<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 thepH 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 ℃. When the heating temperature is 80 ℃ 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 ℃ or less, the methacrylic acid yield of the finally obtained catalyst is improved. The lower limit of the heating temperature is more preferably 120 ℃ or more, further preferably 175 ℃ or more. The upper limit of the heating temperature is more preferably 260 ℃ or less, further preferably 230 ℃ 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

Claims

[Claim 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):

(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 catalyst 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 catalyst 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 catalyst 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 catalyst 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 catalyst 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 catalyst for producing methacrylic acid according to claim 5, further showing 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 catalyst for producing methacrylic acid according to claim 5, further showing 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]

A method for producing the catalyst for producing methacrylic acid according to any one of claims 1 to 8, wherein the method for producing the catalyst for producing methacrylic acid comprises:

(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]

A method for producing the catalyst for producing methacrylic acid according to claim 7 or 8, wherein the method for producing the catalyst for producing methacrylic acid comprises:

(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 the catalyst 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]

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 claims 1 to 8.

[Claim 13]

A method for producing methacrylic acid, comprising: producing the catalyst for producing methacrylic acid by the method according to any one of claims 9 to 11, and producing methacrylic acid by oxidation of methacrolein using the catalyst for producing methacrylic acid.

[Claim 14]

The method for producing methacrylic acid according to claim 12 or 13, 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 15]

The method for producing methacrylic acid according to any one of claims 12 to 14, 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 16]

The method for producing methacrylic acid according to any one of claims 12 to 15, 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 17]

A method for producing methacrylic acid ester, comprising: esterifying methacrylic acid produced by the method according to any one of claims 12 to 16.

[Claim 18]

A method for producing methacrylic acid ester, comprising: producing methacrylic acid by the method according to any one of claims 12 to 16, and esterifying the methacrylic acid.

[Claim 19]

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 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 20]

The catalyst for producing methacrylic acid according to claim 19, 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 21]

The catalyst for producing methacrylic acid according to claim 19 or 20, 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 22]

The catalyst for producing methacrylic acid according to any one of claims 19 to 21, 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 23]

The catalyst for producing methacrylic acid according to any one of claims 19 to 22, 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 24]

The catalyst for producing methacrylic acid according to claim 23, 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 25]

The catalyst for producing methacrylic acid according to claim 23, further showing 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 26]

The catalyst for producing methacrylic acid according to claim 23, further showing 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 27]

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 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 2θ = 22.1° ± 0.3° and 45.2° ± 0.3° in an X-ray diffraction pattern (using Cu-Kα rays).

[Claim 28]

A method for producing the catalyst for producing methacrylic acid according to any one of claims 19 to 27, wherein the method for producing the catalyst for producing methacrylic acid comprises:

(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 29]

A method for producing the catalyst for producing methacrylic acid according to claim 25 or 26, wherein the method for producing the catalyst for producing methacrylic acid comprises:

(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 30]

The method for producing the catalyst for producing methacrylic acid according to claim 28 or 29, 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 31]

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 claims 19 to 27.

[Claim 32]

A method for producing methacrylic acid, comprising: producing the catalyst for producing methacrylic acid by the method according to any one of claims 28 to 30, and

producing methacrylic acid by oxidation of methacrolein using the catalyst for producing methacrylic acid.

[Claim 33]

The method for producing methacrylic acid according to claim 31 or 32, 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 34]

The method for producing methacrylic acid according to any one of claims 31 to 33, 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 35]

The method for producing methacrylic acid according to any one of claims 31 to 34, 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 36]

A method for producing methacrylic acid ester, comprising: esterifying methacrylic acid produced by the method according to any one of claims 31 to 35.

[Claim 37]

A method for producing methacrylic acid ester, comprising: producing methacrylic acid by the method according to any one of claims 31 to 35, and esterifying the methacrylic acid.