

DESCRIPTION

METHOD FOR PRODUCING CATALYST FOR METHACRYLIC-ACID PRODUCTION AND METHODS FOR PRODUCING METHACRYLIC ACID AND METHACRYIC ESTER

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TECHNICAL FIELD

[0001]

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

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BACKGROUND ART

[0002]

As a catalyst for producing methacrylic acid (hereinafter also simply referred to as "catalyst") used when producing methacrylic acid by oxidizing methacrolein, for example, a heteropolyacid catalyst containing molybdenum and phosphorus is known. Examples of the heteropolyacid catalyst include a proton-type heteropolyacid whose counter cation is a proton, and a heteropoly acid salt obtained by substituting a part of the proton with a cation other than a proton (hereinafter, a proton-type heteropolyacid is simply referred to as "heteropolyacid", and proton-type heteropolyacid and/or heteropolyacid salt is also simply referred to as "heteropolyacid (salt)").

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[0003]

The heteropolyacid (salt) is a condensed oxygen acid (salt) formed by a coordination atom (hereinafter referred to as a poly-atom) that forms the basic skeleton of the polyacid and an oxide of a hetero atom. Phosphorus, silicon, arsenic, germanium, titanium, antimony, and the like can be hetero atoms, and tungsten, molybdenum, vanadium, niobium, tantalum, and the like can be poly-atoms. The basic structure of the heteropolyacid (salt) includes Keggin-type, Dawson-type, Preyssler-type, etc. (Non-patent Document 1). Heteropolyacid catalysts have also been improved for the purpose of improving the yield of methacrylic acid. For example, an attempt to improve the yield of methacrylic acid by improving the catalyst by controlling the basic structure and crystal structure of the heteropolyacid

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has been reported (Non-patent Document 2). In Non-Patent Document 2, the heteropolyacids composed of phosphorus and molybdenum have basic structures such as Keggin-type, Dawson-type and their deficient type, and it has been reported that the basic structure varies depending on the ionic strength, pH, etc. of the heteropolyacid aqueous solution.

[0004]

Patent Document 1 discloses that a catalyst prepared using a specific production method contributes to the yield of methacrylic acid. Specifically, a catalyst prepared by a production method including the following steps (i) to (iv) is disclosed:

- (i) adding at least a molybdenum raw material and an element X raw material in water to prepare an aqueous slurry or aqueous solution containing a heteropolyacid;
- (ii) adding an alkali metal compound to the aqueous slurry or aqueous solution to precipitate a heteropolyacid salt which is at least a part of the alkali metal salt of the heteropolyacid;
- (iii) adding a phosphorus raw material selected from the group consisting of orthophosphoric acid, phosphorus pentoxide and ammonium phosphate into the aqueous slurry or aqueous solution in which the heteropolyacid salt is precipitated;
- (iv) drying the aqueous slurry or aqueous solution containing all the raw materials to obtain a dry product; and
- (v) heat-treating the dry product.

PRIOR ART LITERATURE

PATENT DOCUMENT

[0005]

Patent Document 1: WO2010/013749A1

NON-PATENT DOCUMENT

[0006]

Non-Patent Document 1: Makoto Misono, Masato Hashimoto, Catalyst, vol. 34, No. 3 (1992)

Non-Patent Document 2: Lege Pattersson, Ingerarb Andersson, Lars-Oloh

Ohman, Inorganic Chemistry, vol. 25, 4726-4733 (1986)

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

5 **[0007]**

However, further improvement of the catalyst is desired in order to improve the yield of methacrylic acid.

[0008]

10 The present invention provides a method for producing a catalyst for producing methacrylic acid that can be used as an industrial catalyst for the purpose of increasing the yield of methacrylic acid. Another object of the present invention is to provide a method for producing methacrylic acid and methacrylic acid ester using this catalyst.

15 **MEANS FOR SOLVING THE PROBLEMS**

[0009]

As a result of intensive studies in view of the above problems, the present inventors have found that the above problems can be solved by using a catalyst produced by a specific production method as a catalyst for producing methacrylic acid, and completed the invention.

That is, the present invention includes the following aspects [1] to [10].

[1] A method for producing a catalyst used for producing methacrylic acid by oxidizing methacrolein, including:

25 step (I): mixing at least a molybdenum raw material and a phosphorus raw material with a solvent to prepare a solution or slurry;

step (II): drying the solution or slurry to obtain a catalyst precursor; and

step (III): obtaining the catalyst by calcining the catalyst precursor,

wherein in the step (I), triammonium phosphate is used as at least a part of the phosphorus raw material.

30 **[0010]**

[2] The method for producing a catalyst according to [1], wherein the catalyst precursor obtained in the step (II) has a Keggin-type heteropolyacid structure.

[3] The method for producing a catalyst according to [1] or [2], wherein the catalyst obtained in the step (III) satisfies the following formula (1) when the molar ratio of phosphorus to 12 moles of molybdenum is a:

$$0.5 \leq a \leq 3 \quad (1).$$

5 [4] The method for producing a catalyst according to any one of [1] to [3], wherein the catalyst obtained in the step (III) satisfies the following formula (2) when the molar ratio of phosphorus to 12 moles of molybdenum is a, and a molar ratio of phosphorus derived from triammonium phosphate to 12 moles of molybdenum is a':

$$0.1 \leq a'/a \leq 1 \quad (2).$$

10 [5] The method for producing a catalyst according to any one of [1] to [4], wherein the catalyst precursor obtained in the step (II) satisfies the following formula (3) when the molar ratio of ammonium species to 12 moles of molybdenum is h₂, and a molar ratio of ammonium species derived from triammonium phosphate to 12 moles of molybdenum is h₂':

$$15 \quad 0.2 \leq h_2'/h_2 \leq 1 \quad (3)$$

[0011]

[6] The method for producing a catalyst according to any one of [1] to [5], wherein the catalyst obtained in the step (III) has a composition represented by the following formula (4):

$$20 \quad P_a Mo_b V_c Cu_d A_e E_f G_g (NH_4)_h O_i \quad (4)$$

(In the formula (4), P, Mo, V, Cu, NH₄ and O represent phosphorus, molybdenum, vanadium, copper, ammonium species and oxygen, respectively.

A represents at least one element selected from the group consisting of antimony, bismuth, arsenic, germanium, zirconium, tellurium, silver, selenium,
25 silicon, tungsten and boron.

E represents at least one element selected from the group consisting of iron, zinc, chromium, calcium, strontium, tantalum, cobalt, nickel, manganese, titanium, tin, lead, niobium, indium, sulfur, palladium, gallium, cerium and lanthanum.

G represents at least one element selected from the group consisting of
30 potassium, rubidium, cesium, thallium, magnesium and barium.

a to **i** represent the molar ratio of each component, and when **b** = 12, $0.5 \leq a \leq 3$, $0.01 \leq c \leq 3$, $0.01 \leq d \leq 2$, $0 \leq e \leq 3$, $0 \leq f \leq 3$, $0.01 \leq g \leq 3$, $0 \leq h \leq 20$, and **i** is a

molar ratio of oxygen necessary to satisfy the valence of each component.)

[0012]

[7] A method for producing methacrylic acid, including oxidizing methacrolein in the presence of the catalyst produced by the method according to any one of [1] to [6].

[8] A method for producing methacrylic acid, including a step of producing a catalyst by the method according to any one of [1] to [6] and a step of oxidizing methacrolein using the catalyst.

[9] A method for producing methacrylic acid ester, including esterifying methacrylic acid produced by the method according to [7] or [8].

[10] A method for producing methacrylic acid ester, including a step of producing a catalyst by the method according to any one of [1] to [6], a step of oxidizing methacrolein using the catalyst, and a step of esterifying the methacrylic acid.

EFFECTS OF THE INVENTION

[0013]

According to this invention, when oxidizing methacrolein and producing methacrylic acid, the catalyst for producing methacrylic acid, which can be expected to further improve the yield of methacrylic acid. Moreover, methods of producing methacrylic acid and methacrylic acid ester using the catalyst can be provided.

MODE FOR CARRYING OUT THE INVENTION

[0014]

Hereinafter, the present invention will be described in detail.

[Catalyst for methacrylic acid production]

The catalyst obtained by the production method of the present invention is used when methacrylic acid is produced by oxidizing methacrolein. The catalyst contains at least a phosphorus atom and a molybdenum atom, and preferably satisfies the following formula (1) when the molar ratio of the phosphorus atom to 12 moles of the molybdenum atom is a:

$$0.5 \leq a \leq 3 \quad (1)$$

By satisfying the above formula (1), a heteropolyacid structure suitable for methacrylic acid production can be formed.

[0015]

Moreover, it is preferable that a catalyst has a composition represented by following formula (4) from a viewpoint of the yield improvement of methacrylic acid. In addition, the molar ratio of each element in the catalyst can be obtained by analyzing a component in which the catalyst is dissolved in aqueous ammonia by ICP atomic emission spectroscopy. The molar ratio of the ammonium species can be determined by analyzing the catalyst by the Kjeldahl method.

10 [0016]



(In the formula (4), P, Mo, V, Cu, NH₄ and O represent phosphorus, molybdenum, vanadium, copper, ammonium species and oxygen, respectively.

A represents at least one element selected from the group consisting of antimony, bismuth, arsenic, germanium, zirconium, tellurium, silver, selenium, silicon, tungsten and boron.

E represents at least one element selected from the group consisting of iron, zinc, chromium, calcium, strontium, tantalum, cobalt, nickel, manganese, titanium, tin, lead, niobium, indium, sulfur, palladium, gallium, cerium and lanthanum.

20 G represents at least one element selected from the group consisting of potassium, rubidium, cesium, thallium, magnesium and barium.

a to **i** represent the molar ratio of each component, and when **b** = 12, $0.5 \leq a \leq 3$, $0.01 \leq c \leq 3$, $0.01 \leq d \leq 2$, $0 \leq e \leq 3$, $0 \leq f \leq 3$, $0.01 \leq g \leq 3$, $0 \leq h \leq 20$, and **i** is a molar ratio of oxygen necessary to satisfy the valence of each component.)

25 [0017]

The term "ammonium species" as used herein is a generic term for ammonium, that can be ammonium ions (NH₄⁺), contained in ammonia (NH₃) and an ammonium-containing compound such as an ammonium salt.

[0018]

30 In the formula (4), when **b** = 12, the lower limit of **a** is preferably 1 or more. The upper limit is preferably 2.5 or less, and more preferably 2 or less. The lower limit of **c** is preferably 0.1 or more, and the upper limit is preferably 2.5 or less. The

lower limit of **d** is preferably 0.05 or more, and the upper limit is preferably 1.5 or less. The lower limit of **e** is preferably 0.01 or more, and the upper limit is preferably 2.5 or less. The upper limit of **f** is preferably 2 or less, and more preferably 1 or less. The lower limit of **g** is more preferably 0.1 or more, and the upper limit is more preferably 2.5 or less. The upper limit of **h** is preferably 5 or less, and more preferably 3 or less.

[0019]

[Method for producing a catalyst for methacrylic acid production]

The present invention is a method for producing a catalyst used for producing methacrylic acid by oxidizing methacrolein, and includes the following steps (I) to (III):

- step (I): mixing at least a molybdenum raw material and a phosphorus raw material with a solvent to prepare a solution or slurry;
 - step (II): drying the solution or slurry to obtain a catalyst precursor; and
 - step (III): obtaining the catalyst by calcining the catalyst precursor,
- wherein triammonium phosphate is used as at least a part of the phosphorus raw material in the step (I).

[0020]

The method is characterized in that triammonium phosphate is used as at least part of the phosphorus raw material in the step (I). Thereby, the catalyst for methacrylic acid production which can be used as an industrial catalyst can be manufactured. It is known that ammonium phosphate is used in a step of mixing at least a molybdenum raw material and a phosphorus raw material with a solvent to prepare a solution or slurry (for example, Patent Document 1). However, the expression "ammonium phosphate" generally indicates a highly versatile ammonium phosphate salt, that is, ammonium dihydrogen phosphate and diammonium hydrogen phosphate.

The present inventors have now found that a catalyst having a high methacrylic acid yield can be obtained by using triammonium phosphate as at least a part of the phosphorus raw material. This is considered to be because a catalyst precursor having a Keggin-type heteropolyacid structure suitable for a methacrylic acid production reaction can be obtained by maintaining triammonium phosphate as a

buffer solution and keeping the pH stable. The yield of methacrylic acid is improved by using a catalyst obtained by calcining this precursor.

Hereinafter, each step will be described in detail.

[0021]

5 (Step (I))

In step (I), at least a molybdenum raw material and a phosphorus raw material are mixed with a solvent to prepare a solution or slurry. At this time, triammonium phosphate is used as at least a part of the phosphorus raw material.

[0022]

10 <Molybdenum raw material>

Examples of the molybdenum raw material include ammonium paramolybdate, molybdenum trioxide, molybdic acid, and molybdenum chloride.

[0023]

<Phosphorus raw material>

15 Examples of triammonium phosphate include triammonium phosphate anhydride and triammonium phosphate hydrate. By producing a catalyst using these triammonium phosphates as at least a part of the phosphorus raw material, a catalyst exhibiting a high methacrylic acid yield can be obtained. Triammonium phosphate may be used alone or in combination with other phosphorus raw materials.

20 Examples of other phosphorus raw materials include orthophosphoric acid, phosphorus pentoxide, or phosphates such as ammonium phosphate (ammonium dihydrogen phosphate, diammonium hydrogen phosphate) and cesium phosphate.

It is preferable that the amount of the phosphorus raw material containing triammonium phosphate satisfies the formulas (2) and (3) described later. Thereby,
25 the catalyst which shows a high methacrylic acid yield can be obtained.

[0024]

<Other raw materials>

As described above, the catalyst produced in the present invention preferably has a composition represented by the formula (4). Therefore, it is preferable to
30 further use a raw material containing an element constituting the composition. As these raw materials, nitrates, carbonates, acetates, ammonium salts, oxides, halides, oxoacids, oxoacid salts and the like of each element can be used alone or in

combination of two or more.

Specifically, examples of the vanadium raw material include ammonium metavanadate, vanadium pentoxide, and vanadium chloride. Examples of the copper raw material include copper sulfate, copper nitrate, copper oxide, copper carbonate, copper acetate, and copper chloride. The raw material of ammonium species is not particularly limited as long as it is an ammonium-containing compound. Examples thereof include triammonium phosphate and hydrates thereof, ammonium hydroxide, aqueous ammonia, ammonium nitrate, ammonium carbonate, ammonium bicarbonate and the like. These raw materials may be used alone or in combination of two or more.

[0025]

<Solvent>

As the solvent, water, an organic solvent, a mixed solvent of water and an organic solvent, or the like can be used, but water is preferably used from an industrial viewpoint.

<Mixing of raw material and solvent>

The raw materials are mixed by adding a part or all of them to the solvent. The order of addition of the raw materials is not particularly limited, but a catalyst exhibiting a high methacrylic acid yield can be obtained by preferably adding the solution or slurry so that the pH of the solution or slurry is within the range of 0.1 to 6.5. Further, the lower limit of the pH is more preferably 0.5 or more, and even more preferably 1 or more. The upper limit of the pH is more preferably 6 or less, and further preferably 3 or less. The pH of the solution or slurry does not need to be strictly measured and controlled by titration, and can be adjusted while measuring using a commercially available pH meter or the like. For the adjustment of pH, an acid (sulfuric acid, nitric acid, hydrochloric acid, etc.) or base containing the same ions as the raw material can be used as necessary. The temperature of the solvent when adding the raw materials to the solvent is preferably 10 to 60° C, and more preferably 50° C or lower, from the viewpoint of avoiding unnecessary reactions of the respective raw materials. Moreover, if the temperature is within the range, it is also possible to add a raw material with heating up.

[0026]

After adding the raw materials, a solution or slurry is prepared by stirring while heating. The heating temperature is not particularly limited, but is preferably 75 to 130° C, more preferably 95 to 130° C. By setting the heating temperature to 75° C or higher, the reaction rate of the compounds contained in the solution or slurry can be sufficiently increased. Moreover, evaporation of water in the solution or slurry can be suppressed by heating temperature being 130° C or less. Depending on the vapor pressure of the solvent to be used, it may be concentrated and refluxed during heating, or may be heat-treated under pressure conditions by operating in a closed container.

10 [0027]

The rising rate of temperature is not particularly limited, but is preferably 0.8 to 15° C/min. When the rising rate of temperature is 0.8° C/min or more, the time required for the step (I) can be shortened. Moreover, when the rising rate of temperature is 15° C/min or less, the temperature can be increased using conventional temperature increasing equipment. Stirring is preferably performed at a stirring power of 0.01 kW/m³ or more, and more preferably 0.05 kW/m³ or more. By setting the stirring power to 0.01 kW/m³ or more, the temperature, components, and local spots of the temperature of the solution or slurry are reduced, and a structure suitable as a catalyst for methacrylic acid production is stably formed. Further, from the viewpoint of the production cost of the catalyst, the stirring is usually performed with a stirring power of 3.5 kW/m³.

20 [0028]

The pH of the solution or slurry obtained in the above step (I) is preferably 0.2 to 3, the lower limit is preferably 0.5 or more, and the upper limit is more preferably 2.5 or less. Thereby, in the step (II) described later, a catalyst precursor having a Keggin-type heteropolyacid structure suitable for methacrylic acid production can be obtained. Examples of the method for controlling the pH of the solution and slurry within the above range include a method of appropriately selecting the amount of each raw material containing a catalyst constituent and adding nitric acid, oxalic acid or the like as appropriate.

30 [0029]

(Step (II))

In step (II), the solution or slurry obtained in the step (I) is dried to obtain a catalyst precursor.

The drying method is not particularly limited, and examples include drum drying, freeze drying, spray drying, and evaporation to dryness. Among these, drum drying, spray drying, or evaporation to dryness is preferable from the viewpoint of drying ability. The drying temperature is preferably 120 to 500° C, the lower limit is 140° C or higher, and the upper limit is more preferably 350° C or lower. Drying is performed until the solution or slurry is solidified. Here, the moisture content of the catalyst precursor obtained by drying is preferably 0.1 to 4.5% by mass.

The conditions such as the drying method, the drying temperature, and the water content can be appropriately selected depending on the shape and size of the desired catalyst precursor.

[0030]

As described above, the catalyst precursor obtained in the step (II) preferably has a Keggin-type heteropolyacid structure suitable for methacrylic acid production. The structure of the catalyst precursor can be determined by infrared absorption spectrometry. When the catalyst precursor has a Keggin-type heteropolyacid structure, the obtained infrared absorption spectrum has characteristic peaks in the vicinity of 1060, 960, 870, and 780 cm⁻¹.

[0031]

In the catalyst precursor, it is preferable that $1 \leq h_2 \leq 5$ is satisfied, where h_2 is a molar ratio of ammonium species to 12 moles of molybdenum. The value of h_2 is a value obtained by analyzing the catalyst precursor by the Kjeldahl method. The value of h_2 can be controlled by changing the charged amounts of the molybdenum raw material and the ammonium species raw material in the step (I). When h_2 is 1 or more, a catalyst precursor having a crystal structure suitable for methacrylic acid production is obtained in step (II). Moreover, when h_2 is 5 or less, it becomes easy to form a Keggin-type heteropolyacid structure suitable for methacrylic acid production. The lower limit of h_2 is more preferably 1.5 or more, and the upper limit is more preferably 4.5 or less.

[0032]

Moreover, in the catalyst precursor, when the molar ratio of the ammonium

species derived from triammonium phosphate to 12 moles of molybdenum is h_2' , it is preferable in that it can be obtained a catalyst exhibiting a high methacrylic acid yield that satisfies the following formula (3). Note that the value of h_2' is a value obtained from the amounts of the molybdenum raw material and triammonium phosphate charged.

$$0.2 \leq h_2'/h_2 \leq 1 \quad (3)$$

The value of h_2'/h_2 can be controlled by changing the charged amounts of triammonium phosphate and ammonium species raw material in the step (I). The lower limit of h_2'/h_2 is preferably 0.5 or more, more preferably 0.6 or more, particularly preferably 0.7 or more, and most preferably 0.8 or more.

The catalyst precursor obtained in step (II) is then molded by a molding step. However, the molding may be carried out after step (III) described later.

[0033]

(Molding step)

In the molding step, the catalyst precursor or the catalyst obtained in step (III) described later is molded. The molding method is not particularly limited, and a known dry or wet molding method can be applied. For example, tablet molding, extrusion molding, pressure molding, rolling granulation and the like can be mentioned. There is no restriction in particular as a shape of a molded object, arbitrary shapes, such as a spherical granular shape, a ring shape, a columnar pellet shape, a star shape, and the granule shape by pulverizing and classifying after molding, are mentioned.

The pulverization includes, for example, a method using a pulverizer such as a ball mill, a high-speed rotary mill, a jet mill, or a grinding machine. Examples of the classification include a method using a classifier such as a mesh fixed sieve, a vibrating sieve, an in-plane motion sieve or the like.

The size of the molded article is preferably 0.1 to 10 mm in diameter. When the diameter of the molded product is 0.1 mm or more, the pressure loss in the reaction tube can be reduced. In the meantime, when the diameter of the molded product is 10 mm or less, the activity of the catalyst is further improved, and the yield of methacrylic acid is improved. When molding, it may be supported on a carrier or other additives may be mixed.

[0034]

(Step (III))

In the step (III), the catalyst precursor obtained in the step (II) or a molded product of the catalyst precursor obtained in the molding step (hereinafter, also collectively referred to as catalyst precursor) is calcined to obtain a catalyst. The catalyst precursor can be further improved in catalytic activity by calcination.

There is no particular limitation on the calcination method, and a suitable method may be appropriately selected from stationary calcination, fluidized calcination, and the like. Examples of the stationary calcination include a calcination method using a box-type electric furnace, an annular calcination furnace, or the like. Examples of fluidized calcination include a method of calcination using a fluidized calcining furnace, a rotary kiln, or the like.

Calcination is performed, for example, in an oxygen-containing gas such as air or inert gas atmosphere, but is preferably performed in an oxygen-containing gas atmosphere such as air. The “inert gas” means a gas that does not decrease the catalytic activity, and examples thereof include nitrogen, carbon dioxide gas, helium, and argon. These may be used singly or by mixing two or more thereof. As long as the desired calcination gas atmosphere can be maintained, the calcination gas may or may not be flowed.

From the viewpoint of obtaining a catalyst exhibiting a high methacrylic acid yield, the calcination temperature is preferably 200 to 500° C, the lower limit is more preferably 300° C or higher, and the upper limit is more preferably 450° C or lower. The calcination time is preferably 1 to 40 hours, and the lower limit is more preferably 2 hours or more.

[0035]

In the catalyst obtained in the step (III), from the viewpoint of obtaining a catalyst exhibiting a high yield of methacrylic acid, it is preferable to satisfy the above-mentioned formula (1), when the molar ratio of phosphorus to 12 moles of molybdenum is a, and to satisfy the following formula (2), when the molar ratio of phosphorus derived from triammonium phosphate to 12 moles of molybdenum is a'. The value of a' is a value obtained from the charging amounts of molybdenum raw material and triammonium phosphate.

$$0.1 \leq a'/a \leq 1 \quad (2)$$

As described above, the value of a'/a can be controlled by changing the charging amounts of triammonium phosphate and other phosphorus raw materials in the step (I). The lower limit of a'/a is preferably 0.4 or more, more preferably 0.5 or more, particularly preferably 0.6 or more, and most preferably 0.7 or more.

[0036]**[Method for Producing Methacrylic Acid]**

In the presence of the catalyst produced by the method according to the present invention, methacrolein is oxidized, particularly subjected to a gas-phase catalytic oxidation with molecular oxygen. In other words, the method for producing methacrylic acid according to the present invention includes a step of producing a catalyst by the method according to the present invention and a step of gas-phase catalytic oxidation of methacrolein with molecular oxygen using the catalyst. By using the catalyst for methacrylic acid production produced by the method according to the present invention, methacrylic acid can be produced at a higher yield than prior art.

[0037]

The method for producing methacrylic acid according to the present invention produces methacrylic acid by bringing a source gas containing methacrolein and molecular oxygen into contact with the catalyst according to the present invention. In this reaction, a fixed bed reactor can be used. The reaction can be carried out by filling the catalyst in a reaction tube and supplying a source gas to the reactor. The catalyst may be filled as one layer, or a plurality of catalysts having different activities may be divided into a plurality of layers and filled, respectively. In addition, the catalyst for methacrylic acid production may be diluted and filled with an inert carrier to control the activity.

[0038]

The concentration of methacrolein in the source gas is not particularly limited, but is preferably 1 to 20% by volume, the lower limit is more preferably 3% by volume, and the upper limit is more preferably 10% by volume or less. The raw material methacrolein may contain a small amount of impurities such as water and lower saturated aldehydes that do not substantially affect the reaction.

[0039]

The concentration of the molecular oxygen in the source gas is preferably 0.4 to 4 moles per mole of methacrolein, the lower limit is more preferably 0.5 moles or more, and the upper limit is more preferably 3 moles or less. Note that air is preferred as the molecular oxygen source from the viewpoint of economic efficiency. If necessary, a gas enriched with molecular oxygen by adding pure oxygen to air may be used.

[0040]

The source gas may be obtained by diluting methacrolein and molecular oxygen with an inert gas such as nitrogen or carbon dioxide. Further, water vapor may be added to the source gas. By carrying out the reaction in the presence of water vapor, methacrylic acid can be obtained with high yield. The concentration of water vapor in the source gas is preferably 0.1 to 50% by volume, the lower limit is more preferably 1% by volume, and the upper limit is more preferably 40% by volume or less.

[0041]

The contact time between the source gas and the catalyst for producing methacrylic acid is preferably 1.5 to 15 seconds, the lower limit is more preferably 2 seconds or more, and the upper limit is more preferably 10 seconds or less. The reaction pressure is preferably 0.1 to 1 MPa (G). Here, (G) means a gauge pressure. The reaction temperature is preferably 200 to 450° C, the lower limit is more preferably 250° C or higher, and the upper limit is more preferably 400° C or lower.

[0042]**[Method for Producing Methacrylic Acid Ester]**

The method for producing a methacrylic acid ester according to the present invention is to esterify the methacrylic acid produced by the method according to the present invention. In other words, the method for producing a methacrylic acid ester according to the present invention includes a step of producing a catalyst for methacrylic acid production by the method according to the present invention, a step of gas-phase catalytic oxidation of methacrolein with molecular oxygen using the catalyst, and a step of esterifying the methacrylic acid. By using the catalyst for methacrylic acid production according to the present invention, methacrylic acid can

be obtained in high yield by gas phase catalytic oxidation of methacrolein, and therefore, the methacrylic acid ester can be obtained in high yield from the raw material methacrolein.

The alcohol to be reacted with methacrylic acid is not particularly limited, and examples thereof include methanol, ethanol, isopropanol, n-butanol, and isobutanol. Examples of the resulting methacrylic acid ester include methyl methacrylate, ethyl methacrylate, propyl methacrylate, and butyl methacrylate. The reaction can be carried out in the presence of an acidic catalyst such as a sulfonic acid type cation exchange resin. The reaction temperature is preferably 50 to 200° C.

EXAMPLES

[0043]

Hereinafter, the present invention will be explained in detail by examples and comparative examples, but the present invention is not limited to these examples.

“Parts” in Examples and Comparative Examples means parts by mass.

[0044]

The structure of the catalyst precursor was judged by infrared absorption spectrometry using NICOLET 6700 FT-IR (product name, manufactured by Thermo Electron CO., Ltd.).

The molar ratio of each element in the catalyst and the catalyst precursor was calculated by analyzing a component in which the catalyst and the catalyst precursor were dissolved in aqueous ammonia by ICP atomic emission spectroscopy. The molar ratio of the ammonium species was calculated by analyzing the catalyst and the catalyst precursor by the Kjeldahl method. The values of a' and h2' were calculated from the charging amounts of the molybdenum raw material and triammonium phosphate.

[0045]

For the analysis of the source gas and the product, gas chromatography (apparatus: GC-2014 manufactured by Shimadzu Corporation, column: manufactured by Agilent J & W, product name (DB-FFAP, 30 m × 0.32 mm, film thickness 1.0 μm)) was used. From the results of gas chromatography, the yield of methacrylic acid was determined by the following formula.

Yield of methacrylic acid (%) = (number of moles of methacrylic acid produced / number of moles of methacrolein supplied) $\times$ 100

[0046]

[Example 1]

5 To 1,200 parts of pure water at room temperature, 300 parts of molybdenum trioxide and 10.2 parts of ammonium metavanadate were added and dispersed by stirring, and 42.1 parts of triammonium phosphate trihydrate, 8.9 parts of 85% aqueous phosphoric acid solution, a diluted substance of which 40.2 parts of cesium bicarbonate were diluted with 175 parts of pure water, and a diluted substance of
10 which 6.2 parts of copper (II) nitrate trihydrate were dissolved in 9.0 parts of pure water were added. The resulting slurry was heated to 95° C at 2° C/min and stirred for 2 hours while maintaining the temperature at 95° C. The obtained slurry was heated and evaporated to dryness to obtain a catalyst precursor. The obtained catalyst precursor had a Keggin-type heteropolyacid structure.

15 **[0047]**

The catalyst precursor was pressure-molded, pulverized, and classified using a sieve so that the particle diameter was distributed in the range of 710 μ m to 2.36 mm. The obtained molded product was calcined at 380° C for 5 hours under air flow to produce a catalyst. The composition of the resulting catalyst excluding oxygen
20 was $P_{1.6}Mo_{12}V_{0.5}Cu_{0.15}Cs_{1.2}$. The molar ratio of ammonium species in the catalyst was $0 \leq h \leq 1$.

[0048]

The catalyst was filled into a reactor so that the reaction rate of methacrolein was within the range of 37 to 60%, and then a source gas composed of 5% by volume
25 of methacrolein, 10% by volume of oxygen, 30% by volume of water vapor and 55% by volume of nitrogen was circulated and the reaction was performed at a reaction temperature of 285° C. The product was collected and analyzed by gas chromatography to calculate the methacrylic acid yield. The results are shown in Table 1.

30 **[0049]**

[Example 2]

A catalyst precursor was obtained in the same manner as in Example 1,

except that 42.1 parts of triammonium phosphate trihydrate was changed to 38.8 parts. The obtained catalyst precursor had a Keggin-type heteropolyacid structure. The catalyst precursor was molded in the same manner as in Example 1, and calcined to obtain a catalyst. The composition of the resulting catalyst excluding oxygen was $P_{1.5}Mo_{12}V_{0.5}Cu_{0.15}Cs_{1.2}$. The molar ratio of ammonium species in the catalyst was $0 \leq h \leq 1$.

Using this catalyst, methacrylic acid was produced in the same manner as in Example 1, and the methacrylic acid yield was calculated. The results are shown in Table 1.

10 [0050]

[Example 3]

A catalyst precursor was obtained in the same manner as in Example 1, except that 42.1 parts of triammonium phosphate trihydrate was changed to 31.0 parts and no 85% aqueous phosphoric acid solution was added. The obtained catalyst precursor had a Keggin-type heteropolyacid structure.

The catalyst precursor was molded in the same manner as in Example 1, and calcined to obtain a catalyst. The composition of the obtained catalyst excluding oxygen was $P_{0.9}Mo_{12}V_{0.5}Cu_{0.15}Cs_{1.2}$. The molar ratio of ammonium species in the catalyst was $0 \leq h \leq 1$.

20 [0051]

Using this catalyst, methacrylic acid was produced in the same manner as in Example 1, and the methacrylic acid yield was calculated. The results are shown in Table 1.

[0052]

25 [Example 4]

A catalyst precursor was obtained in the same manner as in Example 1, except that 42.1 parts of triammonium phosphate trihydrate was changed to 38.8 parts and 8.9 parts of 85% aqueous phosphoric acid solution was changed to 4.3 parts. The obtained catalyst precursor had a Keggin-type heteropolyacid structure.

The catalyst precursor was molded in the same manner as in Example 1, and calcined to obtain a catalyst. The composition of the obtained catalyst excluding oxygen was $P_{1.3}Mo_{12}V_{0.5}Cu_{0.15}Cs_{1.2}$. The molar ratio of ammonium species in the

catalyst was $0 \leq h \leq 1$.

Using this catalyst, methacrylic acid was produced in the same manner as in Example 1, and the methacrylic acid yield was calculated. The results are shown in Table 1.

5 **[0053]**

[Example 5]

A catalyst precursor was obtained in the same manner as in Example 1, except that 42.1 parts of triammonium phosphate trihydrate was changed to 62.2 parts. The obtained catalyst precursor had a Keggin-type heteropolyacid structure.

10 The catalyst precursor was molded in the same manner as in Example 1, and calcined to obtain a catalyst. The composition of the obtained catalyst excluding oxygen was $P_{2.2}Mo_{12}V_{0.5}Cu_{0.15}Cs_{1.2}$. The molar ratio of ammonium species in the catalyst was $0 \leq h \leq 1$.

Using this catalyst, methacrylic acid was produced in the same manner as in Example 1, and the methacrylic acid yield was calculated. The results are shown in Table 1.

[0054]

[Example 6]

20 A catalyst precursor was obtained in the same manner as in Example 1, except that 38.8 parts of triammonium phosphate trihydrate and 11.6 parts of 28% aqueous ammonia were used instead of 42.1 parts of triammonium phosphate trihydrate. The obtained catalyst precursor had a Keggin-type heteropolyacid structure.

25 The catalyst precursor was molded in the same manner as in Example 1, and calcined to obtain a catalyst. The composition of the resulting catalyst excluding oxygen was $P_{1.5}Mo_{12}V_{0.5}Cu_{0.15}Cs_{1.2}$. The molar ratio of ammonium radicals in the catalyst was $0 \leq h \leq 1$.

Using this catalyst, methacrylic acid was produced in the same manner as in Example 1, and the methacrylic acid yield was calculated. The results are shown in Table 1.

30 **[0055]**

[Comparative Example 1]

A catalyst precursor was obtained in the same manner as in Example 1, except that 23.5 parts of diammonium hydrogen phosphate and 10.6 parts of 28% aqueous ammonia were used instead of 42.1 parts of triammonium phosphate trihydrate. The obtained catalyst precursor had a Keggin-type heteropolyacid structure.

The catalyst precursor was molded in the same manner as in Example 1, and calcined to obtain a catalyst. The composition of the resulting catalyst excluding oxygen was $P_{1.5}Mo_{12}V_{0.5}Cu_{0.15}Cs_{1.2}$. The molar ratio of ammonium species in the catalyst was $0 \leq h \leq 1$.

Using this catalyst, methacrylic acid was produced in the same manner as in Example 1, and the methacrylic acid yield was calculated. The results are shown in Table 1.

[0056]

[Comparative Example 2]

A catalyst precursor was obtained in the same manner as in Example 1, except that 31.6 parts of 28% aqueous ammonia was used instead of 40.2 parts of triammonium phosphate trihydrate, and 8.9 parts of 85% aqueous phosphoric acid solution was changed to 30.6 parts. The obtained catalyst precursor had a Keggin-type heteropolyacid structure.

The catalyst precursor was molded in the same manner as in Example 1, and calcined to obtain a catalyst. The composition of the resulting catalyst excluding oxygen was $P_{1.5}Mo_{12}V_{0.5}Cu_{0.15}Cs_{1.2}$. The molar ratio of ammonium radicals in the catalyst was $0 \leq h \leq 1$.

Using the catalyst, methacrylic acid was produced in the same manner as in Example 1, and the methacrylic acid yield was calculated. The results are shown in Table 1.

[0057]

[Comparative Example 3]

A catalyst precursor was obtained in the same manner as in Example 1, except that 46.7 parts of 28% ammonia water was used instead of 40.2 parts of triammonium phosphate trihydrate, and 8.9 parts of 85% aqueous phosphoric acid solution was changed to 30.6 parts. The obtained catalyst precursor had a Keggin-

type heteropolyacid structure.

The catalyst precursor was molded in the same manner as in Example 1, and calcined to obtain a catalyst. The composition of the resulting catalyst excluding oxygen was $P_{1.5}Mo_{12}V_{0.5}Cu_{0.15}Cs_{1.2}$. The molar ratio of ammonium species in the catalyst was $0 \leq h \leq 1$.

Using the catalyst, methacrylic acid was produced in the same manner as in Example 1, and the methacrylic acid yield was calculated. The results are shown in Table 1.

[0058]

10 [Comparative Example 4]

A catalyst precursor was obtained in the same manner as in Example 1, except that 21.7 parts of ammonium dihydrogen phosphate and 20.5 parts of 28% aqueous ammonia were used instead of 42.1 parts of triammonium phosphate trihydrate. The obtained catalyst precursor had a Keggin-type heteropolyacid structure.

The catalyst precursor was molded in the same manner as in Example 1, and calcined to obtain a catalyst. The composition of the resulting catalyst excluding oxygen was $P_{1.5}Mo_{12}V_{0.5}Cu_{0.15}Cs_{1.2}$. The molar ratio of ammonium species in the catalyst was $0 \leq h \leq 1$.

20 Using this catalyst, methacrylic acid was produced in the same manner as in Example 1, and the methacrylic acid yield was calculated. The results are shown in Table 1.

[0059]

[Table 1]

	Phosphorus raw material	a	a'/a	h ₂	h ₂ '/h ₂	Methacrolein conversion [%]	Selectivity of methacrylic acid [%]	Yield of methacrylic acid [%]
Example 1	Triammonium phosphate / phosphoric acid	1.64	0.73	4.08	0.88	54.3	91.7	49.8
Example 2	Triammonium phosphate / phosphoric acid	1.54	0.71	3.80	0.87	53.7	91.8	49.3
Example 3	Triammonium phosphate	0.88	1.00	3.14	0.84	52.5	91.0	47.8
Example 4	Triammonium phosphate / phosphoric acid	1.31	0.84	3.80	0.87	53.2	91.2	48.5
Example 5	Triammonium phosphate / phosphoric acid	2.21	0.80	5.79	0.91	54.2	87.6	47.5
Example 6	Triammonium phosphate / phosphoric acid	1.54	0.71	4.94	0.67	53.6	87.9	47.1
Comparative Example 1	Diammonium hydrogen phosphate / phosphoric acid	1.47	0.00	3.59	0.00	50.1	89.7	45.0
Comparative Example 2	phosphoric acid	1.53	0.00	3.61	0.00	50.5	90.3	45.6
Comparative Example 3	phosphoric acid	1.53	0.00	5.09	0.00	51.5	86.0	44.3
Comparative Example 4	Ammonium dihydrogen phosphate / phosphoric acid	1.53	0.00	3.60	0.00	50.1	89.1	44.6

[0060]

As shown in Table 1, Examples 1 to 6 using triammonium phosphate as at least a part of the phosphorus raw material were confirmed to be catalysts having a higher methacrylic acid yield than Comparative Examples 1 to 4.

INDUSTRIAL APPLICABILITY**[0061]**

Since the catalyst for methacrylic acid production according to the present invention can produce methacrylic acid at a higher yield than before, it is useful when industrially producing methacrylic acid.

CLAIMS

1. A method for producing a catalyst used for producing methacrylic acid by oxidizing methacrolein, comprising:
 - 5 step (I): mixing at least a molybdenum raw material and a phosphorus raw material with a solvent to prepare a solution or slurry;
 - step (II): drying the solution or slurry to obtain a catalyst precursor; and
 - step (III): obtaining the catalyst by calcining the catalyst precursor,
 - wherein in the step (I), triammonium phosphate is used as at least a part of
 - 10 the phosphorus raw material.
2. The method for producing a catalyst according to claim 1, wherein the catalyst precursor obtained in the step (II) has a Keggin-type heteropolyacid structure.
- 15 3. The method for producing a catalyst according to claim 1 or 2, wherein the catalyst obtained in the step (III) satisfies the following formula (1) when the molar ratio of phosphorus to 12 moles of molybdenum is a:

$$0.5 \leq a \leq 3 \quad (1).$$
- 20 4. The method for producing a catalyst according to any one of claims 1 to 3, wherein the catalyst obtained in the step (III) satisfies the following formula (2) when the molar ratio of phosphorus to 12 moles of molybdenum is a, and a molar ratio of phosphorus derived from triammonium phosphate to 12 moles of molybdenum is a':

$$0.1 \leq a'/a \leq 1 \quad (2).$$
- 25 5. The method for producing a catalyst according to any one of claims 1 to 4, wherein the catalyst precursor obtained in the step (II) satisfies the following formula (3) when the molar ratio of ammonium species to 12 moles of molybdenum is h₂, and a molar ratio of ammonium species derived from triammonium phosphate to 12 moles of molybdenum is h₂':

$$0.2 \leq h_2'/h_2 \leq 1 \quad (3)$$
- 30

6. The method for producing a catalyst according to any one of claims 1 to 5, wherein the catalyst obtained in the step (III) has a composition represented by the following formula (4):



5 (In the formula (4), P, Mo, V, Cu, NH₄ and O represent phosphorus, molybdenum, vanadium, copper, ammonium species and oxygen, respectively.

A represents at least one element selected from the group consisting of antimony, bismuth, arsenic, germanium, zirconium, tellurium, silver, selenium, silicon, tungsten and boron.

10 E represents at least one element selected from the group consisting of iron, zinc, chromium, calcium, strontium, tantalum, cobalt, nickel, manganese, titanium, tin, lead, niobium, indium, sulfur, palladium, gallium, cerium and lanthanum.

G represents at least one element selected from the group consisting of potassium, rubidium, cesium, thallium, magnesium and barium.

15 **a** to **i** represent the molar ratio of each component, and when **b** = 12, $0.5 \leq \mathbf{a} \leq 3$, $0.01 \leq \mathbf{c} \leq 3$, $0.01 \leq \mathbf{d} \leq 2$, $0 \leq \mathbf{e} \leq 3$, $0 \leq \mathbf{f} \leq 3$, $0.01 \leq \mathbf{g} \leq 3$, $0 \leq \mathbf{h} \leq 20$, and **i** is a molar ratio of oxygen necessary to satisfy the valence of each component.)

7. A method for producing methacrylic acid, comprising oxidizing methacrolein
20 in the presence of the catalyst produced by the method according to any one of claims 1 to 6.

8. A method for producing methacrylic acid, comprising a step of producing a
25 catalyst by the method according to any one of claims 1 to 6 and a step of oxidizing methacrolein using the catalyst.

9. A method for producing methacrylic acid ester, comprising esterifying
methacrylic acid produced by the method according to claim 7 or 8.

30 10. A method for producing methacrylic acid ester, comprising a step of producing a catalyst by the method according to any one of claims 1 to 6, a step of oxidizing methacrolein using the catalyst, and a step of esterifying the methacrylic

acid.