

DESCRIPTION

METHOD FOR PRODUCING CATALYST FOR METHACRYLIC ACID PRODUCTION, METHOD FOR PRODUCING METHACRYLIC ACID, AND METHOD FOR PRODUCING METHACRYLIC ACID ESTER

TECHNICAL FIELD

[0001] The present invention relates to a method for producing a catalyst for methacrylic acid production, a method for producing methacrylic acid, and a method for producing a methacrylic acid ester.

BACKGROUND ART

[0002] Heteropoly acid-based catalysts containing molybdenum and phosphorus are known as catalysts for methacrylic acid production to be used when producing methacrylic acid by gas phase catalytic oxidation of methacrolein with molecular oxygen. As such heteropoly acid-based catalysts, there are proton-type heteropoly acids in which the counter cation is proton and heteropoly acid salts in which some of the protons in proton-type heteropoly acids are substituted with cations other than protons. As heteropoly acid salts, an alkali metal salt in which the cation is an alkali metal ion and an ammonium salt in which the cation is an ammonium ion are known (hereinafter, a proton-type heteropoly acid is also referred to simply as a "heteropoly acid" and at least one kind selected from a proton-type heteropoly acid and a heteropoly acid salt is also referred to simply as a "heteropoly acid (salt)").

[0003] As a method for producing a catalyst for methacrylic acid production, for example, Patent Document 1 discloses a method for producing a catalyst for

methacrylic acid production which is for producing methacrylic acid by gas phase catalytic oxidation of methacrolein with molecular oxygen and contains predetermined atoms at predetermined atomic ratios, which includes (i) a step for preparing a solution or slurry (liquid I) containing at least molybdenum (Mo), phosphorus (P), and vanadium (V), (ii) a step for preparing a solution or slurry (liquid II) containing an ammonium radical, (iii) a step for preparing a liquid mixture of the liquid I and the liquid II by charging either liquid (PR liquid) of the liquid I or the liquid II into a tank (tank A) and charging the other liquid (LA liquid) into a continuous liquid surface region having an area to be from 0.01% to 10% with respect to the entire area of the liquid surface of the PR liquid charged in the tank A, and (iv) a step for drying and firing a solution or slurry containing a catalyst precursor containing all of the catalyst components.

PRIOR ART LITERATURE

PATENT LITERATURE

[0004] Patent Document 1: WO 2005/039760 A

SUMMARY OF THE INVENTION

PROBLEM TO BE SOLVED BY THE INVENTION

[0005] However, the catalyst for methacrylic acid production to be produced by the method disclosed in Patent Document 1 is desired to be further improved since the yield of methacrylic acid is not sufficient in the case of using the catalyst in the production of methacrylic acid. It is an object of the invention to provide a catalyst for methacrylic acid production, which has a high methacrylic acid yield.

MEANS FOR SOLVING PROBLEM

[0006] The invention is the following [1] to [18].

[0007] [1] A method for producing a catalyst for methacrylic acid production to be used when producing methacrylic acid by gas phase catalytic oxidation of methacrolein with molecular oxygen, including:

(1) a step for preparing a catalyst starting material liquid A containing at least molybdenum, phosphorus, and vanadium;

(2) a step for preparing a catalyst starting material liquid B containing a cation starting material; and

(3) a step for preparing a liquid containing a heteropoly acid having a Keggin-type structure or a salt of the heteropoly acid by adding one of the catalyst starting material liquid A or the catalyst starting material liquid B to the other and mixing the liquids together, in which

the following Formulas (i) and (ii) are satisfied in the step (3).

$$[0008] \quad 3.0 \leq T/(\sqrt[3]{V}) \leq 13.0 \quad (i)$$

$$0.01 \leq u_1 \leq 1.0 \quad (ii)$$

(In Formulas (i) and (ii), V represents a volume [m³] of the catalyst starting material liquid A, T represents the number of addition ports for adding the other liquid, and u₁ represents a volumetric flow rate [L/min] of the other liquid to be added.

Incidentally, u₁ represents an average value of volumetric flow rates of the other liquid to be added through the respective addition ports in a case where T is 2 or more.)

[0009] [2] A method for producing a catalyst for methacrylic acid production to be used when producing methacrylic acid by gas phase catalytic oxidation of methacrolein with molecular oxygen, including:

(1) a step for preparing a catalyst starting material liquid A containing at least molybdenum, phosphorus, and vanadium;

(2) a step for preparing a catalyst starting material liquid B containing a cation starting material; and

(3) a step for preparing a liquid containing a heteropoly acid having a Keggin-type structure or a salt of the heteropoly acid by adding the catalyst starting material liquid B to the catalyst starting material liquid A and mixing the liquids together, in which

the following Formulas (i) and (iii) are satisfied in the step (3).

$$[0010] \quad 3.0 \leq T/(\sqrt[3]{V}) \leq 13.0 \quad (i)$$

$$0.01 \leq u_2 \leq 8 \quad (iii)$$

(In Formulas (i) and (iii), V represents a volume [m³] of the catalyst starting material liquid A, T represents the number of addition ports for adding the catalyst starting material liquid B, and u₂ represents a flow rate [mol/min] of the cation starting material in the catalyst starting material liquid B. Incidentally, u₂ represents an average value of flow rates of the cation starting material in the catalyst starting material liquid B to be added through the respective addition ports in a case where T is 2 or more.)

[0011] [3] The method for producing a catalyst for methacrylic acid production according to [1] or [2], in which T is 2 or more in Formula (i) above.

[0012] [4] The method for producing a catalyst for methacrylic acid production according to [1], in which one of the catalyst starting material liquid A or the catalyst starting material liquid B is added into a vessel that contains the other and satisfies the following Formula (iv), and mixed with the other in the step (3).

$$[0013] \quad 0.1 \leq S^3/W^2 \leq 50 \quad (iv)$$

(In Formula (iv), S represents a surface area [m²] of a liquid surface of the liquid in the vessel and W represents a volume [m³] of the liquid in the vessel.)

[0014] [5] The method for producing a catalyst for methacrylic acid production according to [2], in which the catalyst starting material liquid B is added into a vessel that contains the catalyst starting material liquid A and satisfies the following Formula (iv), and mixed with the catalyst starting material liquid A in the step (3).

$$[0015] 0.1 \leq S^3/W^2 \leq 50 \quad (\text{iv})$$

(In Formula (iv), S represents a surface area [m^2] of a liquid surface of the liquid in the vessel and W represents a volume [m^3] of the liquid in the vessel.)

[0016] [6] The method for producing a catalyst for methacrylic acid production according to [4] or [5], in which the addition port is disposed above the liquid surface of the liquid in the vessel in the step (3).

[0017] [7] The method for producing a catalyst for methacrylic acid production according to [6], in which the following Formula (v) is satisfied in the step (3).

$$[0018] 2 \leq T/S \leq 100 \quad (\text{v})$$

(In Formula (v), T is synonymous with T in Formula (i) above and S is synonymous with S in Formula (iv) above.)

[0019] [8] The method for producing a catalyst for methacrylic acid production according to [6] or [7], in which one addition port is disposed above each of Y_1 to Y_T , where Y_1 to Y_T respectively represent regions of liquid surfaces to be divided by T straight lines drawn from a center of the liquid surface of the liquid in the vessel toward a wall surface of the vessel to be substantially parallel to the liquid surface so that a central angle is $360^\circ/T$ in the step (3).

[0020] [9] The method for producing a catalyst for methacrylic acid production according to any one of [6] to [8], in which the addition port is not present above a circular region to be drawn with a radius R [m] to be calculated by the following Formula (vi) by having a center of the liquid surface of the liquid in the vessel as a

center in the step (3).

[0021] [Math. 1]

$$R = \frac{\sqrt{S/\pi}}{3} \quad (v \ i)$$

(In Formula (vi), S is synonymous with S in Formula (iv).)

[0022] [10] The method for producing a catalyst for methacrylic acid production according to [1], in which the catalyst starting material liquid B is added into a vessel containing the catalyst starting material liquid A and mixed with the catalyst starting material liquid A in the step (3).

[0023] [11] The method for producing a catalyst for methacrylic acid production according to any one of [1] to [10], in which a total volume of the catalyst starting material liquid A prepared in the step (1) and the catalyst starting material liquid B prepared in the step (2) is 0.2 m³ or more.

[0024] [12] The method for producing a catalyst for methacrylic acid production according to any one of [1] to [11], in which the cation starting material is at least one kind selected from the group consisting of a compound containing an alkali metal and a compound containing an ammonium ion.

[0025] [13] The method for producing a catalyst for methacrylic acid production according to any one of [1] to [12], further including a step for drying the liquid containing a heteropoly acid having a Keggin-type structure or a salt of the heteropoly acid to obtain a catalyst precursor.

[0026] [14] The method for producing a catalyst for methacrylic acid production according to [13], further including a step for subjecting the catalyst precursor to a heat treatment.

[0027] [15] The method for producing a catalyst for methacrylic acid production

according to any one of [1] to [14], in which the catalyst for methacrylic acid production has an elemental composition to be represented by the following Formula (vii).



(In Formula (vii), Mo, P, V, Cu and O are element symbols representing molybdenum, phosphorus, vanadium, copper and oxygen, respectively. A represents at least one kind of element selected from the group consisting of antimony, bismuth, arsenic, germanium, zirconium, tellurium, silver, selenium, silicon, tungsten and boron. E represents at least one kind of element selected from the group consisting of iron, zinc, chromium, magnesium, calcium, strontium, tantalum, cobalt, nickel, manganese, barium, titanium, tin, lead, niobium, indium, sulfur, palladium, gallium, cerium and lanthanum. G represents at least one kind of element selected from the group consisting of lithium, sodium, potassium, rubidium, cesium and thallium. a, b, c, d, e, f, g and h represent atomic ratios of respective elements, and when $a=12$, $b = 0.5$ to 3 , $c = 0.01$ to 3 , $d = 0.01$ to 2 , $e = 0$ to 3 , $f = 0$ to 3 , $g = 0.01$ to 3 , and h is an atomic ratio of oxygen required to satisfy valences of the respective elements.)

[0029] [16] A method for producing methacrylic acid, including conducting gas phase catalytic oxidation of methacrolein with molecular oxygen in the presence of a catalyst for methacrylic acid production produced by the method according to any one of [1] to [15].

[0030] [17] A method for producing methacrylic acid, comprising producing a catalyst for methacrylic acid production by the method according to any one of [1] to [15] and conducting gas phase catalytic oxidation of methacrolein with molecular oxygen in the presence of the catalyst for methacrylic acid production.

[0031] [18] A method for producing a methacrylic acid ester, comprising esterifying methacrylic acid produced by the method for producing methacrylic acid according to

[16] or [17].

EFFECT OF THE INVENTION

[0032] According to the invention, it is possible to provide a catalyst for methacrylic acid production, which has a high methacrylic acid yield.

MODE(S) FOR CARRYING OUT THE INVENTION

[0033] [Method for producing catalyst for methacrylic acid production]

The method for producing a catalyst for methacrylic acid production according to the invention is a method for producing a catalyst for methacrylic acid production to be used when producing methacrylic acid by gas phase catalytic oxidation of methacrolein with molecular oxygen. A first embodiment of the method includes the following steps (1) to (3).

(1) A step for preparing a catalyst starting material liquid A containing at least molybdenum, phosphorus, and vanadium.

(2) A step for preparing a catalyst starting material liquid B containing a cation starting material.

(3) A step for preparing a liquid containing a heteropoly acid having a Keggin-type structure or a salt of the heteropoly acid by adding one of the catalyst starting material liquid A or the catalyst starting material liquid B to the other and mixing the liquids together.

[0034] The following Formulas (i) and (ii) are satisfied in the step (3).

[0035] $3.0 \leq T/(\sqrt[3]{V}) \leq 13.0$ (i)

$0.01 \leq u_1 \leq 1.0$ (ii)

In Formulas (i) and (ii), V represents the volume [m³] of the catalyst starting

material liquid A, T represents the number of addition ports for adding the other liquid, and u1 represents the volumetric flow rate [L/min] of the other liquid to be added. Incidentally, u1 represents the average value of volumetric flow rates of the other liquid to be added through the respective addition ports in a case in which T is 2 or more.

[0036] In addition, a second embodiment of the method includes the following steps (1) to (3).

(1) A step for preparing a catalyst starting material liquid A containing at least molybdenum, phosphorus, and vanadium.

(2) A step for preparing a catalyst starting material liquid B containing a cation starting material.

(3) A step for preparing a liquid containing a heteropoly acid having a Keggin-type structure or a salt of the heteropoly acid by adding the catalyst starting material liquid B to the catalyst starting material liquid A and mixing the liquids together.

[0037] The following Formulas (i) and (iii) are satisfied in the step (3).

$$[0038] \quad 3.0 \leq T/(\sqrt[3]{V}) \leq 13.0 \quad (i)$$

$$0.01 \leq u2 \leq 8 \quad (iii)$$

In Formulas (i) and (iii), V represents the volume [m³] of the catalyst starting material liquid A, T represents the number of addition ports for adding the catalyst starting material liquid B, and u2 represents the flow rate [mol/min] of the cation starting material in the catalyst starting material liquid B. Incidentally, u2 represents the average value of flow rates of the cation starting material in the catalyst starting material liquid B to be added through the respective addition ports in a case in which T is 2 or more.

[0039] In the first and second embodiments of the method according to the invention, it is possible to produce a catalyst for methacrylic acid production with which methacrylic

acid can be produced at a high yield as the method include the steps (1) to (3) and Formulas (i) and (ii) above or Formulas (i) and (iii) above are satisfied in the step (3). It is presumed that catalyst particles effective in the improvement of methacrylic acid yield are likely to be produced although the detailed mechanism thereof is not necessarily clarified.

[0040] The catalyst for methacrylic acid production to be produced by the method according to the invention contains at least molybdenum, phosphorus and vanadium, but it can further contain elements such as copper other than these. From the viewpoint of being able to produce methacrylic acid at a high yield, it is preferable that the catalyst has an elemental composition to be represented by the following Formula (vii).

[0041] $\text{Mo}_a\text{P}_b\text{V}_c\text{Cu}_d\text{A}_e\text{E}_f\text{G}_g\text{O}_h$ (vii)

In Formula (vii), Mo, P, V, Cu and O are element symbols representing molybdenum, phosphorus, vanadium, copper and oxygen, respectively. A represents at least one kind of element selected from the group consisting of antimony, bismuth, arsenic, germanium, zirconium, tellurium, silver, selenium, silicon, tungsten and boron. E represents at least one kind of element selected from the group consisting of iron, zinc, chromium, magnesium, calcium, strontium, tantalum, cobalt, nickel, manganese, barium, titanium, tin, lead, niobium, indium, sulfur, palladium, gallium, cerium and lanthanum. G represents at least one kind of element selected from the group consisting of lithium, sodium, potassium, rubidium, cesium and thallium. a, b, c, d, e, f, g and h represent the atomic ratios of the respective elements, and when $a = 12$, $b = 0.5$ to 3 , $c = 0.01$ to 3 , $d = 0.01$ to 2 , $e = 0$ to 3 , $f = 0$ to 3 , $g = 0.01$ to 3 , and h is the atomic ratio of oxygen required to satisfy the valences of the respective elements. Incidentally, the elemental composition is a value to be calculated by ICP emission spectrometry analysis of the components obtained by dissolving the catalyst in ammonia water.

[0042] (Step (1))

In the step (1), a catalyst starting material liquid A containing at least molybdenum, phosphorus and vanadium is prepared. For example, the catalyst starting material liquid A can be obtained by dissolving or suspending starting material compounds of the catalyst components, containing molybdenum, phosphorus and vanadium in a solvent by using a preparation vessel. It is possible to produce a catalyst for methacrylic acid production, which has a higher methacrylic acid yield as the catalyst starting material liquid A contains at least molybdenum, phosphorus and vanadium.

[0043] The starting material compounds of the catalyst components are not particularly limited, and nitrates, carbonates, acetates, ammonium salts, oxides, halides, oxoacids, oxoates and the like of the respective constituent elements of the catalyst can be used singly or in combination of two or more kinds thereof. Examples of the starting material compound of molybdenum may include molybdenum oxide such as molybdenum trioxide, ammonium molybdate such as ammonium paramolybdate and ammonium dimolybdate. Examples of the starting material compound of phosphorus may include phosphoric acid, phosphorus pentoxide, and ammonium phosphate. Examples of the starting material compound of vanadium may include ammonium metavanadate, vanadium pentoxide, and vanadyl oxalate. Examples of the starting material compound of copper may include copper nitrate, copper oxide, copper carbonate, and copper acetate. As the starting material compounds of the catalyst components, one kind may be used or two or more kinds may be used in combination for each element constituting the catalyst components.

[0044] Examples of the solvent may include water, ethyl alcohol, and acetone. These may be used singly or two or more kinds thereof may be used concurrently. Among

these, it is preferable to use water.

[0045] It is preferable that the catalyst starting material liquid A is prepared by adding the starting material compounds of the catalyst components to a solvent by using a preparation vessel, and stirring the mixture while conducting heating. The heating temperature is preferably from 80°C to 130°C and the lower limit thereof is more preferably 90°C or more. In addition, the pH of the catalyst starting material liquid A is preferably 3.0 or less and more preferably 2.5 or less. Examples of a method for adjusting the pH of the catalyst starting material liquid A to 3.0 or less may include a method in which molybdenum trioxide is used as a molybdenum starting material and the starting material compounds of the catalyst components are selected so as to contain a nitrate ion in a large amount. The concentration of the starting material compounds of the catalyst components in the catalyst starting material liquid A is not particularly limited, but it can be, for example, from 5% to 90% by mass.

[0046] (Step (2))

In the step (2), a catalyst starting material liquid B containing a cation starting material is prepared. For example, the catalyst starting material liquid B can be obtained by dissolving or suspending a cation starting material in a solvent by using a preparation vessel.

[0047] Here, the "cation starting material" refers to at least one kind selected from the group consisting of a compound containing an alkali metal, a compound containing an alkaline earth metal, a compound containing a transition metal, a compound containing a base metal, and a compound containing nitrogen (a compound containing ammonia, an ammonium ion or an alkylammonium ion, or a nitrogen-containing heterocyclic compound). Examples of the alkali metal may include lithium, sodium, potassium, rubidium, and cesium. Examples of the alkaline earth metal may include magnesium,

calcium, strontium, and barium. Examples of the compound containing an alkali metal, the compound containing an alkaline earth metal, the compound containing a transition metal, and the compound containing a base metal may include nitrates, carbonates, bicarbonates, acetates, sulfates, ammonium salts, oxides, hydroxides, halides, oxoacids, and oxoates of an alkali metal, an alkaline earth metal, a transition metal, and a base metal. Examples of the compound containing an ammonium ion may include ammonium bicarbonate, ammonium carbonate, ammonium nitrate, ammonium phosphate, and ammonium vanadate. Examples of the compound containing an alkylammonium ion may include halides or hydroxides such as tetramethylammonium, tetraethylammonium, tetra-n-propylammonium, tetra-n-butylammonium, and triethylmethylammonium. Examples of the nitrogen-containing heterocyclic compound may include pyridine, piperidine, piperazine, pyrimidine, quinoline, isoquinoline and any alkyl derivative thereof. These may be used singly or two or more kinds thereof may be used concurrently. Among these, the cation starting material is preferably at least one kind selected from the group consisting of a compound containing an alkali metal and a compound containing an ammonium ion from the viewpoint of obtaining a catalyst for methacrylic acid production, which has a higher methacrylic acid yield.

[0048] Examples of the solvent may include water, ethyl alcohol, and acetone. These may be used singly or two or more kinds thereof may be used concurrently. Among these, it is preferable to use water.

[0049] Incidentally, in the case of using a plurality of kinds of starting materials as a cation starting material, a plurality of catalyst starting material liquids B, for example, catalyst starting material liquids B1, B2, ... may be prepared by respectively dissolving or suspending the respective cation starting materials in a solvent by using a plurality of

preparation vessels. In the case of adding the catalyst starting material liquid B to the catalyst starting material liquid A, the catalyst starting material liquids B1, B2, ... may be added to the catalyst starting material liquid A in random order or at the same time. In the first embodiment, in the case of adding the catalyst starting material liquid A to the catalyst starting material liquid B, the catalyst starting material liquid A may be added to any one of the catalyst starting material liquids B and the liquid obtained may be mixed with the other catalyst starting material liquids B or the catalyst starting material liquid A may be divided into a plurality of catalyst starting material liquids A, for example, catalyst starting material liquids A1, A2, ... and added to the catalyst starting material liquids B and then the respective liquids obtained may be mixed together. In addition, the concentration of the cation starting material in the catalyst starting material liquid B is not particularly limited, but it can be, for example, from 5% to 90% by mass.

[0050] In addition, in the case of preparing the catalyst starting material liquids A and B in the steps (1) and (2) described above, the total volume of the catalyst starting material liquid A prepared in the step (1) and the catalyst starting material liquid B prepared in the step (2) is preferably 0.2 m³ or more, more preferably 0.8 m³ or more, and still more preferably 1.5 m³ or more from the viewpoint of production cost when the industrial production is taken into consideration. Incidentally, the upper limit of the range of the volume is not particularly limited, but it may be, for example, 5 m³ or less.

[0051] (Step (3))

In the first embodiment, a liquid containing a heteropoly acid having a Keggin-type structure or a salt thereof is prepared by adding one of the catalyst starting material liquid A or the catalyst starting material liquid B to the other and mixing the liquids together in the step (3). In other words, the catalyst starting material liquid B is added

to and mixed with the catalyst starting material liquid A or the catalyst starting material liquid A is added to and mixed with the catalyst starting material liquid B. The catalyst starting material liquid B corresponds to "the other liquid" in the former and the catalyst starting material liquid A corresponds to "the other liquid" in the latter. Hereinafter, the "other liquid" is also referred as an additive liquid. In addition, in the second embodiment, a liquid containing a heteropoly acid having a Keggin-type structure or a salt thereof is prepared by adding the catalyst starting material liquid B to the catalyst starting material liquid A and mixing the liquids together in the step (3). In the first embodiment, both of the conditions of the following Formulas (i) and (ii) are required to be satisfied in the step (3). In addition, in the second embodiment, both of the conditions of the following Formulas (i) and (iii) are required to be satisfied in the step (3).

$$[0052] \quad 3.0 \leq T/(\sqrt[3]{V}) \leq 13.0 \quad (i)$$

$$0.01 \leq u1 \leq 1.0 \quad (ii)$$

$$0.01 \leq u2 \leq 8 \quad (iii)$$

In Formulas (i), (ii), and (iii), V represents the volume [m³] of the catalyst starting material liquid A, T represents the number of addition ports for adding the other liquid, u1 represents the volumetric flow rate [L/min] of the other liquid to be added, and u2 represents the flow rate [mol/min] of the cation starting material in the catalyst starting material liquid B. In addition, the "addition port" is the outlet of the other liquid (catalyst starting material liquid B) provided in order to add the other (catalyst starting material liquid B) to one of the catalyst starting material liquid A or the catalyst starting material liquid B (catalyst starting material liquid A). Incidentally, u1 and u2 respectively represent the average value of volumetric flow rates of the other liquid to be added through the respective addition ports and the average value of flow rates of the

cation starting material in the catalyst starting material liquid B to be added through the respective addition ports in a case in which T is 2 or more. Incidentally, each of the additive liquids is required to satisfy the above conditions in a case in which there are a plurality of additive liquids. In other words, each addition of the respective liquids is all required to satisfy both of the conditions of Formulas (i) and (ii) or both of the conditions of Formulas (i) and (iii) are satisfied in a case in which there are the catalyst starting material liquids B1, B2, ... as the additive liquid. In addition, in the first embodiment, each addition of the respective liquids is all required to satisfy both of the conditions of Formulas (i) and (ii) in the same manner in a case in which there are the catalyst starting material liquids A1, A2, ... as the additive liquid as well.

[0053] A liquid containing a heteropoly acid (salt) having a Keggin-type structure is obtained as the catalyst starting material liquid A is mixed with the catalyst starting material liquid B. In Formula (i) above, $T/(^3\sqrt{V})$ is obtained by dividing the number T of addition ports by the cube root of the volume V of the catalyst starting material liquid A and affects the contact state of the respective liquids when mixing the catalyst starting material liquid A with the catalyst starting material liquid B. Hence, it is presumed that heteropoly acids (salts) effective in the improvement of methacrylic acid yield are likely to be produced among heteropoly acids (salts) as $T/(^3\sqrt{V})$ in Formula (i) above is set to a specific range. Incidentally, the total amount of the heteropoly acids (salts) to be obtained is related to the amount of the catalyst component to be contained in the catalyst starting material liquid A. The value of $T/(^3\sqrt{V})$ satisfies $3.0 \leq T/(^3\sqrt{V}) \leq 13.0$, and the lower limit thereof is preferably 4.0 or more, more preferably 5.0 or more, and still more preferably 6.0 or more. The upper limit thereof is preferably 12.0 or less, more preferably 11.0 or less, and still more preferably 9.0 or less.

[0054] The value of T is preferably 2 or more, more preferably 4 or more, and still more

preferably 8 or more from the viewpoint of obtaining a catalyst for methacrylic acid production, which has a higher methacrylic acid yield. The upper limit of the range of the value of T is not particularly limited, but for example, it can be set to 20 or less. Examples of a method for setting the value of T to 2 or more may include use of a pipe having a plurality of holes and use of a multi-nozzle having a plurality of discharge ports. The diameter of the addition port is preferably from 0.5 to 30 mm, the lower limit thereof is 1 mm or more, and the upper limit thereof is 10 mm or less.

[0055] In Formula (ii) above, the volumetric flow rate u_1 of the additive liquid affects the contact speed of both liquids when mixing the catalyst starting material liquid A with the catalyst starting material liquid B. Hence, it is presumed that catalyst particles effective in the improvement of methacrylic acid yield are likely to be produced as one of the catalyst starting material liquid A or the catalyst starting material liquid B is added to the other so that Formula (ii) above is satisfied. The value of u_1 satisfies $0.01 \leq u_1 \leq 1.0$, and the lower limit thereof is preferably 0.05 or more and more preferably 0.1 or more. The upper limit thereof is preferably 0.5 or less, more preferably 0.4 or less, and still more preferably 0.3 or less.

[0056] In addition, in Formula (iii) above, the flow rate u_2 of the cation starting material in the catalyst starting material liquid B to be added affects the contact speed of both liquids when mixing the catalyst starting material liquid A with the catalyst starting material liquid B. Hence, it is presumed that catalyst particles effective in the improvement of methacrylic acid yield are likely to be produced as the catalyst starting material liquid B is added to the catalyst starting material liquid A so that Formula (iii) above is satisfied. The value of u_2 satisfies $0.01 \leq u_2 \leq 8$, and the lower limit thereof is preferably 0.1 or more and more preferably 0.5 or more. The upper limit thereof is preferably 5 or less, more preferably 4 or less, and still more preferably 2 or less.

[0057] In the first embodiment, it is preferable that one of the catalyst starting material liquid A or the catalyst starting material liquid B is added into a vessel that contains the other and satisfies the following Formula (iv), and mixed with the other in the step (3). In addition, in the second embodiment, it is preferable that the catalyst starting material liquid B is added into a vessel that contains the catalyst starting material liquid A and satisfies the following Formula (iv), and mixed with the catalyst starting material liquid A in the step (3).

$$[0058] \quad 0.1 \leq S^3/W^2 \leq 50 \quad (\text{iv})$$

In Formula (iv), S represents the surface area [m^2] of the liquid surface of the liquid in the vessel and W represents the volume [m^3] of the liquid in the vessel. Here, the "liquid in the vessel" refers to the catalyst starting material liquid A or the catalyst starting material liquid B contained in the vessel.

[0059] S^3/W^2 is a value related to the shape of the vessel for mixing the catalyst starting material liquid A with the catalyst starting material liquid B. The surface area of the liquid surface with respect to the volume of the liquid in the vessel is in a preferred range and a stable stirring state can be maintained as the shape of the vessel for mixing the catalyst starting material liquid A with the catalyst starting material liquid B is adjusted so that Formula (iv) above is satisfied. The lower limit of the value of S^3/W^2 is more preferably 0.5 or more and still more preferably 0.8 or more.

[0060] In the case of respectively preparing the catalyst starting material liquid A and the catalyst starting material liquid B by using a preparation vessel in the steps (1) and (2), one of the catalyst starting material liquid A or the catalyst starting material liquid B (catalyst starting material liquid A) may be contained in the preparation vessel as it is and the other (catalyst starting material liquid B) may be added into the preparation vessel or one of the catalyst starting material liquid A or the catalyst starting material

liquid B (catalyst starting material liquid A) may be transferred to a newly prepared vessel and the additive liquid may be added thereto in order to satisfy Formula (iv) above. In addition, a plurality of vessels may be used and the additive liquid may be added to the liquid in the vessel so that Formula (iv) above is satisfied in each vessel.

[0061] The value of S is not particularly limited, but it is preferably $0.01 \text{ m}^2 \leq S \leq 3 \text{ m}^2$, the lower limit thereof is 0.05 m^2 or more, and the upper limit thereof is more preferably 2 m^2 or less. In addition, the value of W is not particularly limited, but it is preferably $0.1 \text{ m}^3 \leq W \leq 4.5 \text{ m}^3$, the lower limit thereof is 0.5 m^3 or more, and the upper limit thereof is 3.0 m^3 or less.

[0062] It is preferable that the addition port is disposed above the liquid surface of the liquid in the vessel in the step (3). In addition, it is preferable that the value of T/S satisfies the following Formula (v).

[0063] $2 \leq T/S \leq 100$ (v)

In Formula (v), T is synonymous with T in Formula (i) above and S is synonymous with S in Formula (iv) above. T/S represents the number of addition ports per unit surface area of the liquid surface of the liquid in the vessel, and a stable stirring state can be maintained as T/S is adjusted so that Formula (v) above is satisfied. The lower limit of the value of T/S is more preferably 3 or more and still more preferably 4 or more. The upper limit thereof is more preferably 80 or less and still more preferably 60 or less.

[0064] Furthermore, it is more preferable that one addition port is disposed above each of Y_1 to Y_T , where Y_1 to Y_T respectively represent the regions of liquid surfaces to be divided by T straight lines drawn from the center of the liquid surface of the liquid in the vessel toward the wall surface of the vessel to be substantially parallel to the liquid surface so that the central angle is $360^\circ/T$. When the catalyst starting material liquid A

is mixed with the catalyst starting material liquid B as the addition ports are disposed in this manner, the contact surface between both liquids is more uniform and mixed state is stabilized, and it is possible to stably produce catalyst particles effective in the improvement of methacrylic acid yield. Incidentally, the "center of the liquid surface of the liquid in the vessel" refers to the center of gravity of the liquid surface of the liquid in the vessel, and it can be, for example, the center of the circle in a case in which the shape of liquid surface is circular and the intersection point of the diagonal lines in a case in which the shape of liquid surface is rectangular. In addition, to be "substantially parallel" means to be parallel within a range of $\pm 5^\circ$. It is particularly preferable that all addition ports are present above the position at which Z_1 is rotated and moved by $360^\circ/T$ by having the center of the liquid surface of the liquid in the vessel as the axis, where Z_1 represents the contact point when a perpendicular line is drawn from the addition port present above Y_1 onto the liquid surface of the liquid in the vessel.

[0065] It is preferable that the addition port is not present above the circular region to be drawn with a radius R [m] to be calculated by the following Formula (vi) by having the center of the liquid surface of the liquid in the vessel as the center in the step (3).

In other words, it is preferable that the addition ports are all present above the outside of the range of the circular region.

[0066] [Math. 2]

$$R = \frac{\sqrt{S/\pi}}{3} \quad (\text{v i})$$

In Formula (vi), S is synonymous with S in Formula (iv). In a case in which the liquid surface of the liquid in the vessel is circular, R in the following Formula (vi) is $1/3$ of the radius of liquid surface of the liquid in the vessel. When the catalyst

starting material liquid A is mixed with the catalyst starting material liquid B as the addition ports are disposed in this manner, the contact surface between both liquids is more uniform and mixed state is stabilized and it is possible to stably produce catalyst particles effective in the improvement of methacrylic acid yield.

[0067] In addition, in the first embodiment, it is preferable that the catalyst starting material liquid B is added into the vessel containing the catalyst starting material liquid A and mixed with the catalyst starting material liquid A in the step (3). It is presumed that catalyst particles effective in the improvement of methacrylic acid yield are more likely to be produced as the catalyst starting material liquid containing a cation starting material is mixed as the additive liquid.

[0068] The liquid to be obtained in the step (3) contains a heteropoly acid having a Keggin-type structure or a salt thereof. The catalyst particles produced can be stably present not being changed as the liquid contains a heteropoly acid having a Keggin-type structure or a salt thereof, and it is thus possible to obtain a catalyst, which has a high methacrylic acid yield. Incidentally, the fact that the liquid contains a heteropoly acid having a Keggin-type structure or a salt thereof can be confirmed by subjecting one obtained by drying the liquid to the measurement by infrared absorption analysis. The infrared absorption spectrum obtained has characteristic peaks in the vicinity of 1060, 960, 870 and 780 cm^{-1} in the case of containing a heteropoly acid having a Keggin-type structure or a salt thereof.

[0069] The pH of the liquid to be obtained in the step (3) is preferably 3.0 or less and more preferably 2.5 or less. A liquid containing a heteropoly acid having a Keggin-type structure or a salt thereof can be easily obtained as the pH is 3.0 or less.

Examples of a method for adjusting the pH to 3.0 or less may include a method in which the pH of the catalyst starting material liquid A is adjusted to a low value in

advance.

[0070] (Drying step)

It is preferable that the method according to the invention includes a step for drying the liquid which contains a heteropoly acid having a Keggin-type structure or a salt thereof and is obtained in the step (3) to obtain a catalyst precursor. The drying method of the liquid and the conditions such as the drying temperature are not particularly limited, and these can be selected depending on the desired shape and size of the dried material as appropriate. Examples of the drying method may include a drying method using a box type dryer, a drum drying method, a pneumatic conveying drying method, an evaporation drying method, and a spray drying method. The drying temperature can be set to, for example, from 120°C to 500°C, the lower limit thereof is 140°C or more, and the upper limit thereof is 400°C or less. Drying can be conducted until the liquid is dried and solidified.

[0071] (Molding step)

In the method according to the invention, a step of molding the catalyst precursor obtained in the drying step may be carried out before a heat treatment step to be described later. The molding method is not particularly limited, and a known dry or wet molding method can be applied. Examples thereof may include tableting molding, press molding, extrusion molding, and granulation molding. The shape of the molded article is not particularly limited, and examples thereof may include a cylindrical shape, a ring shape, and a spherical shape. In addition, it is preferable to mold the catalyst precursor alone without adding a carrier, a binder and the like to the catalyst precursor at the time of molding, but for example, known additives such as graphite and talc and known binders derived from organic substances and inorganic substances may be added, if necessary. Hereinafter, the catalyst precursor obtained through the drying step and

the molded article of the catalyst precursor obtained through the molding step are collectively referred to as a catalyst precursor.

[0072] (Heat treatment step)

It is preferable that the method according to the invention includes a step for subjecting the catalyst precursor to a heat treatment. For example, the catalyst precursor can be subjected to a heat treatment under the flow of at least either of air or an inert gas. It is preferable that the heat treatment is conducted under the flow of an oxygen-containing gas such as air. In addition, an "inert gas" refers to a gas which does not deteriorate the catalytic activity, and examples thereof may include nitrogen, carbon dioxide gas, helium, and argon. These may be used singly or in mixture of two or more kinds thereof. The shape of the heat treatment vessel is not particularly limited, but it is preferable to use a tubular heat treatment vessel having a cross sectional area of 2 square centimeters or more and 100 square centimeters or less. The heat treatment temperature is preferably 300°C or more and 700°C or less, the lower limit thereof is more preferably 320°C or more, and the upper limit thereof is more preferably 450°C or less.

[0073] It is preferable that the catalyst for methacrylic acid production to be thus obtained contains a heteropoly acid having a Keggin-type structure or a salt thereof from the viewpoint of a higher methacrylic acid yield. The fact that the catalyst contains a heteropoly acid having a Keggin-type structure or a salt thereof can be confirmed by subjecting the catalyst to the measurement by infrared absorption analysis as described above.

[0074] [Method for producing methacrylic acid]

In the method for producing methacrylic acid according to the invention, methacrylic acid is produced by gas phase catalytic oxidation of methacrolein with

molecular oxygen in the presence of the catalyst for methacrylic acid production produced by the method according to the invention. In addition, in the method for producing methacrylic acid according to the invention, a catalyst for methacrylic acid production is produced by the method according to the invention and methacrylic acid is produced by gas phase catalytic oxidation of methacrolein with molecular oxygen in the presence of the catalyst for methacrylic acid production. According to these methods, it is possible to produce methacrylic acid at a high yield. Specifically, methacrylic acid can be produced by bringing a starting material gas containing methacrolein and molecular oxygen into contact with the catalyst for methacrylic acid production according to the invention. This reaction can be conducted in a fixed bed. The catalyst layer may be one layer or two or more layers. The catalyst for methacrylic acid production may be supported on a carrier or may contain other additives. The concentration of methacrolein in the starting material gas is not particularly limited, but it is preferably from 1% to 20% by volume, the lower limit thereof is more preferably 3% by volume or more, and the upper limit thereof is more preferably 10% by volume or less. Methacrolein may contain a small amount of impurities, such as lower saturated aldehydes, which do not substantially affect the present reaction. The concentration of molecular oxygen in the starting material gas is preferably from 0.4 to 4 moles with respect to 1 mole of methacrolein, the lower limit thereof is more preferably 0.5 moles or more, and the upper limit thereof is more preferably 3 moles or less. Incidentally, air is preferable as a molecular oxygen source from the viewpoint of economic efficiency, but a gas in which molecular oxygen is enriched by adding pure oxygen to air, and the like may be used if necessary. The starting material gas may be one obtained by diluting methacrolein and molecular oxygen with an inert gas such as nitrogen or carbon dioxide gas. Furthermore, water vapor may be added to the starting

material gas. It is possible to obtain methacrylic acid at a higher yield by conducting the reaction in the presence of water vapor. The concentration of water vapor in the starting material gas is preferably from 0.1% to 50% by volume, the lower limit thereof is more preferably 1% by volume or more, and the upper limit thereof is more preferably 40% by volume or less. The contact time of the starting material gas with the catalyst for methacrylic acid production is preferably from 1.5 to 15 seconds, the lower limit thereof is more preferably 2 seconds or more, and the upper limit thereof is more preferably 5 seconds or less. The reaction pressure is preferably from 0.1 MPa (G) to 1.0 MPa (G). Incidentally, (G) means the gauge pressure. The reaction temperature is preferably from 200°C to 450°C, the lower limit thereof is more preferably 250°C or more, and the upper limit thereof is more preferably 400°C or less.

[0075] [Method for producing methacrylic acid ester]

In the method for producing a methacrylic acid ester according to the invention, methacrylic acid produced by the method according to the invention is esterified. According to this method, a methacrylic acid ester can be obtained using methacrylic acid to be obtained by gas phase catalytic oxidation of methacrolein. Examples of an alcohol to be reacted with methacrylic acid may include methanol, ethanol, isopropanol, n-butanol, and isobutanol. Examples of the methacrylic acid ester to be obtained may include methyl methacrylate, ethyl methacrylate, propyl methacrylate, and butyl methacrylate. The reaction can be conducted in the presence of an acidic catalyst such as a sulfonic acid-type cation exchange resin. The reaction temperature is preferably from 50°C to 200°C.

EXAMPLES

[0076] Hereinafter, the invention will be described in detail with reference to Examples

and Comparative Examples, but the invention is not limited to these Examples. The term "parts" in Examples and Comparative Examples means parts by mass. The molar ratio of the elemental composition of the catalyst was calculated by ICP emission spectrometry analysis of the components obtained by dissolving the catalyst in ammonia water. The analysis of starting material gases and products was conducted by gas chromatography. From the results of gas chromatography, the percent conversion of methacrolein, the selectivity for methacrylic acid to be produced, and the single flow yield of methacrylic acid were determined by the following formulas.

[0077] Percent conversion of methacrolein (%) = $(B/A) \times 100$

Selectivity for methacrylic acid (%) = $(C/B) \times 100$

Single flow yield of methacrylic acid = $(C/A) \times 100$

In the formulas, A represents the number of carbon atoms in methacrolein supplied, B represents the number of carbon atoms in methacrolein reacted, and C represents the number of carbon atoms in methacrylic acid produced.

[0078] In addition, u_2 was calculated as the product of the molar concentration [mol/L] of the catalyst starting material liquid B and u_1 .

[0079] [Example 1]

In 400 parts of pure water, 100 parts of molybdenum trioxide, 7.5 parts of ammonium metavanadate, 11.4 parts of a 85% by mass aqueous solution of phosphoric acid, and 7.0 parts of copper(II) nitrate trihydrate were dissolved. The temperature of this solution was raised to 95°C while stirring the solution, and the solution was stirred for 2 hours while keeping the liquid temperature at 95°C, thereby obtaining a catalyst starting material liquid A. The pH of the catalyst starting material liquid A was 2.1. Meanwhile, a catalyst starting material liquid B1 was obtained by dissolving 15.7 parts of cesium bicarbonate in 20 parts of pure water. In addition, a catalyst starting

material liquid B2 was obtained by dissolving 20.0 parts of ammonium bicarbonate in 20 parts of pure water. The total volume of the catalyst starting material liquid A, the catalyst starting material liquid B1, and the catalyst starting material liquid B2 was 2.1 m³.

[0080] While the liquid temperature of the catalyst starting material liquid A in the vessel was kept at 95°C, the catalyst starting material liquid B1 was added to the catalyst starting material liquid A while stirring the catalyst starting material liquid A by using a rotary blade stirrer, and the mixture was stirred for 15 minutes. Thereafter, the catalyst starting material liquid B2 was added to the mixture, and this mixture was stirred for 15 minutes. Incidentally, it was set to $T = 10$, $S = 1.54 \text{ m}^2$, $V = 1.9 \text{ m}^3$, $S^3/W^2 = 1.01$, $T/(\sqrt[3]{V}) = 8.1$, $T/S = 6.5$, and $u_1 = 0.20 \text{ L/min}$ when adding the catalyst starting material liquids B1 and B2. At this time, u_2 was 0.62 mol/min for the catalyst starting material liquid B1 and 1.40 mol/min for the catalyst starting material liquid B2. In addition, a ring-shaped pipe which had a radius of $3 \times (\sqrt{(S/\pi)})/7 \text{ [m]}$ and was provided with addition ports having a diameter of 2 mm at regular intervals was disposed so that the center of the ring-shaped pipe is positioned above the center of the liquid surface of the liquid in the vessel and one addition port was disposed above each of the regions Y_1 to Y_{10} . The catalyst starting material liquids B1 and B2 were sequentially added through the addition ports of the ring-shaped pipe. The obtained slurry contained a heteropoly acid having a Keggin-type structure or a salt thereof. Thereafter, the slurry was spray-dried to obtain a catalyst precursor.

[0081] The catalyst precursor was molded and placed in a cylindrical quartz glass firing vessel having an inner diameter of 3 cm. Under the flow of air, the temperature of the catalyst precursor was raised at 10°C/h and the catalyst precursor was subjected to a heat treatment at 380°C for 2 hours, thereby preparing a catalyst for methacrylic acid

production. The catalyst for methacrylic acid production obtained had a Keggin-type structure. In addition, the elemental composition of the catalyst for methacrylic acid production obtained other than oxygen was $\text{Mo}_{12}\text{P}_{1.7}\text{V}_{1.1}\text{Cu}_{0.5}\text{Cs}_{1.4}$.

[0082] The catalyst for methacrylic acid production was filled in a reaction tube, a starting material gas composed of 5% by volume of methacrolein, 10% by volume of oxygen, 30% by volume of water vapor, and 55% by volume of nitrogen was allowed to flow through the reaction tube, and the reaction was conducted at a reaction temperature of 300°C. The product was collected and analyzed by gas chromatography to calculate the methacrylic acid yield. The results are presented in Table 1.

[0083] [Example 2]

The total volume of the catalyst starting material liquid A, the catalyst starting material liquid B1, and the catalyst starting material liquid B2 was changed to 0.10 m³, it was changed to $T = 4$, $S = 0.196 \text{ m}^2$, $V = 0.088 \text{ m}^3$, $S^3/W^2 = 0.97$, $T/(\sqrt[3]{V}) = 9.0$, $T/S = 20.4$, and $u_1 = 0.03 \text{ L/min}$, and a ring-shaped pipe which had a radius of $3 \times (\sqrt{(S/\pi)})/5$ [m] and was provided with addition ports having a diameter of 2 mm at regular intervals was disposed so that one addition port was disposed above each of the regions Y_1 to Y_4 . In addition, u_2 at this time was 0.09 mol/min for the catalyst starting material liquid B1 and 0.21 mol/min for the catalyst starting material liquid B2. A slurry was obtained by the same method as in Example 1 except these. The obtained slurry contained a heteropoly acid having a Keggin-type structure or a salt thereof. Thereafter, a catalyst for methacrylic acid production was prepared in the same manner as in Example 1. The catalyst for methacrylic acid production obtained had a Keggin-type structure. In addition, the elemental composition of the catalyst for methacrylic acid production obtained other than oxygen was $\text{Mo}_{12}\text{P}_{1.7}\text{V}_{1.1}\text{Cu}_{0.5}\text{Cs}_{1.4}$. In addition, methacrylic acid was produced in the same manner as in Example 1 except that this catalyst for

methacrylic acid production was used. The results are presented in Table 1.

[0084] [Example 3]

It was changed to $T = 13$, $S = 1.54 \text{ m}^2$, $V = 1.9 \text{ m}^3$, $S^3/W^2 = 1.01$, $T/(\sqrt[3]{V}) = 10.5$, $T/S = 8.4$, and $u1 = 0.26 \text{ L/min}$, and the addition ports were all disposed above the region having a radius of $5 \times (\sqrt{(S/\pi)})/7 \text{ [m]}$ or more from the center of the liquid surface of the liquid in the vessel in the region Y_1 . In addition, $u2$ at this time was 0.80 mol/min for the catalyst starting material liquid B1 and 1.83 mol/min for the catalyst starting material liquid B2. A slurry was obtained by the same method as in Example 1 except these. The obtained slurry contained a heteropoly acid having a Keggin-type structure or a salt thereof. Thereafter, a catalyst for methacrylic acid production was prepared in the same manner as in Example 1. The catalyst for methacrylic acid production obtained had a Keggin-type structure. In addition, the elemental composition of the catalyst for methacrylic acid production obtained other than oxygen was $\text{Mo}_{12}\text{P}_{1.7}\text{V}_{1.1}\text{Cu}_{0.5}\text{Cs}_{1.4}$. In addition, methacrylic acid was produced in the same manner as in Example 1 except that this catalyst for methacrylic acid production was used. The results are presented in Table 1.

[0085] [Comparative Example 1]

The total volume of the catalyst starting material liquid A, the catalyst starting material liquid B1, and the catalyst starting material liquid B2 was changed to 0.0014 m^3 , it was changed to $T = 1$, $S = 0.0177 \text{ m}^2$, $V = 0.0013 \text{ m}^3$, $S^3/W^2 = 3.28$, $T/(\sqrt[3]{V}) = 9.2$, $T/S = 56.5$, and $u1 = 1.41 \text{ L/min}$, and the addition port was disposed above the position of $4 \times (\sqrt{(S/\pi)})/5 \text{ [m]}$ from the center of the liquid surface of the liquid in the vessel. In addition, $u2$ at this time was 4.35 mol/min for the catalyst starting material liquid B1 and 9.90 mol/min for the catalyst starting material liquid B2. A slurry was obtained by the same method as in Example 1 except these. The obtained slurry contained a

heteropoly acid having a Keggin-type structure or a salt thereof. Thereafter, a catalyst for methacrylic acid production was prepared in the same manner as in Example 1. The catalyst for methacrylic acid production obtained had a Keggin-type structure. In addition, the elemental composition of the catalyst for methacrylic acid production obtained other than oxygen was $\text{Mo}_{12}\text{P}_{1.7}\text{V}_{1.1}\text{Cu}_{0.5}\text{Cs}_{1.4}$. In addition, methacrylic acid was produced in the same manner as in Example 1 except that this catalyst for methacrylic acid production was used. The results are presented in Table 1.

[0086] [Comparative Example 2]

The total volume of the catalyst starting material liquid A, the catalyst starting material liquid B1, and the catalyst starting material liquid B2 was changed to 0.00048 m^3 , it was changed to $T = 1$, $S = 0.00785 \text{ m}^2$, $V = 0.00043 \text{ m}^3$, $S^3/W^2 = 2.62$, $T/(\sqrt[3]{V}) = 13.2$, $T/S = 127.4$, and $u_1 = 0.07 \text{ L/min}$, and the addition port was disposed above the position of $2 \times (\sqrt{(S/\pi)})/5 \text{ [m]}$ from the center of the liquid surface of the liquid in the vessel. In addition, u_2 at this time was 0.22 mol/min for the catalyst starting material liquid B1 and 0.49 mol/min for the catalyst starting material liquid B2. A slurry was obtained by the same method as in Example 1 except these. The obtained slurry contained a heteropoly acid having a Keggin-type structure or a salt thereof. Thereafter, a catalyst for methacrylic acid production was prepared in the same manner as in Example 1. The catalyst for methacrylic acid production obtained had a Keggin-type structure. In addition, the elemental composition of the catalyst for methacrylic acid production obtained other than oxygen was $\text{Mo}_{12}\text{P}_{1.7}\text{V}_{1.1}\text{Cu}_{0.5}\text{Cs}_{1.4}$. In addition, methacrylic acid was produced in the same manner as in Example 1 except that this catalyst for methacrylic acid production was used. The results are presented in Table 1.

[0087] [Comparative Example 3]

In 400 parts of pure water, 100 parts of molybdenum trioxide, 7.5 parts of

ammonium metavanadate, and 11.4 parts of a 85% by mass aqueous solution of phosphoric acid were dissolved. The temperature of this solution was raised to 95°C while stirring the solution, and the solution was stirred for 2 hours while keeping the liquid temperature at 95°C, thereby preparing a catalyst starting material liquid A. The pH of the catalyst starting material liquid A was 6.9. Meanwhile, a catalyst starting material liquid B1 was prepared by dissolving 15.8 parts of cesium nitrate in 20 parts of pure water. In addition, a catalyst starting material liquid B2 was prepared by dissolving 40.0 parts of 30% by mass ammonia water in 20 parts of pure water. In addition, a catalyst starting material liquid B3 was prepared by dissolving 7.0 parts of copper(II) nitrate trihydrate in 40 parts of pure water. The total volume of the catalyst starting material liquid A and the catalyst starting material liquids B1 to B3 was 2.3 m³. [0088] While the liquid temperature of the catalyst starting material liquid A in the vessel was lowered to 50°C and kept at this temperature, the catalyst starting material liquid B1 was added to the catalyst starting material liquid A while stirring the catalyst starting material liquid A by using a rotary blade stirrer, and the mixture was stirred for 15 minutes. Thereafter, the catalyst starting material liquid B2 was added to the mixture, and this mixture was stirred for 15 minutes. Furthermore, the catalyst starting material liquid B3 was added to the mixture. Incidentally, the catalyst starting material liquids B1 to B3 were added in the same manner as in Example 3. In addition, u₂ at this time was 0.80 mol/min for the catalyst starting material liquid B1, 2.87 mol/min for the catalyst starting material liquid B2, and 0.18 mol/min for the catalyst starting material liquid B3. The obtained slurry contained a heteropoly acid having a Dawson-type structure or a salt thereof.

[0089] Thereafter, a catalyst for methacrylic acid production was prepared in the same manner as in Example 1. The catalyst for methacrylic acid production obtained had a

Dawson-type structure. In addition, the elemental composition of the catalyst for methacrylic acid production obtained other than oxygen was $\text{Mo}_{12}\text{P}_{1.7}\text{V}_{1.1}\text{Cu}_{0.5}\text{Cs}_{1.4}$. In addition, methacrylic acid was produced in the same manner as in Example 1 except that this catalyst for methacrylic acid production was used. The results are presented in Table 1.

[0090] [Comparative Example 4]

The catalyst starting material liquids A and B1 to B3 were prepared in the same manner as in Comparative Example 3. While the liquid temperature of the catalyst starting material liquid A in the vessel was lowered to 50°C and kept at this temperature, the catalyst starting material liquid B1 was added to the catalyst starting material liquid A while stirring the catalyst starting material liquid A by using a rotary blade stirrer, and the mixture was stirred for 15 minutes. Thereafter, the catalyst starting material liquid B2 was added to the mixture, and this mixture was stirred for 15 minutes. Furthermore, the catalyst starting material liquid B3 was added to the mixture. Incidentally, the catalyst starting material liquids B1 to B3 were added in the same manner as in Example 1. In addition, u_2 at this time was 0.62 mol/min for the catalyst starting material liquid B1, 2.21 mol/min for the catalyst starting material liquid B2, and 0.14 mol/min for the catalyst starting material liquid B3. The obtained slurry contained a heteropoly acid having a Dawson-type structure or a salt thereof.

[0091] Thereafter, a catalyst for methacrylic acid production was prepared in the same manner as in Example 1. The catalyst for methacrylic acid production obtained had a Dawson-type structure. In addition, the elemental composition of the catalyst for methacrylic acid production obtained other than oxygen was $\text{Mo}_{12}\text{P}_{1.7}\text{V}_{1.1}\text{Cu}_{0.5}\text{Cs}_{1.4}$. In addition, methacrylic acid was produced in the same manner as in Example 1 except that this catalyst for methacrylic acid production was used. The results are presented

in Table 1.

[0092] [Table 1]

[Table 1]

	T	$T/\sqrt[3]{V}$	u1 (L/min)	u2(B1) (mol/min)	u2(B2) (mol/min)	u2(B3) (mol/min)	Disposition of addition port in region Y ₁ to Y ₇	Distance of addition port from center of liquid surface of liquid in vessel	Structure of heteropoly acid in slurry	Percent conversion of methacrolein (%)	Selectivity for methacrylic acid (%)	Single flow yield of methacrylic acid (%)
Example 1	10	8.1	0.20	0.62	1.40	-	Disposed one addition port above each of Y ₁ to Y ₁₀	$\frac{3\sqrt{S/\pi}}{7}$	Keggin type	65.7	92.3	60.6
Example 2	4	9.0	0.03	0.09	0.21	-	Disposed one addition port above each of Y ₁ to Y ₄	$\frac{3\sqrt{S/\pi}}{5}$	Keggin type	62.5	92.7	58.0
Example 3	13	10.5	0.26	0.80	1.83	-	Disposed all addition ports above Y ₁	$\frac{5\sqrt{S/\pi}}{7}$ or more	Keggin type	56.5	92.0	52.0
Comparative Example 1	1	9.2	1.41	4.35	9.90	-	-	$\frac{4\sqrt{S/\pi}}{5}$	Keggin type	33.1	95.2	31.5
Comparative Example 2	1	13.2	0.07	0.22	0.49	-	-	$\frac{2\sqrt{S/\pi}}{5}$	Keggin type	34.6	94.4	32.6
Comparative Example 3	13	10.5	0.26	0.80	2.87	0.18	Disposed all addition ports above Y ₁	$\frac{5\sqrt{S/\pi}}{7}$ or more	Dawson type	65.3	75.3	49.2
Comparative Example 4	10	8.1	0.20	0.62	2.21	0.14	Disposed one addition port above each of Y ₁ to Y ₁₀	$\frac{3\sqrt{S/\pi}}{7}$	Dawson type	61.4	74.6	45.8

[0093] In Examples 1, 2 and 3, it has been confirmed that the value of $T/(^3\sqrt{V})$ and the values of u_1 and u_2 are within the ranges of the invention and the catalysts offer a high yield. Incidentally, in Example 3, the addition ports were disposed only above the region Y1 and thus the catalyst offered a slightly lower yield as compared with the catalysts in Examples 1 and 2. In addition, the values of u_1 and u_2 of the catalyst starting material liquid B2 were respectively outside the ranges of the invention in Comparative Example 1 and the value of $T/(^3\sqrt{V})$ was outside the range of the invention in Comparative Example 2, and thus the yields were lower as compared with those in Examples. In addition, in Comparative Examples 3 and 4, the slurry obtained did not contain a heteropoly acid having a Keggin-type structure or a salt thereof, and thus the yields were lower as compared with those in Examples. Incidentally, it is possible to obtain a methacrylic acid ester by esterifying methacrylic acid obtained in the present Examples.

[0094] This application is based upon and claims the benefit of priority of the prior Japanese Patent Application No. 2016-161888 filed on August 22, 2016, the entire contents of which are incorporated herein by reference.

[0095] The invention has been described with reference to embodiments and Examples, but the invention is not limited to the embodiments and Examples described above. Various changes that can be understood by those skilled in the art can be made to the configuration and details of the invention within the scope of the invention.

INDUSTRIAL APPLICABILITY

[0096] The catalyst for methacrylic acid production to be obtained by the method according to the invention is industrially useful since methacrylic acid can be produced at a high yield using the catalyst.

CLAIMS

1. A method for producing a catalyst for methacrylic acid production to be used when producing methacrylic acid by gas phase catalytic oxidation of methacrolein with molecular oxygen, comprising:

(1) a step for preparing a catalyst starting material liquid A containing at least molybdenum, phosphorus, and vanadium;

(2) a step for preparing a catalyst starting material liquid B containing a cation starting material; and

(3) a step for preparing a liquid containing a heteropoly acid having a Keggin type structure or a salt of the heteropoly acid by adding one of the catalyst starting material liquid A or the catalyst starting material liquid B to the other and mixing the liquids together, wherein

the following Formulas (i) and (ii) are satisfied in the step (3):

$$3.0 \leq T/(3\sqrt{V}) \leq 13.0 \text{ (i)}$$

$$0.01 \leq u_1 \leq 1.0 \text{ (ii)}$$

in Formulas (i) and (ii), V represents a volume [m³] of the catalyst starting material liquid A, T represents the number of addition ports for adding the other liquid and T is 2 or more, u₁ represents a volumetric flow rate [L/min] of the other liquid to be added, and u₁ represents an average value of volumetric flow rates of the other liquid to be added through the respective addition ports,

wherein the catalyst for methacrylic acid production has an elemental composition to be represented by the following Formula (vii):



in Formula (vii), Mo, P, V, Cu and O are element symbols representing molybdenum, phosphorus, vanadium, copper and oxygen, respectively, A represents at least one kind of element selected from the group consisting of antimony, bismuth, arsenic, germanium, zirconium, tellurium, silver, selenium, silicon, tungsten and boron, E represents at least one kind of element selected from the group consisting of iron, zinc, chromium, magnesium, calcium, strontium, tantalum, cobalt, nickel, manganese, barium, titanium, tin, lead, niobium, indium, sulfur, palladium, gallium, cerium and lanthanum, G represents at least one kind of element selected from the group consisting of lithium, sodium, potassium, rubidium, cesium and thallium, a, b, c, d, e, f, g and h represent atomic ratios of respective elements, and when a=12, b = 0.5 to 3, c = 0.01 to 3, d = 0.01 to 2, e = 0 to 3, f = 0 to 3, g = 0.01 to 3, and h is an atomic ratio of oxygen required to satisfy valences of the respective elements.

2. A method for producing a catalyst for methacrylic acid production to be used when producing methacrylic acid by gas phase catalytic oxidation of methacrolein with molecular oxygen, comprising:

(1) a step for preparing a catalyst starting material liquid A containing at least molybdenum, phosphorus, and vanadium;

(2) a step for preparing a catalyst starting material liquid B containing a cation starting material; and

(3) a step for preparing a liquid containing a heteropoly acid having a Keggin type structure or a salt of the heteropoly acid by adding the catalyst starting material liquid B to the catalyst starting material liquid A and mixing the liquids together, wherein

the following Formulas (i) and (iii) are satisfied in the step (3):

$$3.0 \leq T/(3\sqrt{V}) \leq 13.0 \text{ (i)}$$

$$0.01 \leq u_2 \leq 8 \text{ (iii)}$$

in Formulas (i) and (iii), V represents a volume [m³] of the catalyst starting material liquid A, T represents the number of addition ports for adding the catalyst starting material liquid B and T is 2 or more, u₂ represents a flow rate [mol/min] of the cation starting material in the catalyst starting material liquid B, and u₂ represents an average value of flow rates of the cation starting material in the catalyst starting material liquid B to be added through the respective addition ports,

wherein the catalyst for methacrylic acid production has an elemental composition to be represented by the following Formula (vii):



in Formula (vii), Mo, P, V, Cu and O are element symbols representing molybdenum, phosphorus, vanadium, copper and oxygen, respectively, A represents at least one kind of element selected from the group consisting of antimony, bismuth, arsenic, germanium, zirconium, tellurium, silver, selenium, silicon, tungsten and boron, E represents at least one kind of element selected from the group consisting of iron, zinc, chromium, magnesium, calcium, strontium, tantalum, cobalt, nickel, manganese, barium, titanium, tin, lead, niobium, indium, sulfur, palladium, gallium, cerium and lanthanum, G represents at least one kind of element selected from the group consisting of lithium, sodium, potassium, rubidium, cesium and thallium, a, b, c, d, e, f, g and h represent atomic ratios of respective elements, and when a=12, b = 0.5 to 3, c = 0.01 to 3, d = 0.01 to 2, e = 0 to 3, f = 0 to 3, g = 0.01 to 3, and h is an atomic ratio of oxygen required to satisfy valences of the respective elements.

3. The method for producing a catalyst for methacrylic acid production according to claim 1, wherein one of the catalyst starting material liquid A or the catalyst starting material liquid B is added into a vessel that contains the other and satisfies the following Formula (iv), and mixed with the other in the step (3):

$$0.1 \leq S_3/W_2 \leq 50 \text{ (iv)}$$

in Formula (iv), S represents a surface area [m²] of a liquid surface of the liquid in the vessel and W represents a volume [m³] of the liquid in the vessel.

4. The method for producing a catalyst for methacrylic acid production according to claim 2, wherein the catalyst starting material liquid B is added into a vessel that contains the catalyst starting material liquid A and satisfies the following Formula (iv), and mixed with the catalyst starting material liquid A in the step (3):

$$0.1 \leq S_3/W_2 \leq 50 \text{ (iv)}$$

in Formula (iv), S represents a surface area [m²] of a liquid surface of the liquid in the vessel and W represents a volume [m³] of the liquid in the vessel.

5. The method for producing a catalyst for methacrylic acid production according to claim 3 or 4, wherein the addition port is disposed above the liquid surface of the liquid in the vessel in the step (3).

6. The method for producing a catalyst for methacrylic acid production according to claim 5, wherein the following Formula (v) is satisfied in the step (3):

$$2 \leq T/S \leq 100 \text{ (v)}$$

in Formula (v), T is synonymous with T in Formula (i) above and S is synonymous with S in Formula (iv) above.

7. The method for producing a catalyst for methacrylic acid production according to claim 5 or 6, wherein one addition port is disposed above each of Y₁ to Y_T, where Y₁ to Y_T respectively represent regions of liquid surfaces to be divided by T straight lines drawn from a center of the liquid surface of the liquid in the vessel toward a wall

surface of the vessel to be substantially parallel to the liquid surface so that a central angle is $360^\circ/T$ in the step (3).

8. The method for producing a catalyst for methacrylic acid production according to any one of claims 5 to 7, wherein the addition port is not present above a circular region to be drawn with a radius R [m] to be calculated by the following Formula (vi) by having a center of the liquid surface of the liquid in the vessel as a center in the step (3):

[Math. 1]

$$R = \sqrt{\frac{S/\pi}{3}} \quad (\text{v i})$$

in Formula (vi), S is synonymous with S in Formula (iv).

9. The method for producing a catalyst for methacrylic acid production according to claim 1, wherein the catalyst starting material liquid B is added into a vessel containing the catalyst starting material liquid A and mixed with the catalyst starting material liquid A in the step (3).

10. The method for producing a catalyst for methacrylic acid production according to any one of claims 1 to 9, wherein a total volume of the catalyst starting material liquid A prepared in the step (1) and the catalyst starting material liquid B prepared in the step (2) is 0.2 m³ or more.

11. The method for producing a catalyst for methacrylic acid production according to any one of claims 1 to 10, wherein the cation starting material is at least one kind

selected from the group consisting of a compound containing an alkali metal and a compound containing an ammonium ion.

12. The method for producing a catalyst for methacrylic acid production according to any one of claims 1 to 11, further comprising a step for drying the liquid containing a heteropoly acid having a Keggin-type structure or a salt of the heteropoly acid to obtain a catalyst precursor.

13. The method for producing a catalyst for methacrylic acid production according to claim 12, further comprising a step for subjecting the catalyst precursor to a heat treatment.

14. A method for producing methacrylic acid, comprising conducting gas phase catalytic oxidation of methacrolein with molecular oxygen in the presence of a catalyst for methacrylic acid production produced by the method according to any one of claims 1 to 13.

15. A method for producing methacrylic acid, comprising producing a catalyst for methacrylic acid production by the method according to any one of claims 1 to 13 and conducting gas phase catalytic oxidation of methacrolein with molecular oxygen in the presence of the catalyst for methacrylic acid production.

16. A method for producing a methacrylic acid ester, comprising esterifying methacrylic acid produced by the method for producing methacrylic acid according to claim 14 or 15.