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):

$Mo_1V_cX_dZ_e(NH_4)_fO_g$ (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 $0 < c < 0.5$, $0 \leqq d < 0.5$, $0 \leqq e \leqq 0.1$, $0 \leqq f \leqq 0.1$, 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:

$0 \leqq M2/M1 < 0.05$ (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 ± 10 cm^{-1}, 1456 ± 10 cm^{-1}, and 1374 ± 10 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 m^2/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 2θ = 22.1° ± 0.3° and 45.2° ± 0.3° in an X-ray diffraction pattern (using Cu-Kα 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 2θ = 22.1° ± 0.3° and 45.2° ± 0.3° in an X-ray diffraction pattern (using Cu-Kα rays).

[Claim 7]

The method for producing methacrylic acid according to claim 5, wherein the metal oxide further shows diffraction peaks at 2θ = 6.6° ± 0.3°, 7.9° ± 0.3°, 9.0° ± 0.3°, 26.4° ± 0.3°, 26.9° ± 0.3°, 27.2° ± 0.3°, and 27.4° ± 0.3° under condition (g).

[Claim 8]

The method for producing methacrylic acid according to claim 5, wherein the metal oxide further shows diffraction peaks at 2θ = 4.7° ± 0.3°, 8.3° ± 0.3°, 25.3° ± 0.3°, 25.7° ± 0.3°, 27.0° ± 0.3°, 27.9° ± 0.3°, and 28.3° ± 0.3° 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.

[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]

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:

methacrolein:oxygen:water vapor:A = k:l:m:n (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 $0 \leqq m < 45$.

[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):

$15 < W/F < 550$ (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]

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):

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

where, in 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.

[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.

[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):

(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):

$Mo_1V_cX_dZ_e(NH_4)_fO_g$ (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 $0 < c < 0.5$, $0 \leqq d < 0.5$, $0 \leqq e \leqq 0.1$, $0 \leqq f \leqq 0.1$, 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:

$0 \leqq M2/M1 < 0.05$ (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 ± 10 cm^{-1}, 1456 ± 10 cm^{-1}, and 1374 ± 10 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 m^2/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 $2\theta = 22.1° \pm 0.3°$ and $45.2° \pm 0.3°$ in an X-ray diffraction pattern (using Cu-Kα 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 $2\theta = 22.1° \pm 0.3°$ and $45.2° \pm 0.3°$ in an X-ray diffraction pattern (using Cu-Kα rays).

[Claim 22]

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

[Claim 23]

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

[Claim 24]

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):

$Mo_1V_cX_dZ_e(NH_4)_fO_g$ (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 $0 < c < 0.5$, $0 \leqq d < 0.5$, $0 \leqq e \leqq 0.1$, $0 \leqq f \leqq 0.1$, and g is the molar ratio of oxygen required to satisfy the valence of each component; and

(g1) the metal oxide shows diffraction peaks only at $2\theta = 22.1° \pm 0.3°$ and $45.2° \pm 0.3°$ in an X-ray diffraction pattern (using Cu-Kα 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),

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

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

(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:

(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.

[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

(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]

The method for producing methacrylic acid according to any one of claims16 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),

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 $0 \leqq m < 45$.

[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):

$15 < W/F < 550$ (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]

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):

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

where, in 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.

[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.