water at 20 to 150 °C to
30 obtain the solid content.

[0108]

(Step (1b))

In the method for producing a catalyst for producing methacrylic acid according to the present invention, when the metal oxide has the orthorhombic or trigonal crystal structure, the

method may include a step (1b) of subjecting the solid content produced in the step (1) to a dispersion treatment in an aqueous oxalic acid solution, hydrochloric acid, ethylene glycol, or hydrogen peroxide solution. When a component having a hexagonal structure, a pseudo hexagonal structure, or the like is contained in the solid content, the yield may decrease in the production of methacrylic acid. By subjecting the solid content to the dispersion treatment in the aqueous oxalic acid solution, hydrochloric acid, ethylene glycol, or hydrogen peroxide solution, the component having the hexagonal structure or the pseudo hexagonal structure is eluted, and the component can be separated from the solid content.

[0109]

On the other hand, since the component having the amorphous structure is also eluted by step (1b), it is preferable to produce the catalyst for producing methacrylic acid without performing step (1b) when the metal oxide has the amorphous structure.

[0110]

It is preferable that the solid content produced in the step (1) or the solid content after the dispersing treatment obtained in the step (1b) (hereinafter collectively referred to as the "solid content") satisfies the following conditions (h) and (i).

(h) The solid content having an average length of crystals of 2 to 50 μm observed by an electron microscope.

(i) The solid content having an average aspect ratio of crystals of 2 to 30 observed by an electron microscope.

(Note that average aspect ratio = (average length of crystals)/(average diameter of crystals))

[0111]

<Condition (h) and condition (i)>

There is no limitation on the electron microscope used to observe the average length and the average aspect ratio of crystals, as long as it can distinguish between 0.1 and 50 μm , at least between 2 and 50 μm , and it can measure the length. As examples, the solid content can be observed by fixing it on carbon tapes, grids or meshes for the electron microscope, using a scanning electron microscope (SEM), a transmission electron microscope (TEM), a scanning transmission electron microscope (STEM), or the like.

[0112]

In conditions (h) and (i), the average length of crystals indicates the average value of the length of the observed crystal in the major axis direction, the average diameter of crystals indicates the average value of the length of the observed crystal in the minor axis direction. The

lengths in the major axis direction and minor axis direction of crystals can be obtained by manually measuring the length in consideration of the scale or by measuring the length by image analysis. In both manual and image analysis cases, at least 500 different crystals with identifiable crystal lengths are extracted, and the lengths in the major axis direction and minor axis direction measured for all the extracted crystals are obtained. The average length of crystals is calculated by obtaining the average value of the length in the major axis direction, and the average diameter of crystals is calculated by obtaining the average value of the length in the minor axis direction. However, if the cross-section in the minor axis direction of the crystal is not a perfect circle, calculate the length in the minor axis direction using the following formula from the cross-sectional area in the minor axis direction.

[0113]

[Math. 1]

length in the minor axis direction of crystals

$$= 2 \times \sqrt{\text{cross-sectional area in the minor axis direction} / 3.14}$$

[0114]

The average diameter of crystals and the average aspect ratio of crystals can be controlled by adding a surfactant as the catalyst raw material in the step (1). When the amount of the surfactant added is increased, the average diameter of crystals of the solid content becomes large, and the average aspect ratio becomes small. Further, the average length of crystals and the average aspect ratio of crystals can be controlled by subjecting the solid content to a pulverization treatment. Long pulverization time physically destroys crystals, the average length of crystals becomes small, and the average aspect ratio becomes small. Examples of the pulverization include a method using a mortar, a ball mill, a high-speed rotation mill, a jet mill, a mortar machine, and the like.

[0115]

The average length of crystals is preferably 0.1 μm or more, more preferably 0.2 μm or more, further preferably 1 μm or more, and particularly preferably satisfies the condition (h) (2 μm or more), from the viewpoint of stably maintaining the cyclic structure.

In the condition (h), when the average length of crystals is 2 μm or more, the cyclic structure satisfying the conditions (a) and (b) can be stably maintained, and the continuous operation time in the production of methacrylic acid can be improved by a simple method. In addition, since the average length of crystals is 50 μm or less, the cross section of crystals in the minor axis direction can be effectively used in the production of methacrylic acid, and the yield of methacrylic acid is improved. From these viewpoints, the average length of crystals is more

preferably 3 μm or more, further preferably 5 μm or more, and is preferably 40 μm or less, more preferably 30 μm or less.

[0116]

In the condition (i), when the average aspect ratio of crystals is 2 to 30, the collapse of the cyclic structure satisfying the conditions (a) and (b) is easily suppressed, and since the cyclic structure can effectively contribute to the reaction in the production of methacrylic acid, the yield of methacrylic acid is improved.

[0117]

(Molding step)

The method for producing a catalyst for producing methacrylic acid according to the present invention may include a molding step of molding the solid content prior to the step (2) or the step (2b) described later. By molding the solid content, the pressure loss in the reactor is reduced in the production of methacrylic acid, and the influence of the raw material gas diffusion is suppressed, thereby improving the selectivity of methacrylic acid.

[0118]

The molding method is not particularly limited, and a known dry or wet molding method can be applied. Examples of the molding method include tablet molding, extrusion molding, pressure molding, rolling granulation, and the like. There is no particular limitation on the shape of the solid content after molding, and examples thereof include any shape such as a spherical granular shape, a ring shape, a cylindrical pellet shape, a star shape, and a granular shape obtained by crushing and classifying after molding. The size of the solid content after molding is preferably 0.1 to 10 mm in diameter. When the diameter is 0.1 mm or more, the pressure loss in the reactor can be sufficiently reduced in the production of methacrylic acid. Further, when the diameter is 10 mm or less, the methacrolein conversion is improved. More preferably, the diameter has a lower limit of 3 mm or more and an upper limit of 8 mm or less.

[0119]

(Step (2) and step (2b))

In the step (2) and step (2b), the solid content or the solid content after molding obtained in the molding step is calcinated to obtain the metal oxide. By calcinating the solid content or the solid content after molding obtained in the molding step, it is possible to improve the methacrolein conversion in the production of methacrylic acid. Note that the step (2) shows a case where the solid content is the solid content produced in the step (1), and the step (2b) shows a case where the solid content is the solid content after the dispersion treatment obtained in the step (1b).

[0120]

The calcinating method is not particularly limited, and a suitable method may be appropriately selected from static calcinating, fluid calcinating, and the like. Examples of the static calcinating include a method of calcinating using a box-type electric furnace, an annular
 5 calcinating furnace, or the like. Examples of the fluid calcinating include a method of calcinating using a fluid calcinating furnace, a rotary kiln, or the like. The calcinating gas is performed under an atmosphere of an oxygen-containing gas such as air or an inert gas, for example. It is noted that, the "inert gas" refers to a gas which does not reduce the catalyst activity in the production of methacrylic acid, and includes, for example, nitrogen, carbon dioxide, helium, argon, and the
 10 like. These may be used alone or admixture of two or more. As for the calcinating atmosphere, the calcinating gas may or may not be circulated as long as the desired calcinating gas atmosphere can be maintained. From the viewpoint of forming the metal oxide having the cyclic structure satisfying the conditions (a) and (b), the calcinating temperature is preferably 200 to 500 °C. The lower limit of the calcinating temperature is more preferably 300 °C or more and the
 15 upper limit is more preferably 470 °C or less. The calcinating time is preferably 1 to 40 hours.

[0121]

[Method for producing methacrylic acid]

A method for producing methacrylic acid according to the present invention is a method, comprising: producing methacrylic acid by oxidation of methacrolein using the catalyst for
 20 producing methacrylic acid according to the present invention. In addition, a method for producing methacrylic acid according to the present invention is a method, comprising: producing the catalyst for producing methacrylic acid by the method according to the present invention, and producing methacrylic acid by oxidation of methacrolein using the catalyst for producing methacrylic acid. The oxidation can be carried out by filling the catalyst for producing
 25 methacrylic acid including the metal oxide in the reactor and supplying the raw material gas containing methacrolein to the reactor.

[0122]

<Catalyst loading>

Although the catalyst for producing methacrylic acid may contain a known oxidation
 30 catalyst such as polyoxometalate in addition to the metal oxide, it is preferable that the catalyst for producing methacrylic acid contains 80% by mass or more of the metal oxide, and more preferably 90% or more of the metal oxide from the viewpoint of continuous operation time in the production of methacrylic acid. The catalyst layer may be one layer, and a plurality of catalysts having different activities may be divided into a plurality of layers and loaded. Further,

for heat removal, it is preferable to use it in admixture with an inert diluent such as sea sand or silicon carbide.

[0123]

<Supply of raw material gas>

- 5 The raw material gas may be obtained by diluting methacrolein and molecular oxygen with an inert gas such as nitrogen or carbon dioxide gas. Further, water vapor may be added to the raw material gas.

[0124]

- 10 As the raw material gas, a gas having a composition represented by the following formula (IV) is preferably supplied.

Methacrolein:Oxygen:Water vapor:A = k:l:m:n (IV)

(In the formula (IV), A represents nitrogen or helium. k to n represent the molar ratio of each gas, and when $k + l + m + n = 100$, $0.5 < k < 8.0$, $2.0 < l < 20.0$, and $0 \leq m < 45$.)

- 15 In the formula (IV), k to m are preferably $2.0 < k < 4.0$, $5.0 < l < 12.0$, and $0 \leq m < 25$, from the viewpoint of methacrylic acid selectivity.

In addition, from the viewpoint of the utility cost, the upper limit of m is preferably 10 or less. This reduces the raw material cost in the production of methacrylic acid. Moreover, the reduced amount of wastewater reduces the cost required for wastewater treatment. The upper limit of m is more preferably 5 or less, and $m = 0$ is further preferred.

20 [0125]

Further, it is preferable to supply the raw material gas containing methacrolein so as to satisfy at least one selected from the following formulae (V) and (VI), and it is more preferable to supply the raw material gas containing methacrolein so as to satisfy the following formulae (V) and (VI).

25 $15 < W/F < 550$ (V)

(In the formula (V), W represents the mass (g) of the metal oxide charged in the reactor, and F represents the feed amount (mol/h) of methacrolein per unit time.)

$0.00002 < F/(S \times W) < 0.008$ (VI)

- 30 (In the formula (VI), S represents the BET-specific surface area (m^2/g) of the metal oxide calculated by nitrogen-adsorption, W represents the mass (g) of the metal oxide charged in a reactor, and F represents the feed amount (mol/h) of methacrolein per unit time.)

[0126]

In the formula (V), W/F represents a contact time between a catalyst filled in the reactor and methacrolein. When W/F exceeds 15, excessive heat generation of the catalyst in the

production of methacrylic acid can be suppressed. Further, when W/F is less than 550, catalyst cost can be suppressed. The lower limit of W/F is more preferably 20 or more, further preferably 40 or more, particularly preferably 50 or more, and most preferably 80 or more. The upper limit of W/F is more preferably 500 or less, further preferably 400 or less, and particularly preferably 270 or less.

[0127]

In the formula (VI), $F/(S \times W)$ represents a feed amount of methacrolein per specific surface area of the catalyst. When $F/(S \times W)$ exceeds 0.00002, the size of the reactor required for ensuring the desired methacrylic acid production amount can be suppressed. Further, when $F/(S \times W)$ is less than 0.008, catalyst cost can be suppressed. The lower limit of $F/(S \times W)$ is more preferably 0.00007 or more. The upper limit of $F/(S \times W)$ is more preferably 0.005 or less, still more preferably 0.001 or less, and particularly preferably 0.0008 or less.

[0128]

<Reaction temperature and pressure>

The reaction temperature is preferably 180 to 500 °C, the lower limit is more preferably 200 °C or more, and the upper limit is more preferably 400 °C or less. The reaction pressure is preferably 0.1 to 1 MPa (G). Here, (G) means gauge pressure.

[0129]

[Method for producing methacrylic acid ester]

A method for producing methacrylic ester according to the present invention is a method, comprising: esterifying methacrylic acid produced by the method according to the present invention. Further, a method for producing methacrylic acid ester according to the present invention is a method, comprising: producing methacrylic acid by the method according to the present invention, and esterifying the methacrylic acid. According to these methods, methacrylic acid obtained by oxidation of methacrolein can be used to obtain methacrylic acid ester. The alcohol to be reacted with methacrylic acid is not particularly limited, and examples thereof include methanol, ethanol, isopropanol, n-butanol, and isobutanol. Examples of the obtained methacrylate ester include methyl methacrylate, ethyl methacrylate, propyl methacrylate, butyl methacrylate, and the like. The reaction can be carried out in the presence of an acidic catalyst, such as a sulfonic acid type cation exchange resin. The reaction temperature is preferably 50 to 200 °C.

EXAMPLES

[0130]

Hereinafter, the present invention will be specifically described using Examples and Comparative Examples, but the present invention is not limited to these Examples.

[0131]

(Measurement of average length and average aspect ratio of crystals)

5 The average length and the average aspect ratio of crystals in the solid content were calculated by manually measuring the length in the major axis direction and the minor axis direction of at least 500 crystals using SEM (product name: JSM-7400F, manufactured by JEOL) and calculating the average values.

[0132]

10 (Measurement of pore diameter by molecular probe method)

Pore diameter of the metal oxide was calculated using the DA method after preprocessing the metal oxide at 300 °C, and an adsorb isotherm is created by the molecular probe method using CO₂, CH₄, or C₂H₆ (product name: BELSORP-MAX, manufactured by MicrotracBEL, Inc.).

15 [0133]

(Measurement of X-ray diffraction pattern)

X-ray diffraction pattern of the metal oxide was measured using a Cu-K α ray by an X-ray structural analyzer (product name: RINT Ultima+, manufactured by Rigaku, tube voltage: 40 kV, tube current: 20 mA). Regarding the obtained X-ray diffraction pattern, when diffraction peaks
20 were shown only at $2\theta = 22.1^\circ \pm 0.3^\circ$ and $45.2^\circ \pm 0.3^\circ$, it was specified to have the amorphous structure. In addition, when diffraction peaks were observed at $2\theta = 6.6^\circ \pm 0.3^\circ$, $7.9^\circ \pm 0.3^\circ$, $9.0^\circ \pm 0.3^\circ$, $26.4^\circ \pm 0.3^\circ$, $26.9^\circ \pm 0.3^\circ$, $27.2^\circ \pm 0.3^\circ$, and $27.4^\circ \pm 0.3^\circ$ other than $2\theta = 22.1^\circ \pm 0.3^\circ$ and $45.2^\circ \pm 0.3^\circ$, it was specified to have the orthorhombic crystal structure. Further, when
25 diffraction peaks were observed at $2\theta = 4.7^\circ \pm 0.3^\circ$, $8.3^\circ \pm 0.3^\circ$, $25.3^\circ \pm 0.3^\circ$, $25.7^\circ \pm 0.3^\circ$, $27.0^\circ \pm 0.3^\circ$, $27.9^\circ \pm 0.3^\circ$, and $28.3^\circ \pm 0.3^\circ$ other than $2\theta = 22.1^\circ \pm 0.3^\circ$ and $45.2^\circ \pm 0.3^\circ$, it was specified to have the trigonal crystal structure. Except for the amorphous structure, the crystal structure of orthorhombic, and the crystal structure of trigonal, the crystal structure was identified by performing the search-and-match analysis with the previously reported XRD pattern. The search-and-match analysis was performed using the previously reported XRD
30 pattern data recorded in ICDD2017 with analysis software JADE9. 8.

[0134]

(Calculation of molar ratio)

The molar ratio of each element in the metal oxide was calculated by dissolving the metal oxide component in ammonia water or an aqueous solution of hydrofluoric acid and analyzing it

by ICP atomic emission spectroscopy. Further, the molar ratio of the ammonium species was set to a value determined by analyzing the metal oxide by a Kjeldahl method. Note that when the solid content is collected by suction filtration, since some of the metal components elute to the filtrate side, the molar ratio calculated from the charge ratio of the raw material and the molar ratio calculated by performing the above-described analysis on the obtained metal oxide do not necessarily match each other.

[0135]

(Calculation of difference spectrum by FT-IR measurement)

FT-IR measurement (product name: FT/IR-6100, manufactured by JASCO) of the metal oxide was performed by the transmission method. First, a pellet of 40 to 50 mg of the metal oxide in a diameter of 20 mm was placed in the device, and the temperature was raised to 400 °C at 10 °C/min under helium flow, and pretreatment was performed for 10 minutes. Thereafter, the metal oxide was cooled to 100 °C, and the infrared absorption spectrum was measured (FT-IR measurement 1). Then, the metal oxide was held under a water vapor atmosphere of 20% by volume for 10 seconds, and methacrolein was further introduced so as to have a methacrolein atmosphere of 2.0% by volume or more, and after the flowing gas was switched to oxygen and held for 60 minutes, the infrared absorption spectrum was measured (FT-IR measurement 2). The difference spectrum was calculated by subtracting the infrared absorption spectrum obtained by FT-IR measurement 1 from the infrared absorption spectrum obtained by FT-IR measurement 2.

[0136]

(Measurement of BET-specific surface area)

The BET-specific surface area S of the metal oxide was calculated using the BET method after pretreatment of the metal oxide at 300 °C by creating an adsorption isotherm for nitrogen (product name: BELSORP-MAX, manufactured by MicrotracBEL).

[0137]

(Analysis of raw material gas and product)

Analysis of the raw material gas and the product were performed using gas chromatography (device: GC-14B manufactured by Shimadzu Corporation, column: Porapak-QS). From the results of gas chromatography, the conversion of methacrolein, the selectivity of methacrylic acid produced and the yield of methacrylic acid were determined by the following formula.

$$\text{Methacrolein conversion (\%)} = (\beta/\alpha) \times 100$$

$$\text{Methacrylic acid selectivity (\%)} = (\gamma/\beta) \times 100$$

$$\text{Methacrylic acid yield (\%)} = (\gamma/\alpha) \times 100$$

In the above formulae, α represents the number of moles of supplied methacrolein, β represents the number of moles of reacted methacrolein, and γ represents the number of moles of methacrylic acid produced.

5 [0138]

[Production Example 1]

To a solution obtained by adding 8.83 g of ammonium heptamolybdate 4 hydrate to 120 g of pure water and stirring at room temperature, a solution obtained by adding 3.29 g of vanadyl sulfate to 120 g of pure water and stirring at room temperature was mixed and stirred for 10 minutes. The pH at this time was 3.19. The resulting solution after mixing was transferred into an autoclave made of Teflon in which a Teflon sheet was placed in advance, and bubbling was performed at a nitrogen flow rate of 50 l/min for 10 minutes. Thereafter, the production of a solid content using a hydrothermal method was carried out in an oven at 175 °C for 48 hours. Thereafter, the solid content was collected by suction filtration and dried in an oven at 80 °C to remove water.

15

[0139]

Subsequently, the solid content obtained after drying was mixed with 1.26 g of oxalic acid 2 hydrate and 25 g of pure water with respect to 1.0 g of the solid content, and dispersed and mixed at 60 °C for 30 minutes. Thereafter, while washing well with 500 g of pure water, the solid content was collected by suction filtration and dried in an oven at 80 °C to remove water.

20

[0140]

Subsequently, the obtained solid content after the dispersion treatment was subjected to a pulverization treatment using an agate mortar for 5 minutes. For the obtained solid content after the pulverization treatment, the average length and the average aspect ratio of crystals were measured. The results are shown in Table 1.

25

[0141]

Subsequently, the solid content after the pulverization treatment was calcined at 400 °C for 2 hours under a nitrogen flow of 50 ml/min to obtain a metal oxide.

[0142]

The obtained metal oxide was measured for pore diameter by molecular probe method. Further, the crystal structure was specified by X-ray diffraction measurement, and the molar ratio of each element was calculated by ICP atomic emission spectroscopy. The results are shown in Table 1. From these measurement results, it was confirmed that the obtained metal oxide had a cyclic structure that satisfied the formula (I) and in which each of the seven metal-oxygen

30

octahedrons (octahedral structures) was bonded by sharing oxygen at adjacent vertices. Further, it was confirmed that the metal oxide satisfied the formula (II). The mass ratio M2/M1 of inert ingredients, the difference spectrum by FT-IR measurement, and BET-specific surface area S for the metal oxide are shown in Table 1.

5 [0143]

[Production Example 2]

The solid content after the dispersion treatment was obtained in the same manner as in Production Example 1. For the solid content after the dispersion treatment, no pulverization treatment was performed to measure the average length and average aspect ratio of crystals. The results are shown in Table 1.

10 [0144]

Subsequently, the solid content after the dispersion treatment was calcined in the same manner as in Production Example 1 to obtain a metal oxide.

[0145]

15 The obtained metal oxide was measured for pore diameter by molecular probe method. Further, the crystal structure was specified by X-ray diffraction measurement, and the molar ratio of each element was calculated by ICP atomic emission spectroscopy. The results are shown in Table 1. From these measurement results, it was confirmed that the obtained metal oxide had a cyclic structure that satisfied the formula (I) and in which each of the seven metal-oxygen octahedrons (octahedral structures) was bonded by sharing oxygen at adjacent vertices. Further, it was confirmed that the metal oxide satisfied the formula (II). The mass ratio M2/M1 of inert ingredients, the difference spectrum by FT-IR measurement, and BET-specific surface area S for the metal oxide are shown in Table 1.

20 [0146]

25 [Production Example 3]

To a solution obtained by adding 8.83 g of ammonium heptamolybdate 4 hydrate to 120 g of pure water and stirring at room temperature, a solution obtained by adding 3.29 g of vanadyl sulfate to 120 g of pure water and stirring at room temperature was mixed and stirred for 10 minutes. Subsequently, 2 M sulfuric acid was added to adjust the pH to 2.30. The resulting solution after mixing was transferred into an autoclave made of Teflon in which a Teflon sheet was placed in advance, and bubbling was performed at a nitrogen flow rate of 50 l/min for 10 minutes. Thereafter, the production of a solid content using a hydrothermal method was carried out in an oven at 175 °C for 20 hours. Thereafter, the solid content was collected by suction filtration and dried in an oven at 80 °C to remove water.

30

[0147]

Subsequently, the solid content obtained after drying was mixed with 1.26 g of oxalic acid 2 hydrate and 25 g of pure water with respect to 1.0 g of the solid content, and dispersed and mixed at 60 °C for 30 minutes. Thereafter, while washing well with 500 g of pure water, the solid content was collected by suction filtration and dried in an oven at 80 °C to remove water.

[0148]

Subsequently, the solid content obtained after the dispersion treatment was subjected to a pulverization treatment using an agate mortar for 5 minutes. For the obtained solid content after the pulverization treatment, the average length and the average aspect ratio of crystals were measured. The results are shown in Table 1.

[0149]

Subsequently, the solid content after the pulverization treatment was calcined in the same manner as in Production Example 1 to obtain a metal oxide.

[0150]

The obtained metal oxide was measured for pore diameter by molecular probe method. Further, the crystal structure was specified by X-ray diffraction measurement, and the molar ratio of each element was calculated by ICP atomic emission spectroscopy. The results are shown in Table 1. From these measurement results, it was confirmed that the obtained metal oxide had a cyclic structure that satisfied the formula (I) and in which each of the seven metal-oxygen octahedrons (octahedral structures) was bonded by sharing oxygen at adjacent vertices. Further, it was confirmed that the metal oxide satisfied the formula (II). The mass ratio M2/M1 of inert ingredients, the difference spectrum by FT-IR measurement, and BET-specific surface area S for the metal oxide are shown in Table 1.

[0151]

[Production Example 4]

To a solution obtained by adding 17.7 g of ammonium heptamolybdate 4 hydrate to 120 g of pure water and stirring at room temperature, a solution obtained by adding 6.58 g of vanadyl sulfate to 120 g of pure water and stirring at room temperature was mixed and stirred for 10 minutes. The pH at this time was 3.26. The resulting solution after mixing was transferred into an autoclave made of Teflon, and bubbling was performed at a nitrogen flow rate of 50 l/min for 10 minutes. Thereafter, the production of a solid content using a hydrothermal method was carried out in an oven at 175 °C for 48 hours. Thereafter, the solid content was collected by suction filtration and dried in an oven at 80 °C to remove water.

[0152]

Subsequently, the solid content obtained after drying was subjected to a pulverization treatment using an agate mortar for 5 minutes.

[0153]

Subsequently, the solid content after the pulverization treatment was calcined in the same manner as in Production Example 1 to obtain a metal oxide.

[0154]

The obtained metal oxide was measured for pore diameter by molecular probe method. Further, the crystal structure was specified by X-ray diffraction measurement, and the molar ratio of each element was calculated by ICP atomic emission spectroscopy. The results are shown in Table 1. From these measurement results, it was confirmed that the obtained metal oxide had a cyclic structure that satisfied the formula (I) and in which each of the seven metal-oxygen octahedrons (octahedral structures) was bonded by sharing oxygen at adjacent vertices. Further, it was confirmed that the metal oxide satisfied the formula (II) and had an amorphous structure showing diffraction peaks only at $2\theta = 22.1^\circ \pm 0.3^\circ$ and $45.2^\circ \pm 0.3^\circ$ in the X-ray diffraction pattern. The mass ratio M2/M1 of inert ingredients, the difference spectrum by FT-IR measurement, and BET-specific surface area S for the metal oxide are shown in Table 1.

[0155]

[Production Example 5]

21.594 g of molybdenum trioxide was added to a solution of 28.04 mL of a 70% ethylamine solution to which 28.04 g of pure water was added, and the molybdenum trioxide was completely dissolved, followed by evaporation to obtain a $(C_2H_5NH_3)Mo_3O_{10}$. To a solution obtained by dissolving 1.799 g of the obtained $(C_2H_5NH_3)Mo_3O_{10}$ in 20 g of pure water, a solution obtained by adding 0.658 g of vanadyl sulfate to 20 g of pure water and stirring at room temperature was mixed and stirred for 10 minutes. Subsequently, 0.327 g of bismuth oxychloride was added and stirred for an additional 10 minutes, and 2 M sulfuric acid was added to adjust the pH to 2.0. The resulting solution after mixing was transferred into an autoclave made of Teflon in which a Teflon sheet was placed in advance, and bubbling was performed at a nitrogen flow rate of 50 l/min for 10 minutes. Thereafter, while the autoclave was rotated at 1 rpm, a solid content was produced using a hydrothermal method in an oven at 175 °C for 48 hours. Thereafter, the solid content was collected by suction filtration and dried in an oven at 80 °C to remove water.

[0156]

Subsequently, the solid content obtained after drying was mixed with 20 ml of 1.2 M hydrochloric acid with respect to 1.0 g of the solid content, and dispersed and mixed at room

temperature for 30 minutes. Thereafter, while washing well with 1000 g of pure water, the solid content was collected by suction filtration and dried in an oven at 80 °C to remove water.

[0157]

Subsequently, the solid content obtained after the dispersion treatment was subjected to a pulverization treatment using an agate mortar for 5 minutes.

[0158]

Subsequently, the solid content after the pulverization treatment was calcined in the same manner as in Production Example 1 to obtain a metal oxide.

[0159]

The obtained metal oxide was measured for pore diameter by molecular probe method. Further, the crystal structure was specified by X-ray diffraction measurement, and the molar ratio of each element was calculated by ICP atomic emission spectroscopy. The results are shown in Table 1. From these measurement results, it was confirmed that the obtained metal oxide had a cyclic structure that satisfied the formula (I) and in which each of the seven metal-oxygen octahedrons (octahedral structures) was bonded by sharing oxygen at adjacent vertices. Further, it was confirmed that the metal oxide satisfied the formula (II). The mass ratio M2/M1 of inert ingredients, the molar ratio excluding oxygen, the difference spectrum by FT-IR measurement, and BET-specific surface area S for the metal oxide are shown in Table 1.

[0160]

[Production Example 6]

To a solution of 33.2 ml of a 40% methylamine was added 21.594 g of molybdenum trioxide, which was completely dissolved, followed by evaporation to obtain a $(\text{CH}_3\text{NH}_3)_6\text{Mo}_7\text{O}_{24}$. To a solution obtained by dissolving 1.780 g of the obtained $(\text{CH}_3\text{NH}_3)_6\text{Mo}_7\text{O}_{24}$ in 20 g of pure water, a solution obtained by adding 0.658 g of vanadyl sulfate to 20 g of pure water and stirring at room temperature was mixed and stirred for 10 minutes. Subsequently, 0.156 g of copper sulfate 5 hydrate was added and stirred for an additional 10 minutes. The pH at this time was 3.2. The resulting solution after mixing was transferred into an autoclave made of Teflon in which a Teflon sheet was placed in advance, and bubbling was performed at a nitrogen flow rate of 50 l/min for 10 minutes. Thereafter, while rotating the autoclave at 1 rpm, a solid content was produced using a hydrothermal method in an oven at 175 °C for 20 hours. Thereafter, the solid content was collected by suction filtration and dried in an oven at 80 °C to remove water.

[0161]

Subsequently, the solid content obtained after drying was mixed with 1.26 g of oxalic acid

2 hydrate and 25 g of pure water with respect to 1.0 g of the solid content, and dispersed and mixed at 60 °C for 30 minutes. Thereafter, while washing well with 500 g of pure water, the solid content was collected by suction filtration and dried in an oven at 80 °C to remove water.
[0162]

5 Subsequently, the solid content obtained after the dispersion treatment was subjected to a pulverization treatment using an agate mortar for 5 minutes.
[0163]

Subsequently, the solid content after the pulverization treatment was calcined in the same manner as in Production Example 1 to obtain a metal oxide.

10 [0164]

The obtained metal oxide was measured for pore diameter by molecular probe method. Further, the crystal structure was specified by X-ray diffraction measurement, and the molar ratio of each element was calculated by ICP atomic emission spectroscopy. The results are shown in Table 1. From these measurement results, it was confirmed that the obtained metal oxide had a
15 cyclic structure that satisfied the formula (I) and in which each of the seven metal-oxygen octahedrons (octahedral structures) was bonded by sharing oxygen at adjacent vertices. Further, it was confirmed that the metal oxide satisfied the formula (II). The mass ratio M2/M1 of inert ingredients, the difference spectrum by FT-IR measurement, and BET-specific surface area S for the metal oxide are shown in Table 1.

20 [0165]

[Production Example 7]

21.594 g of molybdenum trioxide was added to a solution prepared by adding 28.04 g of distilled water to 28.04 ml of a 70% ethylamine solution, and the molybdenum trioxide was completely dissolved, followed by evaporation to obtain a $(C_2H_5NH_3)Mo_3O_{10}$. To a solution
25 obtained by dissolving 1.799 g of the obtained $(C_2H_5NH_3)Mo_3O_{10}$ in 20 g of pure water, a solution obtained by adding 0.658 g of vanadyl sulfate to 20 g of pure water and stirring at room temperature was mixed and stirred for 10 minutes. Subsequently, 0.161 g of ammonium metatungstate was added and stirred for an additional 10 minutes. The pH at this time was 2.4. The resulting solution after mixing was transferred into an autoclave made of Teflon in which a
30 Teflon sheet was placed in advance, and bubbling was performed at a nitrogen flow rate of 50 l/min for 10 minutes. Thereafter, the production of a solid content using a hydrothermal method was carried out in an oven at 175 °C for 48 hours. Thereafter, the solid content was collected by suction filtration and dried in an oven at 80 °C to remove water.

[0166]

Subsequently, the solid content obtained after drying was mixed with 1.26 g of oxalic acid 2 hydrate and 25 g of pure water with respect to 1.0 g of the solid content, and dispersed and mixed at 60 °C for 30 minutes. Thereafter, while washing well with 500 g of pure water, the solid content was collected by suction filtration and dried in an oven at 80 °C to remove water.

5 [0167]

Subsequently, the solid content obtained after the dispersion treatment was subjected to a pulverization treatment using an agate mortar for 5 minutes.

[0168]

Subsequently, the solid content after the pulverization treatment was calcined in the same
10 manner as in Production Example 1 to obtain a metal oxide.

[0169]

The obtained metal oxide was measured for pore diameter by molecular probe method. Further, the crystal structure was specified by X-ray diffraction measurement, and the molar ratio of each element was calculated by ICP atomic emission spectroscopy. The results are shown in
15 Table 1. From these measurement results, it was confirmed that the obtained metal oxide had a cyclic structure that satisfied the formula (I) and in which each of the seven metal-oxygen octahedrons (octahedral structures) was bonded by sharing oxygen at adjacent vertices. Further, it was confirmed that the metal oxide satisfied the formula (II). The mass ratio M2/M1 of inert ingredients, the difference spectrum by FT-IR measurement, and BET-specific surface area S for
20 the metal oxide are shown in Table 1.

[0170]

[Production Example 8]

To a solution obtained by dissolving 1.780 g of $(\text{CH}_3\text{NH}_3)_6\text{Mo}_7\text{O}_{24}$ obtained in the same manner as in Production Example 6 into 20 g of pure water, a solution obtained by adding 0.642
25 g of vanadyl sulfate to 20 g of pure water and stirring at room temperature was mixed and stirred for 10 minutes. Subsequently, 0.176 g of iron sulfate 7 hydrate was added and stirred for an additional 10 minutes. The pH at this time was 2.84. The resulting solution after mixing was transferred into an autoclave made of Teflon, and bubbling was performed at a nitrogen flow rate of 50 l/min for 10 minutes. Thereafter, while rotating the autoclave at 1 rpm, a solid content was
30 produced using a hydrothermal method in an oven at 175 °C for 20 hours. Thereafter, the solid content was collected by suction filtration and dried in an oven at 80 °C to remove water.

[0171]

Subsequently, the solid content obtained after drying was mixed with 1.26 g of oxalic acid 2 hydrate and 25 g of pure water with respect to 1.0 g of the solid content, and dispersed and

mixed at 60 °C for 30 minutes. Thereafter, while washing well with 500 g of pure water, the solid content was collected by suction filtration and dried in an oven at 80 °C to remove water. [0172]

Subsequently, the solid content obtained after the dispersion treatment was subjected to a pulverization treatment using an agate mortar for 5 minutes. [0173]

Subsequently, the solid content after the pulverization treatment was calcined in the same manner as in Production Example 1 to obtain a metal oxide. [0174]

10 The obtained metal oxide was measured for pore diameter by molecular probe method. Further, the crystal structure was specified by X-ray diffraction measurement, and the molar ratio of each element was calculated by ICP atomic emission spectroscopy. The results are shown in Table 1. From these measurement results, it was confirmed that the obtained metal oxide had a cyclic structure that satisfied the formula (I) and in which each of the seven metal-oxygen
15 octahedrons (octahedral structures) was bonded by sharing oxygen at adjacent vertices. Further, it was confirmed that the metal oxide satisfied the formula (II). The mass ratio M2/M1 of inert ingredients and the difference spectrum by FT-IR measurement are shown in Table 1. [0175]

[Production Example 9]

20 The solid content after the pulverization treatment obtained in the same manner as in Production Example 1 is calcined at 400 °C for 2 hours under an air flow of 50 ml/min, and is further calcined at 550 °C for 2 hours under a nitrogen flow of 50 ml/min to obtain a metal oxide. [0176]

25 The obtained metal oxide was measured for pore diameter by molecular probe method. Further, the crystal structure was specified by X-ray diffraction measurement, and the molar ratio of each element was calculated by ICP atomic emission spectroscopy. The results are shown in Table 1. From these measurement results, it was confirmed that the obtained metal oxide did not have a cyclic structure in which each of the seven metal-oxygen octahedrons (octahedral
30 structures) was bonded by sharing oxygen at adjacent vertices. The mass ratio M2/M1 of inert ingredients, a molar ratio excluding oxygen, the difference spectrum by FT-IR measurement, and BET-specific surface area S for the metal oxide are shown in Table 1. [0177]

[Production Example 10]

To a solution obtained by adding 1.766 g of ammonium heptamolybdate 4 hydrate to 120 g of pure water and stirring at room temperature, a solution obtained by adding 0.658 g of vanadyl sulfate to 20 g of pure water and stirring at room temperature was mixed and stirred for 10 minutes. Subsequently, 2 M sulfuric acid was added to adjust the pH to 1.20. The resulting solution after mixing was transferred into an autoclave made of Teflon, and bubbling was performed at a nitrogen flow rate of 50 l/min for 10 minutes. Thereafter, the production of a solid content using a hydrothermal method was carried out in an oven at 175 °C for 20 hours. Thereafter, the solid content was collected by suction filtration and dried in an oven at 80 °C to remove water.

[0178]

Subsequently, the solid content obtained after drying was subjected to a pulverization treatment using an agate mortar for 5 minutes.

[0179]

Subsequently, the solid content after the pulverization treatment was calcined at 400 °C for 2 hours under a nitrogen flow of 50 ml/min to obtain a metal oxide.

[0180]

The obtained metal oxide was measured for pore diameter by molecular probe method. Further, X-ray diffraction measurement was performed to identify the crystal structure from the X-ray diffraction pattern obtained. The results are shown in Table 1. From these measurement results, it was confirmed that the obtained metal oxide did not have a cyclic structure in which each of the seven metal-oxygen octahedrons (octahedral structures) was bonded by sharing oxygen at adjacent vertices. The mass ratio M2/M1 of inert ingredients, a molar ratio excluding oxygen and the difference spectrum by FT-IR measurement for the metal oxide are shown in Table 1.

[0181]

[Production Example 11]

To a solution obtained by adding 1.766 g of ammonium heptamolybdate 4 hydrate to 20 g of pure water and stirring at room temperature, a solution obtained by adding 0.159 g of ammonium metavanadate to 20 g of pure water and stirring at room temperature was mixed and stirred for 10 minutes. The pH of the resulting solution was 2.21. The obtained solution after mixing was evaporated to recover the solid content obtained and dried in an oven at 80 °C to remove water.

[0182]

Subsequently, the solid content obtained after drying was subjected to a pulverization

treatment using an agate mortar for 5 minutes.

[0183]

Subsequently, the solid content after the pulverization treatment was calcined in the same manner as in Production Example 1 to obtain a metal oxide.

5 [0184]

For the obtained metal oxide, measurement of pore diameter by a molecular probe method, and calculation of the molar ratio of each element by ICP atomic emission spectroscopy were performed. The results are shown in Table 1. From these measurement results, it was confirmed that the obtained metal oxide did not have a cyclic structure in which each of the seven metal-
 10 oxygen octahedrons (octahedral structures) was bonded by sharing oxygen at adjacent vertices. In addition, X-ray diffraction measurement was performed, and a crystallographic structure analysis was performed from the resulting X-ray diffraction pattern, and it was shown that the obtained metal oxide was a mixture containing at least three compounds of MoO_3 , $(\text{V}_{0.12}\text{Mo}_{0.88})\text{O}_{2.94}$, and $\text{V}_{0.95}\text{Mo}_{0.97}\text{O}_5$. The mass ratio M2/M1 of inert ingredients, a molar ratio
 15 excluding oxygen and the difference spectrum by FT-IR measurement for the metal oxide are shown in Table 1.

[0185]

[Production Example 12]

To a solution obtained by adding 5.30 g of ammonium heptamolybdate 4 hydrate to 30 g
 20 of pure water and stirring at room temperature, 1.40 g of antimony sulfate was added and stirred for 15 minutes. Subsequently, a solution obtained by adding 2.35 g of vanadyl sulfate to 20 g of pure water and stirring at room temperature was mixed and stirred for 5 minutes. The pH at this time was 1.80. The obtained solution after mixing was transferred into an autoclave made of Teflon, and the production of a solid content using a hydrothermal method was carried out in an
 25 oven at 175 °C for 24 hours while rotating the autoclave at 1 rpm. Thereafter, the solid content was collected by suction filtration and dried in an oven at 80 °C to remove water.

[0186]

Subsequently, the solid content obtained after drying was subjected to a pulverization treatment using an agate mortar for 5 minutes. For the solid content obtained after the
 30 pulverization treatment, the average length and the average aspect ratio of crystals were measured. The results are shown in Table 1.

[0187]

Subsequently, the solid content after the pulverization treatment was calcined in the same manner as in Production Example 1 to obtain a metal oxide.

[0188]

The obtained metal oxide was measured for pore diameter by molecular probe method. Further, the crystal structure was specified by X-ray diffraction measurement, and the molar ratio of each element was calculated by ICP atomic emission spectroscopy. The results are shown in Table 1. From these measurement results, it was confirmed that the obtained metal oxide had a cyclic structure that satisfied the formula (I) and in which each of the seven metal-oxygen octahedrons (octahedral structures) was bonded by sharing oxygen at adjacent vertices. Further, it was confirmed that the metal oxide satisfied the formula (II). The mass ratio M2/M1 of inert ingredients, the difference spectrum by FT-IR measurement and BET-specific surface area S for the metal oxide are shown in Table 1.

[0189]

[Production Example 13]

The solid content obtained after drying in the same manner as in Production Example 1 was subjected to a pulverization treatment using an agate mortar for 5 minutes. For the solid content obtained after the pulverization treatment, the average length and the average aspect ratio of crystals were measured. The results are shown in Table 1.

[0190]

Subsequently, the solid content after the pulverization treatment was calcined in the same manner as in Production Example 1 to obtain a metal oxide.

[0191]

The obtained metal oxide was measured for pore diameter by molecular probe method. Further, the crystal structure was specified by X-ray diffraction measurement, and the molar ratio of each element was calculated by ICP atomic emission spectroscopy. The results are shown in Table 1. From these measurement results, it was confirmed that the obtained metal oxide had a cyclic structure that satisfied the formula (I) and in which each of the seven metal-oxygen octahedrons (octahedral structures) was bonded by sharing oxygen at adjacent vertices. Further, it was confirmed that the metal oxide satisfied the formula (II). The mass ratio M2/M1 of inert ingredients and the difference spectrum by FT-IR measurement are shown in Table 1.

[0192]

[Production Example 14]

The solid content obtained after drying in the same manner as in Production Example 1 was calcined in the same manner as in Production Example 1 to obtain a metal oxide.

[0193]

The obtained metal oxide was measured for pore diameter by molecular probe method.

Further, the crystal structure was specified by X-ray diffraction measurement, and the molar ratio of each element was calculated by ICP atomic emission spectroscopy. The results are shown in Table 1. From these measurement results, it was confirmed that the obtained metal oxide had a cyclic structure that satisfied the formula (I) and in which each of the seven metal-oxygen octahedrons (octahedral structures) was bonded by sharing oxygen at adjacent vertices. Further, it was confirmed that the metal oxide satisfied the formula (II). The mass ratio M2/M1 of inert ingredients and the difference spectrum by FT-IR measurement are shown in Table 1.

[0194]

[Production Example 15]

To a solution obtained by adding 1.766 g of ammonium heptamolybdate 4 hydrate to 20 g of pure water and stirring at room temperature, a solution obtained by adding 0.642 g of vanadyl sulfate to 20 g of pure water and stirring at room temperature was mixed and stirred for 10 minutes. The pH at this time was 3.16. The obtained solution after mixing was evaporated to recover the solid content obtained and dried in an oven at 80 °C to remove water.

[0195]

Subsequently, the solid content obtained after drying was subjected to a pulverization treatment using an agate mortar for 5 minutes.

[0196]

Subsequently, the solid content after the pulverization treatment was calcined in the same manner as in Production Example 1 to obtain a metal oxide.

[0197]

The obtained metal oxide was measured for pore diameter by molecular probe method. Further, the crystal structure was specified by X-ray diffraction measurement, and the molar ratio of each element was calculated by ICP atomic emission spectroscopy. The results are shown in Table 1. From these measurement results, it was confirmed that the obtained metal oxide had a cyclic structure that satisfied the formula (I) and in which each of the seven metal-oxygen octahedrons (octahedral structures) was bonded by sharing oxygen at adjacent vertices. Further, it was confirmed that the metal oxide satisfied the formula (II) and had an amorphous structure showing diffraction peaks only at $2\theta = 22.1^\circ \pm 0.3^\circ$ and $45.2^\circ \pm 0.3^\circ$ in the X-ray diffraction pattern. The mass ratio M2/M1 of inert ingredients, the molar ratio excluding oxygen and the difference spectrum by FT-IR measurement for the metal oxide are shown in Table 1.

[0198]

[Examples 1 to 6]

Using the metal oxide obtained in Production Example 1 as a catalyst, 4.5 g of sea sand

was mixed with respect to 0.5 g of the catalyst and charged into the reactor. Subsequently, a raw material gas composed of methacrolein, oxygen, water vapor, and nitrogen was supplied to carry out the reaction. The composition of the raw material gas, the supply conditions, the reaction temperature, and the reaction result are shown in Table 2.

5 [0199]

[Examples 7 to 14]

Using the metal oxide obtained in Production Example 1 as a catalyst, 4.5 g of sea sand was mixed with respect to 0.1 g of the catalyst and charged into the reactor. Subsequently, a raw material gas composed of methacrolein, oxygen, water vapor, and nitrogen was supplied to carry out the reaction. The composition of the raw material gas, the supply conditions, the reaction temperature, and the reaction result are shown in Table 2.

10

[0200]

[Examples 15 to 17]

Using the metal oxide obtained in Production Example 2 as a catalyst, 4.5 g of sea sand was mixed with respect to 0.5 g of the catalyst and charged into the reactor. Subsequently, a raw material gas composed of methacrolein, oxygen, water vapor, and nitrogen was supplied to carry out the reaction. The composition of the raw material gas, the supply conditions, the reaction temperature, and the reaction result are shown in Table 2.

15

[0201]

20 [Examples 18 to 20]

Using the metal oxide obtained in Production Example 3 as a catalyst, 4.5 g of sea sand was mixed with respect to 0.5 g of the catalyst and charged into the reactor. Subsequently, a raw material gas composed of methacrolein, oxygen, water vapor, and nitrogen was supplied to carry out the reaction. The composition of the raw material gas, the supply conditions, the reaction temperature, and the reaction result are shown in Table 2.

25

[0202]

[Examples 21 to 23]

Using the metal oxide obtained in Production Example 4 as a catalyst, 4.5 g of sea sand was mixed with respect to 0.5 g of the catalyst and charged into the reactor. Subsequently, a raw material gas composed of methacrolein, oxygen, water vapor, and nitrogen was supplied to carry out the reaction. The composition of the raw material gas, the supply conditions, the reaction temperature, and the reaction result are shown in Table 2.

30

[0203]

[Examples 24 to 28]

Using the metal oxide obtained in Production Example 5 as a catalyst, 4.5 g of sea sand was mixed with respect to 0.5 g of the catalyst and charged into the reactor. Subsequently, a raw material gas composed of methacrolein, oxygen, water vapor, and nitrogen was supplied to carry out the reaction. The composition of the raw material gas, the supply conditions, the reaction temperature, and the reaction result are shown in Table 3.

[0204]

[Examples 29 to 32]

Using the metal oxide obtained in Production Example 6 as a catalyst, 4.5 g of sea sand was mixed with respect to 0.5 g of the catalyst and charged into the reactor. Subsequently, a raw material gas composed of methacrolein, oxygen, water vapor, and nitrogen was supplied to carry out the reaction. The composition of the raw material gas, the supply conditions, the reaction temperature, and the reaction result are shown in Table 3.

[0205]

[Examples 33 to 37]

Using the metal oxide obtained in Production Example 7 as a catalyst, 4.5 g of sea sand was mixed with respect to 0.5 g of the catalyst and charged into the reactor. Subsequently, a raw material gas composed of methacrolein, oxygen, water vapor, and nitrogen was supplied to carry out the reaction. The composition of the raw material gas, the supply conditions, the reaction temperature, and the reaction result are shown in Table 3.

[0206]

[Examples 38 to 40]

Using the metal oxide obtained in Production Example 8 as a catalyst, 4.5 g of sea sand was mixed with respect to 0.5 g of the catalyst and charged into the reactor. Subsequently, a raw material gas composed of methacrolein, oxygen, water vapor, and nitrogen was supplied to carry out the reaction. The composition of the raw material gas, the supply conditions, the reaction temperature, and the reaction result are shown in Table 3.

[0207]

[Comparative Examples 1 to 3]

Using the metal oxide obtained in Production Example 9 as a catalyst, 4.5 g of sea sand was mixed with respect to 0.5 g of the catalyst and charged into the reactor. Subsequently, a raw material gas composed of methacrolein, oxygen, water vapor, and nitrogen was supplied to carry out the reaction. The composition of the raw material gas, the supply conditions, the reaction temperature, and the reaction result are shown in Table 3.

[0208]

[Comparative Examples 4 to 6]

Using the metal oxide obtained in Production Example 10 as a catalyst, 4.5 g of sea sand was mixed with respect to 0.5 g of the catalyst and charged into the reactor. Subsequently, a raw material gas composed of methacrolein, oxygen, water vapor, and nitrogen was supplied to carry out the reaction. The composition of the raw material gas, the supply conditions, the reaction temperature, and the reaction result are shown in Table 3.

[0209]

[Comparative Examples 7 to 8]

Using the metal oxide obtained in Production Example 11 as a catalyst, 4.5 g of sea sand was mixed with respect to 0.5 g of the catalyst and charged into the reactor. Subsequently, a raw material gas composed of methacrolein, oxygen, water vapor, and nitrogen was circulated to carry out the reaction. The composition of the raw material gas, the supply conditions, the reaction temperature, and the reaction result are shown in Table 3.

[0210]

[Examples 41 to 45]

Using the metal oxide obtained in Production Example 12 as a catalyst, 4.5 g of sea sand was mixed with respect to 0.5 g of the catalyst and charged into the reactor. Subsequently, a raw material gas composed of methacrolein, oxygen, water vapor, and nitrogen was circulated to carry out the reaction. The composition of the raw material gas, the supply conditions, the reaction temperature, and the reaction result are shown in Table 4.

[0211]

[Examples 46 to 50]

Using the metal oxide obtained in Production Example 13 as a catalyst, 4.5 g of sea sand was mixed with respect to 0.5 g of the catalyst and charged into the reactor. Subsequently, a raw material gas composed of methacrolein, oxygen, water vapor, and nitrogen was circulated to carry out the reaction. The composition of the raw material gas, the supply conditions, the reaction temperature, and the reaction result are shown in Table 4.

[0212]

[Examples 51 to 54]

Using the metal oxide obtained in Production Example 14 as a catalyst, 4.5 g of sea sand was mixed with respect to 0.5 g of the catalyst and charged into the reactor. Subsequently, a raw material gas composed of methacrolein, oxygen, water vapor, and nitrogen was circulated to carry out the reaction. The composition of the raw material gas, the supply conditions, the reaction temperature, and the reaction result are shown in Table 4.

[0213]

[Examples 55 and 56]

Using the metal oxide obtained in Production Example 15 as a catalyst, 4.5 g of sea sand was mixed with respect to 0.5 g of the catalyst and charged into the reactor. Subsequently, a raw material gas composed of methacrolein, oxygen, water vapor, and nitrogen was circulated to carry out the reaction. The composition of the raw material gas, the supply conditions, the reaction temperature, and the reaction result are shown in Table 4.

[0214]

[Example 57]

Using the metal oxide obtained in Production Example 1 as a catalyst, 4.5 g of sea sand was mixed with respect to 0.5 g of the catalyst and charged into the reactor. Subsequently, a raw material gas composed of methacrolein, oxygen, water vapor, and nitrogen was circulated to carry out the reaction. The composition of the raw material gas, the supply conditions, the reaction temperature, and the reaction result are shown in Table 4.

[0215]

[Example 58]

Using the metal oxide obtained in Production Example 1 as a catalyst, 4.5 g of sea sand was mixed with respect to 0.5 g of the catalyst and charged into the reactor. Subsequently, a raw material gas composed of methacrolein, oxygen, and nitrogen was circulated to carry out the reaction. The composition of the raw material gas, the supply conditions, the reaction temperature, and the reaction result are shown in Table 4.

[0216]

[Examples 59 to 60]

Using the metal oxide obtained in Production Example 2 as a catalyst, 4.5 g of sea sand was mixed with respect to 0.5 g of the catalyst and charged into the reactor. Subsequently, a raw material gas composed of methacrolein, oxygen, water vapor, and nitrogen was circulated to carry out the reaction. The composition of the raw material gas, the supply conditions, the reaction temperature, and the reaction result are shown in Table 4.

[0217]

Table 1

(Table 1)

	Crystal in solid content		Pore diameter of metal oxide [nm]	X-ray diffraction pattern of metal oxide		Crystal structure of metal oxide	Composition of metal oxide (excluding oxygen) [molar ratio]							M2/M1	Difference spectrum of metal oxide			S [m ² /g]
	Average length [μm]	Average aspect ratio		22.1°±0.3°	45.2°±0.3°		Mo	V	Bi	Cu	W	Fe	Sb		1557±10 cm ⁻¹	1456±10 cm ⁻¹	1374±10 cm ⁻¹	
Production Example 1	1.8	4.5	0.40	with peak	with peak	orthorhombic	1	0.34	—	—	—	—	—	0	with peak	with peak	with peak	40
Production Example 2	7.9	22.3	0.40	with peak	with peak	orthorhombic	1	0.34	—	—	—	—	—	0	with peak	with peak	with peak	28.5
Production Example 3	0.2	2.9	0.40	with peak	with peak	trigonal	1	0.36	—	—	—	—	—	0	with peak	with peak	with peak	23.2
Production Example 4			0.40	with peak	with peak	amorphous	1	0.38	—	—	—	—	—	0	with peak	with peak	with peak	5.1
Production Example 5			0.40	with peak	with peak	orthorhombic	1	0.31	0.04	—	—	—	—	0	with peak	with peak	with peak	47.3
Production Example 6			0.40	with peak	with peak	orthorhombic	1	0.38	—	0.05	—	—	—	0	with peak	with peak	with peak	20.2
Production Example 7			0.40	with peak	with peak	trigonal	1	0.30	—	—	0.07	—	—	0	with peak	with peak	with peak	21.4
Production Example 8			0.40	with peak	with peak	orthorhombic	1	0.24	—	—	—	0.09	—	0	with peak	with peak	with peak	
Production Example 9	1.8	4.5	<0.30	with peak	with peak	tetragonal	1	0.34	—	—	—	—	—	0	no peak	no peak	no peak	3
Production Example 10			<0.30	no peak	no peak	pseudo hexagonal	1	0.13	—	—	—	—	—	0	no peak	no peak	no peak	
Production Example 11			<0.30	no peak	no peak	—	1	0.06	—	—	—	—	—	0	no peak	no peak	no peak	
Production Example 12			0.40	with peak	with peak	orthorhombic	1	0.31	—	—	—	—	0.15	0	with peak	with peak	with peak	27.3
Production Example 13			0.40	with peak	with peak	orthorhombic	1	0.38	—	—	—	—	—	0	with peak	with peak	with peak	10
Production Example 14			0.40	with peak	with peak	orthorhombic	1	0.38	—	—	—	—	—	0	with peak	with peak	with peak	6.8
Production Example 15			0.40	with peak	with peak	amorphous	1	0.25	—	—	—	—	—	0	with peak	with peak	with peak	

[0218]

Table 2

(Table 2)

	Metal oxide	Catalyst loading	Reaction temperature	Supply conditions of raw material gas			Composition of raw material gas [molar ratio]				Methacrylic acid yield [%]
		W [g]	[°C]	F [mol/h]	W/F	F/(S×W)	Methacrolein	Oxygen	Water vapor	Nitrogen	
Example 1	Production Example 1	0.5	305.5	0.001875	266.7	0.000094	2.7	6.6	20.5	70.3	29.1
Example 2	Production Example 1	0.5	284.5	0.001875	266.7	0.000094	2.7	6.6	20.5	70.3	40.7
Example 3	Production Example 1	0.5	242.8	0.001875	266.7	0.000094	2.7	6.6	20.5	70.3	23.2
Example 4	Production Example 1	0.5	219.4	0.001875	266.7	0.000094	2.7	6.6	20.5	70.3	18.2
Example 5	Production Example 1	0.5	300.0	0.001875	266.7	0.000094	3.0	6.0	15.0	76.0	30.7
Example 6	Production Example 1	0.5	290.0	0.001875	266.7	0.000094	3.0	6.0	15.0	76.0	28.9
Example 7	Production Example 1	0.1	280.0	0.000804	124.4	0.000201	0.6	3.7	10.0	85.7	19.1
Example 8	Production Example 1	0.1	280.0	0.002143	46.7	0.000536	1.6	3.6	11.0	83.8	10.2
Example 9	Production Example 1	0.1	280.0	0.002143	46.7	0.000536	1.6	3.2	12.5	82.7	11.5
Example 10	Production Example 1	0.1	280.0	0.002143	46.7	0.000536	1.6	7.0	12.5	78.9	13.2
Example 11	Production Example 1	0.1	280.0	0.002143	46.7	0.000536	1.6	10.0	12.0	76.4	15.7
Example 12	Production Example 1	0.1	280.0	0.002143	46.7	0.000536	1.6	3.7	7.0	87.7	10.4
Example 13	Production Example 1	0.1	280.0	0.002143	46.7	0.000536	1.6	3.6	24.0	70.8	14.6
Example 14	Production Example 1	0.1	280.0	0.002143	46.7	0.000536	1.6	3.6	41.0	53.8	13.6
Example 15	Production Example 2	0.5	290.0	0.001875	266.7	0.000132	3.0	6.0	15.0	76.0	26.3
Example 16	Production Example 2	0.5	280.0	0.001875	266.7	0.000132	3.0	6.0	15.0	76.0	23.8
Example 17	Production Example 2	0.5	270.0	0.001875	266.7	0.000132	3.0	6.0	15.0	76.0	19.7
Example 18	Production Example 3	0.5	284.4	0.001875	266.7	0.000162	2.7	6.6	20.5	70.3	13.7
Example 19	Production Example 3	0.5	263.4	0.001875	266.7	0.000162	2.7	6.6	20.5	70.3	27.3
Example 20	Production Example 3	0.5	242.8	0.001875	266.7	0.000162	2.7	6.6	20.5	70.3	20.1
Example 21	Production Example 4	0.5	303.8	0.001875	266.7	0.000735	2.7	6.6	20.5	70.3	34.0
Example 22	Production Example 4	0.5	283.4	0.001875	266.7	0.000735	2.7	6.6	20.5	70.3	30.3
Example 23	Production Example 4	0.5	242.4	0.001875	266.7	0.000735	2.7	6.6	20.5	70.3	13.4

[0219]

Table 3

(Table 3)

	Metal oxide	Catalyst loading	Reaction temperature	Supply conditions of raw material gas			Composition of raw material gas [molar ratio]				Methacrylic acid yield [%]
		W [g]	[°C]	F [mol/h]	W/F	F/(S×W)	Methacrolein	Oxygen	Water vapor	Nitrogen	
Example 24	Production Example 5	0.5	311.2	0.001875	266.7	0.000079	2.7	6.6	20.5	70.3	15.4
Example 25	Production Example 5	0.5	300.3	0.001875	266.7	0.000079	2.7	6.6	20.5	70.3	20.1
Example 26	Production Example 5	0.5	289.0	0.001875	266.7	0.000079	2.7	6.6	20.5	70.3	27.9
Example 27	Production Example 5	0.5	266.0	0.001875	266.7	0.000079	2.7	6.6	20.5	70.3	32.7
Example 28	Production Example 5	0.5	243.9	0.001875	266.7	0.000079	2.7	6.6	20.5	70.3	16.7
Example 29	Production Example 6	0.5	308.1	0.001875	266.7	0.000186	2.7	6.6	20.5	70.3	22.9
Example 30	Production Example 6	0.5	296.4	0.001875	266.7	0.000186	2.7	6.6	20.5	70.3	24.6
Example 31	Production Example 6	0.5	285.4	0.001875	266.7	0.000186	2.7	6.6	20.5	70.3	22.9
Example 32	Production Example 6	0.5	261.0	0.001875	266.7	0.000186	2.7	6.6	20.5	70.3	12.9
Example 33	Production Example 7	0.5	310.3	0.001875	266.7	0.000175	2.7	6.6	20.5	70.3	16.9
Example 34	Production Example 7	0.5	299.0	0.001875	266.7	0.000175	2.7	6.6	20.5	70.3	26.1
Example 35	Production Example 7	0.5	288.0	0.001875	266.7	0.000175	2.7	6.6	20.5	70.3	31.5
Example 36	Production Example 7	0.5	266.5	0.001875	266.7	0.000175	2.7	6.6	20.5	70.3	23.9
Example 37	Production Example 7	0.5	245.5	0.001875	266.7	0.000175	2.7	6.6	20.5	70.3	13.1
Example 38	Production Example 8	0.5	292.3	0.001875	266.7		2.7	6.6	20.5	70.3	15.1
Example 39	Production Example 8	0.5	270.9	0.001875	266.7		2.7	6.6	20.5	70.3	27.6
Example 40	Production Example 8	0.5	249.6	0.001875	266.7		2.7	6.6	20.5	70.3	23.1
Comparative Example 1	Production Example 9	0.5	300.8	0.001875	266.7	0.001250	2.7	6.6	20.5	70.3	7.5
Comparative Example 2	Production Example 9	0.5	280.7	0.001875	266.7	0.001250	2.7	6.6	20.5	70.3	5.9
Comparative Example 3	Production Example 9	0.5	240.6	0.001875	266.7	0.001250	2.7	6.6	20.5	70.3	1.6
Comparative Example 4	Production Example 10	0.5	300.9	0.001875	266.7		2.7	6.6	20.5	70.3	1.7
Comparative Example 5	Production Example 10	0.5	280.8	0.001875	266.7		2.7	6.6	20.5	70.3	1.4
Comparative Example 6	Production Example 10	0.5	240.7	0.001875	266.7		2.7	6.6	20.5	70.3	0.0
Comparative Example 7	Production Example 11	0.5	290.3	0.001875	266.7		2.7	6.6	20.5	70.3	4.7
Comparative Example 8	Production Example 11	0.5	270.4	0.001875	266.7		2.7	6.6	20.5	70.3	6.3

[0220]

Table 4

(Table 4)

	Metal oxide	Catalyst loading	Reaction temperature	Supply conditions of raw material gas			Composition of raw material gas [molar ratio]				Methacrylic acid yield [%]
		W [g]	[°C]	F [mol/h]	W/F	F/(S×W)	Methacrolein	Oxygen	Water vapor	Nitrogen	
Example 41	Production Example 12	0.5	308.0	0.001875	266.7	0.000137	2.7	6.6	20.5	70.3	38.4
Example 42	Production Example 12	0.5	287.4	0.001875	266.7	0.000137	2.7	6.6	20.5	70.3	44.0
Example 43	Production Example 12	0.5	265.3	0.001875	266.7	0.000137	2.7	6.6	20.5	70.3	35.7
Example 44	Production Example 12	0.5	244.5	0.001875	266.7	0.000137	2.7	6.6	20.5	70.3	22.5
Example 45	Production Example 12	0.5	244.5	0.001875	266.7	0.000137	2.7	6.6	20.5	70.3	11.0
Example 46	Production Example 13	0.5	319.0	0.001875	266.7	0.000375	2.7	6.6	20.5	70.3	32.2
Example 47	Production Example 13	0.5	295.0	0.001875	266.7	0.000375	2.7	6.6	20.5	70.3	40.1
Example 48	Production Example 13	0.5	273.0	0.001875	266.7	0.000375	2.7	6.6	20.5	70.3	36.3
Example 49	Production Example 13	0.5	253.0	0.001875	266.7	0.000375	2.7	6.6	20.5	70.3	19.4
Example 50	Production Example 13	0.5	232.0	0.001875	266.7	0.000375	2.7	6.6	20.5	70.3	14.8
Example 51	Production Example 14	0.5	318.0	0.001875	266.7	0.000551	2.7	6.6	20.5	70.3	33.7
Example 52	Production Example 14	0.5	295.0	0.001875	266.7	0.000551	2.7	6.6	20.5	70.3	35.7
Example 53	Production Example 14	0.5	273.0	0.001875	266.7	0.000551	2.7	6.6	20.5	70.3	28.4
Example 54	Production Example 14	0.5	253.0	0.001875	266.7	0.000551	2.7	6.6	20.5	70.3	19.1
Example 55	Production Example 15	0.5	306.2	0.001875	266.7		2.7	6.6	20.5	70.3	16.4
Example 56	Production Example 15	0.5	287.2	0.001875	266.7		2.7	6.6	20.5	70.3	11.6
Example 57	Production Example 1	0.5	317.0	0.001875	266.7	0.000094	2.7	6.6	20.5	70.3	18.8
Example 58	Production Example 1	0.5	280.0	0.001875	266.7	0.000094	2.7	6.6	0.0	90.7	12.8
Example 59	Production Example 2	0.5	318.0	0.001875	266.7	0.000132	2.7	6.6	20.5	70.3	29.8
Example 60	Production Example 2	0.5	291.0	0.001875	266.7	0.000132	2.7	6.6	20.5	70.3	35.9

[0221]

As shown in Tables 1 to 4, methacrylic acid was obtained in high yield in Examples 1 to 60 in which the metal oxide having the specific composition ratio containing at least molybdenum and including the specific cyclic structure was used as a catalyst. In addition, from the X-ray diffraction peaks, the metal oxides obtained in Production Examples 1, 2, 5, 6, 8, and 12 to 14 were identified as orthorhombic, the metal oxides obtained in Production Examples 3 and 7 were identified as trigonal, and the metal oxides obtained in Production Examples 4 and 15 were identified as amorphous structures.

On the other hand, in Comparative Examples 1 to 8 using the metal oxide not including the cyclic structure as a catalyst, the yield of methacrylic acid was lower than that of Examples.

[0222]

In Production Example 2, the metal oxide was obtained without performing the pulverization treatment on the solid content after drying in which an average length of crystals was 7.9 μm . That is, the metal oxide can be obtained by a simple method as compared with Production Example 1, and it can be expected that when such a metal oxide is used as a catalyst, an effect that a continuous operation time is improved in the production of methacrylic acid as described above can be obtained. This can also be inferred from Examples 1 to 4 and 57, and Examples 59 and 60, in which the reaction was carried out using the metal oxides obtained in Production Example 1 and Production Example 2 as catalysts at the same W/F and raw material gas composition. From Examples 1 to 4 and 57 using the metal oxide obtained in Production Example 1 as a catalyst, it can be seen that when the reaction temperature becomes high, the methacrylic acid yield decreases greatly, and in Example 57 in which the reaction temperature is 317.0 $^{\circ}\text{C}$, the methacrylic acid yield decreases up to 18.8%. On the other hand, from Examples 59 and 60 using the metal oxide obtained in Production Example 2 as a catalyst, it can be seen that a decrease in methacrylic acid yield is suppressed when the reaction temperature is high, and a methacrylic acid yield as high as 29.8% is maintained even in Example 59 in which the reaction temperature is 318.0 $^{\circ}\text{C}$. Therefore, when the average length of crystals in the solid content is within a specific range, it can be said that the specific cyclic structure can be stably maintained even at a high reaction temperature, and that the catalyst that is advantageous for continuous operation for a long period of time was obtained by a simple method.

Claims

[Claim 1]

A method for producing methacrylic acid, comprising: producing methacrylic acid by oxidation of methacrolein using a catalyst for producing methacrylic acid by oxidation of methacrolein, wherein the catalyst comprises a metal oxide containing molybdenum, and the metal oxide has a cyclic structure satisfying the following conditions (a) and (b):

(a) the cyclic structure satisfies the following formula (I):

(sum of number of moles of Mo, V, and X):(number of moles of O) = 7:35 (I),

where, in formula (I), Mo, V, and O represent molybdenum, vanadium, and oxygen, respectively; and X represents at least one element selected from the group consisting of niobium, tantalum, tungsten, titanium, aluminum, zirconium, chromium, manganese, iron, copper, cobalt, rhodium, nickel, palladium, platinum, phosphorus, arsenic, antimony, tellurium, bismuth, boron, indium, zinc, magnesium, and cerium; and

(b) the cyclic structure in which each of the seven metal-oxygen octahedrons (octahedral structures) is bonded by sharing oxygen at adjacent vertices;

and wherein the metal oxide satisfies the following condition (c):

(c) the metal oxide has a composition represented by the following formula (II):

$\text{Mo}_1\text{V}_c\text{X}_d\text{Z}_e(\text{NH}_4)_f\text{O}_g$ (II),

where, in formula (II), Mo, V, NH_4 , and O represent molybdenum, vanadium, an ammonium species, and oxygen, respectively; X represents at least one element selected from the group consisting of niobium, tantalum, tungsten, titanium, aluminum, zirconium, chromium, manganese, iron, copper, cobalt, rhodium, nickel, palladium, platinum, phosphorus, arsenic, antimony, tellurium, bismuth, boron, indium, zinc, magnesium, and cerium; Z represents at least one element selected from the group consisting of lithium, sodium, potassium, rubidium, cesium, and calcium; and c to g represent the molar ratio of each component, where $0 < c < 0.5$, $0 \leq d < 0.5$, $0 \leq e \leq 0.1$, $0 \leq f \leq 0.1$, and g is the molar ratio of oxygen required to satisfy the valence of each component.

[Claim 2]

The method for producing methacrylic acid according to claim 1, wherein the metal oxide satisfies the following condition (d):

(d) the metal oxide satisfies the following formula (III), where M1 is the mass of the metal oxide and M2 is the mass of inert ingredients contained in the metal oxide:

$0 \leq \text{M2/M1} < 0.05$ (III).

[Claim 3]

The method for producing methacrylic acid according to claim 1 or 2, wherein the metal oxide satisfies the following condition (e):

- (e) the metal oxide has absorption peaks at $1557 \pm 10 \text{ cm}^{-1}$, $1456 \pm 10 \text{ cm}^{-1}$, and $1374 \pm 10 \text{ cm}^{-1}$ in a difference spectrum between an infrared absorption spectrum obtained by FT-IR measurement of the metal oxide and an infrared absorption spectrum obtained by FT-IR measurement after holding the metal oxide under a methacrolein atmosphere of 2.0% by volume or more for 60 minutes.

[Claim 4]

- The method for producing methacrylic acid according to any one of claims 1 to 3, wherein the metal oxide satisfies the following condition (f):

(f) the metal oxide has a BET-specific surface area S of 1.5 to $60 \text{ m}^2/\text{g}$ calculated by nitrogen-adsorption.

[Claim 5]

- The method for producing methacrylic acid according to any one of claims 1 to 4, wherein the metal oxide satisfies the following condition (g):

(g) the metal oxide shows diffraction peaks at $2\theta = 22.1^\circ \pm 0.3^\circ$ and $45.2^\circ \pm 0.3^\circ$ in an X-ray diffraction pattern (using $\text{Cu-K}\alpha$ rays).

[Claim 6]

- The method for producing methacrylic acid according to claim 5, wherein the metal oxide satisfies the following condition (g1):

(g1) the metal oxide shows diffraction peaks only at $2\theta = 22.1^\circ \pm 0.3^\circ$ and $45.2^\circ \pm 0.3^\circ$ in an X-ray diffraction pattern (using $\text{Cu-K}\alpha$ rays).

[Claim 7]

- The method for producing methacrylic acid according to claim 5, wherein the metal oxide further shows diffraction peaks at $2\theta = 6.6^\circ \pm 0.3^\circ$, $7.9^\circ \pm 0.3^\circ$, $9.0^\circ \pm 0.3^\circ$, $26.4^\circ \pm 0.3^\circ$, $26.9^\circ \pm 0.3^\circ$, $27.2^\circ \pm 0.3^\circ$, and $27.4^\circ \pm 0.3^\circ$ under condition (g).

[Claim 8]

- The method for producing methacrylic acid according to claim 5, wherein the metal oxide further shows diffraction peaks at $2\theta = 4.7^\circ \pm 0.3^\circ$, $8.3^\circ \pm 0.3^\circ$, $25.3^\circ \pm 0.3^\circ$, $25.7^\circ \pm 0.3^\circ$, $27.0^\circ \pm 0.3^\circ$, $27.9^\circ \pm 0.3^\circ$, and $28.3^\circ \pm 0.3^\circ$ under condition (g).

[Claim 9]

The method for producing methacrylic acid according to any one of claims 1 to 8, wherein the catalyst for producing methacrylic acid is produced by a method comprising:

- (1) a step of heating an aqueous solution or slurry containing at least molybdenum at 80 to 300°C for 3 to 200 hours to produce a solid content; and
- (2) a step of calcining the solid content to obtain the metal oxide.

[Claim 10]

The method for producing methacrylic acid according to claim 7 or 8, wherein the catalyst for producing methacrylic acid is produced by a method comprising:

- (1) a step of heating an aqueous solution or slurry containing at least molybdenum at 80 to 300°C for 3 to 200 hours to produce a solid content;
- (1b) a step of dispersing the solid content in an aqueous oxalic acid solution, hydrochloric acid, ethylene glycol, or hydrogen peroxide solution to obtain the solid content; and
- (2b) a step of calcining the solid content obtained in (1b) to obtain the metal oxide.

15 [Claim 11]

The method for producing methacrylic acid according to claim 9 or 10, wherein the solid content satisfies the following conditions (h) and (i):

- (h) the solid content has an average length of crystals of 2 to 50 μm as observed by an electron microscope; and
 - (i) the solid content has an average aspect ratio of crystals of 2 to 30 as observed by an electron microscope,
- noting that average aspect ratio = (average length of crystals)/(average diameter of crystals).

[Claim 12]

25 The method for producing methacrylic acid according to any one of claims 1 to 11, wherein a gas having a composition represented by the following formula (IV) is supplied as a raw material gas:

$$\text{methacrolein: oxygen: water vapor: A} = \text{k:l:m:n} \quad (\text{IV}),$$

where, in formula (IV), A represents nitrogen or helium; k to n represent the molar ratio of each gas; and when $k + l + m + n = 100$, $0.5 < k < 8.0$, $2.0 < l < 20.0$ and $0 \leq m < 45$.

[Claim 13]

The method for producing methacrylic acid according to any one of claims 1 to 12, wherein the reaction temperature is 180 to 500°C and a raw material gas containing methacrolein is supplied so as to satisfy the following formula (V):

$$15 < W/F < 550 \quad (V),$$

where, in formula (V), W represents the mass (g) of the metal oxide charged in a reactor and F represents the feed amount (mol/h) of methacrolein per unit time.

[Claim 14]

5 The method for producing methacrylic acid according to any one of claims 1 to 13, wherein the reaction temperature is 180 to 500°C and a raw material gas containing methacrolein is supplied so as to satisfy the following formula (VI):

$$0.00002 < F/(S \times W) < 0.008 \quad (VI),$$

10 where, in formula (VI), S represents the BET-specific surface area (m²/g) of the metal oxide calculated by nitrogen-adsorption; W represents the mass (g) of the metal oxide charged in a reactor; and F represents the feed amount (mol/h) of methacrolein per unit time.

[Claim 15]

A method for producing methacrylic acid ester, comprising: producing methacrylic acid by the method according to any one of claims 1 to 14, and esterifying the methacrylic acid.

15 [Claim 16]

A method for producing methacrylic acid, comprising: producing methacrylic acid by oxidation of methacrolein using a catalyst for producing methacrylic acid by oxidation of methacrolein, wherein the catalyst comprises a metal oxide satisfying the following conditions (b') and (c):

20 (b') the metal oxide includes a cyclic structure in which each of the seven metal-oxygen octahedrons (octahedral structures) is bonded; and

(c) the metal oxide has a composition represented by the following formula (II):



25 where, in formula (II), Mo, V, NH₄, and O represent molybdenum, vanadium, an ammonium species, and oxygen, respectively; X represents at least one element selected from the group consisting of niobium, tantalum, tungsten, titanium, aluminum, zirconium, chromium, manganese, iron, copper, cobalt, rhodium, nickel, palladium, platinum, phosphorus, arsenic, antimony, tellurium, bismuth, boron, indium, zinc, magnesium, and cerium; Z represents at least one element selected from the group consisting of lithium, sodium, potassium, rubidium, cesium, and calcium; and c to g represent the molar ratio of each component, where $0 < c < 0.5$, $0 \leq d < 0.5$, $0 \leq e \leq 0.1$, $0 \leq f \leq 0.1$, and g is the molar ratio of oxygen required to satisfy the valence of each component.

[Claim 17]

The method for producing methacrylic acid according to claim 16, wherein the metal oxide satisfies the following condition (d):

(d) the metal oxide satisfies the following formula (III), where M1 is the mass of the metal oxide and M2 is the mass of inert ingredients contained in the metal oxide:

$$0 \leq M2/M1 < 0.05 \quad (\text{III}).$$

[Claim 18]

The method for producing methacrylic acid according to claim 16 or 17, wherein the metal oxide satisfies the following condition (e):

(e) the metal oxide has absorption peaks at $1557 \pm 10 \text{ cm}^{-1}$, $1456 \pm 10 \text{ cm}^{-1}$, and $1374 \pm 10 \text{ cm}^{-1}$ in a difference spectrum between an infrared absorption spectrum obtained by FT-IR measurement of the metal oxide and an infrared absorption spectrum obtained by FT-IR measurement after holding the metal oxide under a methacrolein atmosphere of 2.0% by volume or more for 60 minutes.

[Claim 19]

The method for producing methacrylic acid according to any one of claims 16 to 18, wherein the metal oxide satisfies the following condition (f):

(f) the metal oxide has a BET-specific surface area S of 1.5 to $60 \text{ m}^2/\text{g}$, as calculated by nitrogen-adsorption.

[Claim 20]

The method for producing methacrylic acid according to any one of claims 16 to 19, wherein the metal oxide satisfies the following condition (g):

(g) the metal oxide shows diffraction peaks at $2\theta = 22.1^\circ \pm 0.3^\circ$ and $45.2^\circ \pm 0.3^\circ$ in an X-ray diffraction pattern (using Cu-K α rays).

[Claim 21]

The method for producing methacrylic acid according to claim 20, wherein the metal oxide satisfies the following condition (g1):

(g1) the metal oxide shows diffraction peaks only at $2\theta = 22.1^\circ \pm 0.3^\circ$ and $45.2^\circ \pm 0.3^\circ$ in an X-ray diffraction pattern (using Cu-K α rays).

[Claim 22]

The method for producing methacrylic acid according to claim 20, wherein the metal oxide further shows diffraction peaks at $2\theta = 6.6^\circ \pm 0.3^\circ$, $7.9^\circ \pm 0.3^\circ$, $9.0^\circ \pm 0.3^\circ$, $26.4^\circ \pm 0.3^\circ$, $26.9^\circ \pm 0.3^\circ$, $27.2^\circ \pm 0.3^\circ$, and $27.4^\circ \pm 0.3^\circ$ under condition (g).

[Claim 23]

The method for producing methacrylic acid according to claim 20, wherein the metal oxide further shows diffraction peaks at $2\theta = 4.7^\circ \pm 0.3^\circ$, $8.3^\circ \pm 0.3^\circ$, $25.3^\circ \pm 0.3^\circ$, $25.7^\circ \pm 0.3^\circ$, $27.0^\circ \pm 0.3^\circ$, $27.9^\circ \pm 0.3^\circ$, and $28.3^\circ \pm 0.3^\circ$ under condition (g).

[Claim 24]

5 A method for producing methacrylic acid, comprising: producing methacrylic acid by oxidation of methacrolein using a catalyst for producing methacrylic acid by oxidation of methacrolein, wherein the catalyst comprises a metal oxide satisfying the following conditions (c) and (g1):

(c) the metal oxide has a composition represented by the following formula (II):

10 $\text{Mo}_1\text{V}_c\text{X}_d\text{Z}_e(\text{NH}_4)_f\text{O}_g$ (II),

where, in formula (II), Mo, V, NH_4 , and O represent molybdenum, vanadium, an ammonium species, and oxygen, respectively; X represents at least one element selected from the group consisting of niobium, tantalum, tungsten, titanium, aluminum, zirconium, chromium, manganese, iron, copper, cobalt, rhodium, nickel, palladium, platinum, phosphorus, arsenic, 15 antimony, tellurium, bismuth, boron, indium, zinc, magnesium, and cerium; Z represents at least one element selected from the group consisting of lithium, sodium, potassium, rubidium, cesium, and calcium; and c to g represent the molar ratio of each component, where $0 < c < 0.5$, $0 \leq d < 0.5$, $0 \leq e \leq 0.1$, $0 \leq f \leq 0.1$, and g is the molar ratio of oxygen required to satisfy the valence of each component; and

20 (g1) the metal oxide shows diffraction peaks only at $2\theta = 22.1^\circ \pm 0.3^\circ$ and $45.2^\circ \pm 0.3^\circ$ in an X-ray diffraction pattern (using Cu-K α rays);

wherein the metal oxide has a cyclic structure satisfying the following condition (a):

(a) the cyclic structure satisfies the following formula (I):

(sum of number of moles of Mo, V, and X):(number of moles of O) = 7:35 (I),

25 where, in formula (I), Mo, V, and O represent molybdenum, vanadium, and oxygen, respectively; and X represents at least one element selected from the group consisting of niobium, tantalum, tungsten, titanium, aluminum, zirconium, chromium, manganese, iron, copper, cobalt, rhodium, nickel, palladium, platinum, phosphorus, arsenic, antimony, tellurium, bismuth, boron, indium, zinc, magnesium, and cerium; and

30 wherein the metal oxide satisfies the following condition (b'):

(b') the metal oxide includes a cyclic structure in which each of the seven metal-oxygen octahedrons (octahedral structures) is bonded.

[Claim 25]

The method for producing methacrylic acid according to any one of claims 16 to 24, wherein the catalyst for producing methacrylic acid is produced by a method comprising:

(1) a step of heating an aqueous solution or slurry containing at least molybdenum at 80 to 300 °C for 3 to 200 hours to produce a solid content; and

5 (2) a step of calcining the solid content to obtain the metal oxide.

[Claim 26]

The method for producing methacrylic acid according to claim 22 or 23, wherein the catalyst for producing methacrylic acid is produced by a method comprising:

10 (1) a step of heating an aqueous solution or slurry containing at least molybdenum at 80 to 300 °C for 3 to 200 hours to produce a solid content;

(1b) a step of dispersing the solid content in an aqueous oxalic acid solution, hydrochloric acid, ethylene glycol, or an hydrogen peroxide solution to obtain the solid content; and

(2b) a step of calcining the solid content obtained in (1b) to obtain the metal oxide.

15 [Claim 27]

The method for producing methacrylic acid according to claim 25 or 26, wherein the solid content satisfies the following conditions (h) and (i):

(h) the solid content has an average length of crystals of 2 to 50 μm as observed by an electron microscope; and

20 (i) the solid content has an average aspect ratio of crystals of 2 to 30 as observed by an electron microscope,

noting that average aspect ratio = (average length of crystals)/(average diameter of crystals).

[Claim 28]

25 The method for producing methacrylic acid according to any one of claims 16 to 27, wherein a gas having a composition represented by the following formula (IV) is supplied as a raw material gas:

methacrolein:oxygen:water vapor:A = k:l:m:n (IV),

30 where, in formula (IV), A represents nitrogen or helium; k to n represent the molar ratio of each gas; and when $k + l + m + n = 100$, $0.5 < k < 8.0$, $2.0 < l < 20.0$ and $0 \leq m < 45$.

[Claim 29]

The method for producing methacrylic acid according to any one of claims 16 to 28, wherein the reaction temperature is 180 to 500 °C, and a raw material gas containing methacrolein is supplied so as to satisfy the following formula (V):

$$15 < W/F < 550 \quad (V),$$

where, in formula (V), W represents the mass (g) of the metal oxide charged in a reactor and F represents the feed amount (mol/h) of methacrolein per unit time.

[Claim 30]

5 The method for producing methacrylic acid according to any one of claims 16 to 29, wherein the reaction temperature is 180 to 500 °C, and a raw material gas containing methacrolein is supplied so as to satisfy the following formula (VI):

$$0.00002 < F/(S \times W) < 0.008 \quad (VI),$$

10 where, in formula (VI), S represents the BET-specific surface area (m²/g) of the metal oxide calculated by nitrogen-adsorption; W represents the mass (g) of the metal oxide charged in a reactor; and F represents the feed amount (mol/h) of methacrolein per unit time.

[Claim 31]

 A method for producing methacrylic acid ester, comprising: producing methacrylic acid by the method according to any one of claims 16 to 30, and esterifying the methacrylic acid.

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