

DESCRIPTION

Title of Invention:

METHOD FOR PRODUCING CATALYST PRECURSOR FOR PRODUCING α,β -UNSATURATED CARBOXYLIC ACID, METHOD FOR PRODUCING CATALYST FOR PRODUCING α,β -UNSATURATED CARBOXYLIC ACID, METHOD FOR PRODUCING α,β -UNSATURATED CARBOXYLIC ACID, AND METHOD FOR PRODUCING α,β -UNSATURATED CARBOXYLIC ACID ESTER

Technical Field

[0001]

The present invention relates to a method for producing a catalyst precursor for production of α,β -unsaturated carboxylic acid, a method for producing a catalyst for production of α,β -unsaturated carboxylic acid, a method for producing α,β -unsaturated carboxylic acid, and a method for producing α,β -unsaturated carboxylic acid ester.

Background Art

[0002]

Known as a catalyst for use in production of α,β -unsaturated carboxylic acid through gas-phase catalytic oxidation of α,β -unsaturated aldehyde with molecular oxygen are catalysts containing heteropolyacid or a salt thereof such as phosphomolybdic acid or phosphomolybdate as a main component. Numerous examinations have been made on methods for producing such catalysts, and in most of the methods an aqueous solution or slurry containing elements to constitute a catalyst is first prepared, and then dried and calcined to produce the catalyst.

[0003]

The basic performance of such a catalyst depends primarily on the elemental composition, crystal structure, particle size, and so forth, and control of them requires to control conditions for a process of preparing an aqueous slurry, in particular, conditions such as pH and temperature. For catalysts containing heteropolyacid or a salt thereof as a main component, a partially neutralized salt of alkali metal such as potassium, rubidium, and cesium is commonly used as a main component. In actual preparation of a catalyst, however, it may be difficult to form a crystal structure optimum for production of α,β -unsaturated carboxylic acid merely by forming a partially neutralized salt of alkali metal. For this reason, in some cases of actual preparation of a catalyst, a complex salt of an alkali metal salt and an ammonium salt or the like

is formed and then calcined to decompose the ammonium salt or the like, thereby forming a partially neutralized salt of alkali metal. Here, aqueous ammonia, ammonium nitrate, ammonium bicarbonate, or the like is used for the ammonium source material. However, each of these ammonium source materials has a problem. Ammonium salts of heteropolyacid are known to generally have larger particle size than alkali metal salts. Larger particle size gives a smaller specific surface area, and hence results in lower catalytic activity in production of α,β -unsaturated carboxylic acid.

[0004]

Patent Literature 1 discloses use of ammonium nitrate as an ammonium source material. In using ammonium nitrate as an ammonium source material, a crystal structure preferred for production of α,β -unsaturated carboxylic acid can be formed by reducing the pH of a slurry of heteropolyacid (salt) to a low value (Non-Patent Literature 1). However, it is known that if an organic forming aid is added, the ammonium nitrate coexisting may generate a large amount of heat in calcination (Patent Literature 2).

[0005]

Patent Literature 3 discloses use of ammonium bicarbonate as an ammonium source material. However, use of ammonium bicarbonate results in low catalytic activity, and sufficient yields are not achieved for α,β -unsaturated carboxylic acid.

Citation List

Patent Literature

[0006]

Patent Literature 1: JP2014-226614A

Patent Literature 2: JP6-86933A

Patent Literature 3: JP2013-128878A

Non Patent Literature

[0007]

Non-Patent Literature 1: T. OKUHARA, N. MIZUNO, M. MISONO ADVANCES IN CATALYSIS, 1996, VOLUME 41, 113-252

Summary of Invention

Technical Problem

[0008]

An object of the present invention is to provide a catalyst precursor for production of

α,β -unsaturated carboxylic acid to enable production of α,β -unsaturated carboxylic acid at a high yield.

Solution to Problem

[0009]

The present invention relates to the following [1] to [13].

[0010]

[1] A method for producing a catalyst precursor for production of α,β -unsaturated carboxylic acid, wherein the catalyst precursor is a precursor of a catalyst for use in production of α,β -unsaturated carboxylic acid through gas-phase catalytic oxidation of α,β -unsaturated aldehyde with molecular oxygen, the precursor contains an ammonium species, and the method includes:

- (i) a step of providing an aqueous slurry or aqueous solution (I) containing molybdenum-containing heteropolyacid;
- (ii) a step of adding an ammonium compound to the aqueous slurry or aqueous solution (I) to obtain a slurry (II) including a precipitated ammonium salt of heteropolyacid; and
- (iii) a step of drying the slurry (II) including the precipitated ammonium salt of heteropolyacid to obtain the precursor, wherein

the ammonium compound used in the step (ii) is an ammonium compound containing 30% by mass or more of ammonium carbamate.

[0011]

[2] A method for producing a catalyst precursor for production of α,β -unsaturated carboxylic acid, wherein the catalyst precursor is a precursor of a catalyst for use in production of α,β -unsaturated carboxylic acid through gas-phase catalytic oxidation of α,β -unsaturated aldehyde with molecular oxygen, the precursor contains an ammonium species, and the method includes:

- (i) a step of providing an aqueous slurry or aqueous solution (I) containing molybdenum-containing heteropolyacid;
- (ii) a step of adding an ammonium compound to the aqueous slurry or aqueous solution (I) to obtain a slurry (II) including a precipitated ammonium salt of heteropolyacid; and
- (iii) a step of drying the slurry (II) including the precipitated ammonium salt of heteropolyacid to obtain the precursor, wherein

the ammonium compound used in the step (ii) satisfies the following expression (1).

[0012]

$$0.048 \leq W1/W2 \leq 0.2 \quad (1)$$

In the expression (1), W1 represents the mass of ammonium carbamate in the ammonium compound, and W2 represents the mass of molybdenum element contained in the aqueous slurry or aqueous solution (I).

[0013]

[3] The method for producing a catalyst precursor for production of α,β -unsaturated carboxylic acid according to [1], wherein the ammonium compound in the step (ii) satisfies the following expression (1).

[0014]

$$0.048 \leq W1/W2 \leq 0.2 \quad (1)$$

In the expression (1), W1 represents the mass of ammonium carbamate in the ammonium compound, and W2 represents the mass of molybdenum element contained in the aqueous slurry or aqueous solution (I).

[0015]

[4] The method for producing a catalyst precursor for production of α,β -unsaturated carboxylic acid according to any one of [1] to [3], wherein the catalyst precursor has a composition represented by the following formula (2).

[0016]



In the formula (2), 'P', 'Mo', 'V', 'Cu', 'NH₄', and 'O' represent phosphorus, molybdenum, vanadium, copper, an ammonium ion, 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; 'G' represents at least one element selected from the group consisting of potassium, rubidium, cesium, thallium, magnesium, and barium; 'a' to 'h' each represent a mole ratio of the corresponding component, provided that if $b = 12$, then $a = 0.5$ 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 $h = 0.1$ to 20; and 'i' represents a mole ratio of oxygen required to satisfy the valences of the components.

[0017]

[5] The method for producing a catalyst precursor for production of α,β -unsaturated carboxylic acid according to any one of [1] to [4], wherein the ammonium compound is added to the aqueous slurry or aqueous solution (I) heated to a temperature of higher than 90°C and 105°C

or lower in the step (ii).

[0018]

[6] The method for producing a catalyst precursor for production of α,β -unsaturated carboxylic acid according to any one of [1] to [5], wherein the ammonium compound in the step (ii) is a mixture of ammonium carbamate and ammonium bicarbonate.

[0019]

[7] The method for producing a catalyst precursor for production of α,β -unsaturated carboxylic acid according to any one of [1] to [6], wherein the α,β -unsaturated aldehyde is (meth)acrolein and the α,β -unsaturated carboxylic acid is (meth)acrylic acid.

[0020]

[8] A method for producing a catalyst for production of α,β -unsaturated carboxylic acid, including a step of heat treatment of a catalyst precursor for production of α,β -unsaturated carboxylic acid, wherein the catalyst precursor is produced by using the method according to any one of [1] to [7].

[0021]

[9] The method for producing a catalyst for production of α,β -unsaturated carboxylic acid according to [8], wherein temperature in the heat treatment is 200 to 500°C.

[0022]

[10] A method for producing α,β -unsaturated carboxylic acid, wherein α,β -unsaturated aldehyde is subjected to gas-phase catalytic oxidation with molecular oxygen in the presence of a catalyst for production of α,β -unsaturated carboxylic acid, and the catalyst is produced by using the method according to [8] or [9].

[0023]

[11] A method for producing α,β -unsaturated carboxylic acid, wherein a catalyst for production of α,β -unsaturated carboxylic acid is produced by using the method according to [8] or [9], and α,β -unsaturated aldehyde is subjected to gas-phase catalytic oxidation with molecular oxygen with use of the catalyst.

[0024]

[12] A method for producing α,β -unsaturated carboxylic acid ester, wherein α,β -unsaturated carboxylic acid produced by using the method according to [10] or [11] is esterified.

[0025]

[13] A method for producing α,β -unsaturated carboxylic acid ester, wherein

α,β -unsaturated carboxylic acid is produced by using the method according to [10] or [11], and the α,β -unsaturated carboxylic acid is esterified.

Advantageous Effects of Invention

[0026]

The present invention can provide a catalyst precursor for production of α,β -unsaturated carboxylic acid to enable production of α,β -unsaturated carboxylic acid at a high yield.

Description of Embodiments

[0027]

[Method for producing catalyst precursor for production of α,β -unsaturated carboxylic acid]

A method for producing a catalyst precursor for production of α,β -unsaturated carboxylic acid (hereinafter, also referred to as a catalyst precursor) according to the present invention is a method for producing a catalyst precursor for production of α,β -unsaturated carboxylic acid, wherein the catalyst precursor is a precursor of a catalyst for use in production of α,β -unsaturated carboxylic acid through gas-phase catalytic oxidation of α,β -unsaturated aldehyde with molecular oxygen, and the precursor contains an ammonium species. The method includes the following steps (i) to (iii):

- (i) a step of providing an aqueous slurry or aqueous solution (I) containing molybdenum-containing heteropolyacid;
- (ii) a step of adding an ammonium compound to the aqueous slurry or aqueous solution (I) to obtain a slurry (II) including a precipitated ammonium salt of heteropolyacid; and
- (iii) a step of drying the slurry (II) including the precipitated ammonium salt of heteropolyacid to obtain the precursor.

[0028]

The ammonium compound in the step (ii) contains 30% by mass or more of ammonium carbamate, or satisfies the following expression (1).

[0029]

$$0.048 \leq W1/W2 \leq 0.2 \quad (1)$$

In the expression (1), W1 represents the mass of ammonium carbamate in the ammonium compound, and W2 represents the mass of molybdenum element contained in the aqueous slurry or aqueous solution (I).

[0030]

The method according to the present invention can reduce only the particle size of the

catalyst particle in the aqueous slurry to increase the specific surface area, without any change in the elemental composition and crystal structure of the catalyst and the chemical properties of the aqueous slurry such as pH and residual counter anions, through the steps (i) to (iii) included in the method and use of the ammonium compound containing 30% by mass or more of ammonium carbamate or satisfying the expression (1) in the step (ii). This results in improved catalytic activity, and the yield of α,β -unsaturated carboxylic acid can be improved in production of α,β -unsaturated carboxylic acid through gas-phase catalytic oxidation of α,β -unsaturated aldehyde with molecular oxygen. In summary, the present inventors found that a high yield can be achieved by using ammonium carbamate with a specific content ratio as an ammonium source material for use in catalyst production, thus completing the present invention. In the present invention, the term "ammonium species" is a generic term of ammonia (NH_3) that can become ammonium ion (NH_4^+), and ammonium that is contained in ammonium-containing compounds such as ammonium salts. In the method according to the present invention, an ammonium compound containing 30% by mass or more of ammonium carbamate and satisfying the expression (1) may be used in the step (ii).

[0031]

The catalyst precursor for production of α,β -unsaturated carboxylic acid to be produced by using the method according to the present invention preferably contains at least phosphorus and molybdenum, and more preferably has a composition represented by the below-described formula (2), because α,β -unsaturated carboxylic acid can be produced at a high yield in production of α,β -unsaturated carboxylic acid. The mole ratios of elements in the catalyst precursor are values determined in analysis with ICP emission spectrometry for components of the catalyst precursor dissolved in aqueous ammonia. The mole ratio of ammonium ions is a value determined in analysis with the Kjeldahl method for the catalyst precursor.

[0032]



In the formula (2), 'P', 'Mo', 'V', 'Cu', 'NH₄', and 'O' represent phosphorus, molybdenum, vanadium, copper, an ammonium ion, 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; 'G' represents at least one element selected from the group consisting of potassium, rubidium, cesium, thallium, magnesium, and barium; 'a' to 'h' each represent a mole ratio of the

corresponding component, provided that if $b = 12$, then $a = 0.5$ 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 $h = 0.1$ to 20 ; and 'i' represents a mole ratio of oxygen required to satisfy the valences of the components.

[0033]

The method for producing a catalyst precursor for production of α,β -unsaturated carboxylic acid according to the present invention includes the following steps (i) to (iii): (i) a step of providing an aqueous slurry or aqueous solution (I) containing molybdenum-containing heteropolyacid; (ii) a step of adding an ammonium compound to the aqueous slurry or aqueous solution (I) to obtain a slurry (II) including a precipitated ammonium salt of heteropolyacid; and (iii) a step of drying the slurry (II) including the precipitated ammonium salt of heteropolyacid to obtain the catalyst precursor. Here, the ammonium compound used in the step (ii) is an ammonium compound containing 30% by mass or more of ammonium carbamate or satisfying the expression (1). The method for producing a catalyst precursor for production of methacrylic acid according to the present invention may further include a forming step described later.

[0034]

(Step (i))

In step (i), an aqueous slurry or aqueous solution (I) containing molybdenum-containing heteropolyacid is provided. To obtain the aqueous slurry or aqueous solution (I), for example, source compounds of the catalyst components are dissolved or suspended in a solvent with a container for preparation. The aqueous slurry or aqueous solution (I) preferably contains at least phosphorus and molybdenum, and more preferably contains elements contained in the composition represented by the formula (2).

[0035]

For each of the source compounds, one of a nitrate, carbonate, acetate, ammonium salt, oxide, halide, oxoacid, and oxoacid salt of the corresponding catalyst element, or combination of two or more of them can be used. Examples of the molybdenum source material include ammonium paramolybdate, molybdenum trioxide, molybdic acid, and molybdenum chloride. Examples of the phosphorus source material include orthophosphoric acid, phosphorus pentoxide, and phosphates such as ammonium phosphate and cesium phosphate. Examples of the copper source material include copper sulfate, copper nitrate, copper oxide, copper carbonate, copper acetate, and copper chloride. Examples of the vanadium source material include ammonium vanadate, ammonium metavanadate, vanadium pentoxide, and vanadium chloride. Only one of them may be used, and two or more of them may be used in combination.

[0036]

For the source material of molybdenum, phosphorus, or vanadium, heteropolyacid containing at least one element of molybdenum, phosphorus, and vanadium can be used. Examples of such heteropolyacid include phosphomolybdic acid, phosphovanadomolybdic acid, and silicomolybdic acid. Only one of them may be used, and two or more of them may be used in combination.

[0037]

When an ammonium salt is used as a source material compound of the catalyst components in the step (i), the amount of ammonium species derived from the source material compound contained in the catalyst precursor is preferably 3 moles or less, more preferably 1.5 moles or less, even more preferably 1 mole or less, and particularly preferably 0.6 mole or less, as the amount of molybdenum is set to 12 moles. With setting the amount of ammonium radicals derived from the source material compound to 3 moles or less as the amount of molybdenum is set to 12 moles, the advantageous effects of the present invention can be sufficiently achieved.

[0038]

In the preparation of the aqueous slurry or aqueous solution (I), it is preferred for simplicity to add some or all of source materials of the elements constituting the catalyst precursor to water and stir the resultant with heating. Alternatively, an aqueous solution, aqueous slurry, or aqueous sol of source materials of the elements constituting the catalyst precursor can be added to water. The heating temperature for the aqueous slurry or aqueous solution (I) is preferably 80 to 130°C, and more preferably 90 to 130°C. Setting the heating temperature for the aqueous slurry or aqueous solution (I) to 80°C or higher can provide a sufficiently high formation rate of molybdenum-containing heteropolyacid. Setting the heating temperature for the aqueous slurry or aqueous solution (I) to 130°C or lower can reduce the evaporation of water in the aqueous slurry or aqueous solution (I). The pH of the aqueous slurry or aqueous solution (I) to be prepared is preferably 4 or lower, and more preferably 2 or lower. By sufficiently lowering the pH of the aqueous slurry or aqueous solution (I), molybdenum-containing heteropolyacid with a preferred structure can be formed. The pH of the aqueous slurry or aqueous solution (I) can be measured by using a pH meter (produced by HORIBA, Ltd., product name: D-21). Infrared absorption analysis with a NICOLET 6700FT-IR (product name, produced by Thermo Electron Corporation) can be used to determine whether molybdenum-containing heteropolyacid has been formed.

[0039]

(Step (ii))

In the step (ii), an ammonium compound is added to the aqueous slurry or aqueous solution (I) to obtain a slurry (II) including a precipitated ammonium salt of heteropolyacid.

[0040]

The ammonium compound used is an ammonium compound containing 30% by mass or more of ammonium carbamate or satisfying the following expression (1).

[0041]

$$0.048 \leq W1/W2 \leq 0.2 \quad (1)$$

In the expression (1), W1 represents the mass of ammonium carbamate in the ammonium compound, and W2 represents the mass of molybdenum element contained in the aqueous slurry or aqueous solution (I).

[0042]

The step (ii) provides the catalyst to be obtained with a larger specific surface area to increase catalytic activity in production of α,β -unsaturated carboxylic acid, and thus the yield of α,β -unsaturated carboxylic acid can be improved. The content of ammonium carbamate in the ammonium compound is preferably 40% by mass or more, more preferably 60% by mass or more, even more preferably 70% by mass or more, and particularly preferably 80% by mass or more. Although the yield of α,β -unsaturated carboxylic acid can be improved to a higher degree as the content of ammonium carbamate is higher, the upper limit of the content of ammonium carbamate is preferably 95% by mass or less for production cost. The lower limit of W1/W2 is preferably 0.055 or higher, more preferably 0.078 or higher, even more preferably 0.085 or higher, and particularly preferably 0.092 or higher. The upper limit of W1/W2 is preferably 0.15 or lower, more preferably 0.13 or lower, and even more preferably 0.12 or lower.

[0043]

When the ammonium compound used is combination of ammonium carbamate and an additional ammonium compound other than ammonium carbamate, examples of the additional ammonium compound include ammonium bicarbonate, ammonium nitrate, and aqueous ammonia, and ammonium bicarbonate is preferably used in combination for the yield of a targeted product. That is, the ammonium compound is preferably a mixture of ammonium carbamate and ammonium bicarbonate. One of such additional ammonium compounds may be used, and two or more of them may be used in combination. The ammonium compound contains ammonium carbamate and ammonium bicarbonate preferably with a total content of 80 to 100% by mass, more preferably with a total content of 90 to 100% by mass. The term "ammonium compound" in the present invention refers to an ammonium compound without any

of the catalyst elements.

[0044]

Regarding the temperature of the aqueous slurry or aqueous solution (I) to which the ammonium compound is added, it is preferable for preventing hot spots in production of α,β -unsaturated carboxylic acid that the lower limit be higher than 90°C and the upper limit be 105°C or lower. The lower limit is more preferably 93°C or higher.

[0045]

In this step, a source material of the element G in the formula (2) may be added in addition to the ammonium compound to precipitate at least part of the heteropolyacid as a salt of the element G.

[0046]

The source materials of the ammonium compound and the element G, which is to be added as necessary, are preferably dissolved or suspended in a solvent before addition. Examples of the solvent include water, ethyl alcohol, and acetone, and water is preferably used as the solvent, like the aqueous slurry or aqueous solution (I) obtained in the step (i). The stirring time after the source materials of the ammonium compound and the element G, which is to be added as necessary, are added is preferably 5 to 60 minutes, and it is more preferable that the lower limit be 10 minutes or longer and the upper limit be 30 minutes or shorter. The temperature of the slurry (II) in stirring is preferably 80 to 100°C. Setting the stirring time to 5 minutes or longer and the temperature to 80°C or higher allows an ammonium salt of heteropolyacid and a salt of the element G to be sufficiently formed. Meanwhile, setting the stirring time to 60 minutes or shorter and the temperature to 100°C or lower can suppress side reactions accompanying formation of a targeted ammonium salt of heteropolyacid and salt of the element G.

[0047]

The ammonium salt of heteropolyacid and salt of the element G to be precipitated may each have Keggin-type structure or another structure differing from Keggin-type structure such as Dawson-type structure, but each preferably have Keggin-type structure. If the ammonium salt of heteropolyacid and salt of the element G to be precipitated each have Keggin-type structure, the yield of α,β -unsaturated carboxylic acid is further improved. Examples of methods for precipitating an ammonium salt of heteropolyacid and salt of the element G each having Keggin-type structure include a method such that molybdenum trioxide is used as a molybdenum source material and the pH of the slurry (II) in the step (ii) is adjusted to 3 or lower. The structures of the ammonium salt of heteropolyacid and salt of the element G precipitated can

be determined through infrared absorption analysis with a NICOLET 6700FT-IR (product name, produced by Thermo Electron Corporation) and X-ray diffraction analysis with the X-ray diffractometer X' Pert PRO MPD (product name, produced by PANalytical).

[0048]

(Step (iii))

In the step (iii), the slurry (II) including the precipitated ammonium salt of heteropolyacid is dried to obtain a catalyst precursor. Examples of the drying method include drum drying, flush drying, evaporation to dryness, and spray drying. The drying temperature is preferably 120 to 500°C, and it is more preferable that the lower limit be 140°C or higher and the upper limit be 350°C or lower. Drying can be continued until the slurry (II) is dried into solid. The moisture content of the catalyst precursor is preferably 0.1 to 4.5% by mass. These conditions can be appropriately selected in accordance with intended shape or size for the catalyst precursor.

[0049]

(Molding step)

In the molding step, the catalyst precursor or a heat-treated catalyst obtained in a heat treatment step described later is molded. The molding method is not limited, and any known dry or wet molding method can be applied. Examples thereof include tableting, extrusion, pressure molding, and tumbling granulation. The shape of the molded article is not limited and may be any shape, such as spherical particles, rings, cylindrical pellets, pentagrams, and granules obtained by milling and classifying after molding. The size of the catalyst is preferably 0.1 to 10 mm in catalyst diameter. Setting the catalyst diameter to 0.1 mm or larger can reduce pressure loss in a reaction tube. Setting the catalyst diameter to 10 mm or smaller can provide more improved catalyst activity. The catalyst may be supported on a carrier in molding, and other additives may be mixed.

[0050]

[Method for producing catalyst for production of α,β -unsaturated carboxylic acid]

A method for producing a catalyst for production of α,β -unsaturated carboxylic acid according to the present invention preferably includes a step of heat treatment (hereinafter, also referred to as the heat treatment step) of the catalyst precursor obtained in the step (iii) or the molded product of the catalyst precursor obtained in the molding step (hereinafter, also referred to as the catalyst precursor, collectively).

[0051]

(Step of heat treating)

In the step of heat treating, the catalyst precursor is heat-treated to obtain a catalyst for production of α,β -unsaturated carboxylic acid. Conditions for heat treating are not limited, and, for example, the heat treatment can be performed under flow of at least one of oxygen-containing gas such as air and inert gas. The heat treatment is preferably performed under flow of oxygen-containing gas such as air. The term "inert gas" refers to gas which does not lower catalyst activity, and examples thereof include nitrogen, carbon dioxide gas, helium, and argon. One of them, or a mixture of two or more of them may be used. The heat treatment temperature is preferably 200 to 500°C, and it is more preferable that the lower limit be 300°C or higher and the upper limit be 450°C or lower. The lower limit of the heat treatment time is preferably 0.5 hours or longer, and more preferably 1 hour or longer. The upper limit of the heat treatment time is preferably 40 hours or shorter. The specific surface area of a catalyst to be obtained is preferably 4.6 m²/g or larger. The specific surface area of a catalyst is a value determined by using a nitrogen adsorption method, specifically, determined in a manner described later.

[0052]

[Method for producing α,β -unsaturated carboxylic acid]

In a method for producing α,β -unsaturated carboxylic acid according to the present invention, α,β -unsaturated aldehyde is subjected to gas-phase catalytic oxidation with molecular oxygen in the presence of a catalyst for production of α,β -unsaturated carboxylic acid, and the catalyst is produced by using the method according to the present invention. In the method for producing α,β -unsaturated carboxylic acid according to the present invention, in another mode, a catalyst for production of α,β -unsaturated carboxylic acid is produced by using the method according to the present invention, and α,β -unsaturated aldehyde is subjected to gas-phase catalytic oxidation with molecular oxygen with use of the catalyst.

[0053]

Examples of the α,β -unsaturated aldehyde in the method according to the present invention include (meth)acrolein, crotonaldehyde (β -methylacrolein), and cinnamaldehyde (β -phenylacrolein). Among them, (meth)acrolein is preferred, and methacrolein is more preferred for the yield of a targeted product. The α,β -unsaturated carboxylic acid to be produced is α,β -unsaturated carboxylic acid resulting from conversion of an aldehyde group of α,β -unsaturated aldehyde into a carboxy group. Specifically, when the α,β -unsaturated aldehyde is (meth)acrolein, (meth)acrylic acid is obtained. The term "(meth)acrolein" refers to acrolein and methacrolein, and the term "(meth)acrylic acid" refers to acrylic acid and

methacrylic acid.

[0054]

Hereinafter, a method will be described as a representative example, in which methacrylic acid is produced by subjecting methacrolein to gas-phase catalytic oxidation with molecular oxygen in the presence of a catalyst for production of methacrylic acid, and the catalyst is produced by using the method according to the present invention.

[0055]

In this method, methacrylic acid is produced by contacting source gas containing methacrolein and molecular oxygen with the catalyst according to the present invention. A fixed bed reactor can be used for this reaction. For this reaction, a reaction tube is packed with the catalyst, and the source gas is fed to the reactor. A single catalyst layer, or a plurality of separated layers packed with catalysts with different activities may be used. To control activity, the catalyst for production of methacrylic acid may be diluted with an inert carrier and then packed.

[0056]

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

[0057]

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

[0058]

The source gas may be a mixture of methacrolein and molecular oxygen diluted with inert gas such as nitrogen and carbon dioxide gas. Water vapor may be further added to the source gas. Reaction in the presence of water vapor can provide methacrylic acid at a higher yield. The concentration of water vapor in the source gas is preferably 0.1 to 50% by volume, and it is more preferable that the lower limit be 1% by volume or more and the upper limit be 40% by volume.

[0059]

The contact time for the source gas and the catalyst for production of methacrylic acid is preferably 1.5 to 15 seconds. The reaction pressure is preferably 0.1 to 1 MPa (G). Here, (G) indicates gauge pressure. The reaction temperature is preferably 200 to 450°C, and it is more preferable that the lower limit be 250°C or higher and the upper limit be 400°C or lower.

[0060]

[Method for producing α,β -unsaturated carboxylic acid ester]

In a method for producing α,β -unsaturated carboxylic acid ester according to the present invention, α,β -unsaturated carboxylic acid produced by using the method according to the present invention is esterified. In the method for producing α,β -unsaturated carboxylic acid ester according to the present invention, in another mode, α,β -unsaturated carboxylic acid is produced by using the method according to the present invention, and the α,β -unsaturated carboxylic acid is esterified. By using the method in any of these modes, α,β -unsaturated carboxylic acid ester can be obtained from α,β -unsaturated carboxylic acid obtained through gas-phase catalytic oxidation of α,β -unsaturated aldehyde. Alcohol to be reacted with α,β -unsaturated carboxylic acid is not limited, and examples thereof include methanol, ethanol, isopropanol, n-butanol, and isobutanol. Examples of α,β -unsaturated carboxylic acid ester to be obtained include methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, and butyl (meth)acrylate. The reaction can be performed in the presence of an acidic catalyst such as sulfonic cation-exchange resin. The reaction temperature is preferably 50 to 200°C.

Examples

[0061]

Hereinafter, the present invention will be described in detail with reference to Examples and Comparative Examples; however, the present invention is not limited to these Examples. The term "parts" in Examples and Comparative Examples means parts by mass. Gas chromatography was used for analysis of source material gas and products. Yields of methacrylic acid were determined from results of gas chromatography by using the following expression.

[0062]

$$\text{Yield of methacrylic acid (\%)} = (B/A) \times 100$$

In the expression, A represents the number of moles of methacrolein fed into a reactor, and B represents the number of moles of methacrylic acid generated.

[0063]

Specific surface areas of catalysts were determined by using a nitrogen adsorption method. Specifically, a TriStar 3000 (product name, produced by Micromeritics Instrument Corp.) was used in measurement. In measurement, 1.5 g of a catalyst was used, and the specific surface area was calculated by using a BET five-point method.

[0064]

(Example 1)

To 400 parts of pure water, a diluted product obtained by diluting 100 parts of molybdenum trioxide, 3.4 parts of ammonium metavanadate, and 9.4 parts of 85% by mass aqueous solution of phosphoric acid with 6.0 parts of pure water, and a dissolved product obtained by dissolving 2.1 parts of copper (II) nitrate trihydrate in 4.5 parts of pure water were added. The temperature of the resulting aqueous slurry was raised from 25°C to 95°C with stirring, and the aqueous slurry was stirred for 2 hours with the solution temperature kept at 95°C to afford an aqueous slurry (I) containing molybdenum-containing heteropolyacid. The pH of the aqueous slurry (I) was 0.6. Further, a dissolved product obtained by dissolving 13.5 parts of cesium bicarbonate in 24 parts of pure water and a dissolved product obtained by dissolving 6.9 parts of ammonium carbamate in 70 parts of pure water were added dropwise thereto with stirring with the solution temperature kept at 95°C, and the resultant was stirred for 15 minutes to precipitate a cesium salt and ammonium salt of heteropolyacid. The cesium salt and ammonium salt of heteropolyacid each had Keggin-type structure. The slurry (II) obtained was subjected to evaporation to dryness by heating with water vapor at 140°C to afford a catalyst precursor. The composition of the thus-obtained catalyst precursor, excluding oxygen, was $\text{P}_{1.4}\text{Mo}_{12}\text{V}_{0.5}\text{Cu}_{0.15}\text{Cs}_{1.2}(\text{NH}_4)_{3.6}$. The catalyst precursor was pressure-molded and the resultant was then crushed, and the resultant product was heat-treated under air flow at 380°C for 5 hours to afford a catalyst.

[0065]

A reaction tube was packed with the catalyst, and source gas consisting 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 pass therethrough at a reaction temperature of 285°C for a contact time of 2.4 seconds for the source gas and the catalyst for production of methacrylic acid. A product obtained from the reactor was collected, and analyzed with gas chromatography to calculate the yield of methacrylic acid. The specific surface area of the catalyst had been calculated by using the nitrogen adsorption method before use for the catalytic reaction. The results are shown in Table 1.

[0066]

(Example 2)

A catalyst precursor was produced in the same manner as in Example 1, except that a dissolved product obtained by dissolving a mixture of 2.0 parts of ammonium bicarbonate and 5.9 parts of ammonium carbamate in 70 parts of pure water was used instead of the dissolved product obtained by dissolving 6.9 parts of ammonium carbamate in 70 parts of pure water. The composition of the thus-obtained catalyst precursor, excluding oxygen, was $\text{P}_{1.4}\text{Mo}_{12}\text{V}_{0.5}\text{Cu}_{0.15}\text{Cs}_{1.2}(\text{NH}_4)_{3.6}$. The catalyst precursor was molded and heat-treated in the same manner as in Example 1 to afford a catalyst. Reaction was performed by using the catalyst in the same manner as in Example 1, and the yield of methacrylic acid was calculated. The results are shown in Table 1.

[0067]

(Example 3)

A catalyst precursor was produced in the same manner as in Example 1, except that a dissolved product obtained by dissolving a mixture of 4.6 parts of ammonium bicarbonate and 4.6 parts of ammonium carbamate in 70 parts of pure water was used instead of the dissolved product obtained by dissolving 6.9 parts of ammonium carbamate in 70 parts of pure water. The composition of the thus-obtained catalyst precursor, excluding oxygen, was $\text{P}_{1.4}\text{Mo}_{12}\text{V}_{0.5}\text{Cu}_{0.15}\text{Cs}_{1.2}(\text{NH}_4)_{3.6}$. The catalyst precursor was molded and heat-treated in the same manner as in Example 1 to afford a catalyst. Reaction was performed by using the catalyst in the same manner as in Example 1, and the yield of methacrylic acid was calculated. The results are shown in Table 1.

[0068]

(Example 4)

A catalyst precursor was produced in the same manner as in Example 1, except that a dissolved product obtained by dissolving a mixture of 5.9 parts of ammonium bicarbonate and 4.0 parts of ammonium carbamate in 70 parts of pure water was used instead of the dissolved product obtained by dissolving 6.9 parts of ammonium carbamate in 70 parts of pure water. The composition of the thus-obtained catalyst precursor, excluding oxygen, was $\text{P}_{1.4}\text{Mo}_{12}\text{V}_{0.5}\text{Cu}_{0.15}\text{Cs}_{1.2}(\text{NH}_4)_{3.6}$. The catalyst precursor was molded and heat-treated in the same manner as in Example 1 to afford a catalyst. Reaction was performed by using the catalyst in the same manner as in Example 1, and the yield of methacrylic acid was calculated. The results are shown in Table 1.

[0069]

(Comparative Example 1)

A catalyst precursor was produced in the same manner as in Example 1, except that a dissolved product obtained by dissolving a mixture of 8.3 parts of ammonium bicarbonate and 2.8 parts of ammonium carbamate in 70 parts of pure water was used instead of the dissolved product obtained by dissolving 6.9 parts of ammonium carbamate in 70 parts of pure water. The composition of the thus-obtained catalyst precursor, excluding oxygen, was $P_{1.4}Mo_{12}V_{0.5}Cu_{0.15}Cs_{1.2}(NH_4)_{3.6}$. The catalyst precursor was molded and heat-treated in the same manner as in Example 1 to afford a catalyst. Reaction was performed by using the catalyst in the same manner as in Example 1, and the yield of methacrylic acid was calculated. The results are shown in Table 1.

[0070]

(Comparative Example 2)

A catalyst precursor was produced in the same manner as in Example 1, except that a dissolved product obtained by dissolving 14.0 g of ammonium bicarbonate in 70 parts of pure water was used instead of the dissolved product obtained by dissolving 6.9 parts of ammonium carbamate in 70 parts of pure water. The composition of the thus-obtained catalyst precursor, excluding oxygen, was $P_{1.4}Mo_{12}V_{0.5}Cu_{0.15}Cs_{1.2}(NH_4)_{3.6}$. The catalyst precursor was molded and heat-treated in the same manner as in Example 1 to afford a catalyst. Reaction was performed by using the catalyst in the same manner as in Example 1, and the yield of methacrylic acid was calculated. The results are shown in Table 1.

[0071]

[Table 1]

	Mass ratio of ammonium carbamate (% by mass)	W1/W2	Specific surface area of catalyst (m ² /g)	Yield of methacrylic acid (%)
Example 1	100	0.104	5.11	51.5
Example 2	75	0.089	4.91	50.3
Example 3	50	0.069	5.09	49.3
Example 4	40	0.060	4.90	50.0
Comparative Example 1	25	0.042	4.37	44.1
Comparative Example 2	0	0.000	4.51	46.0

[0072]

As shown in Table 1, the mass ratio of ammonium carbamate and the value of W1/W2 were each within the range of the present invention in each of Examples 1 to 4, and hence the

catalysts were confirmed to provide a high yield of methacrylic acid. In contrast, the mass ratio of ammonium carbamate and the value of W1/W2 were each out of the range of the present invention in each of Comparative Examples 1 and 2, and hence the yields of methacrylic acid were lower than those in Examples. Methacrylate can be obtained by esterifying methacrylic acid obtained in the present Examples.

[0073]

The present application claims priority to Japanese Patent Application No.2016-240355 filed on December 12, 2016, and the entire of the disclosure is incorporated herein.

[0074]

Thus, the invention of the present application has been described with reference to embodiments and Examples in the above; however, the invention of the present application is not limited to the above-described embodiments and Examples. Various modifications which those skilled in the art can appreciate may be made for the configuration or details of the invention of the present application, without departing from the scope of the invention of the present application.

Industrial Applicability

[0075]

The present invention can provide a catalyst precursor for production of α,β -unsaturated carboxylic acid to enable production of α,β -unsaturated carboxylic acid from α,β -unsaturated aldehyde at a high yield, and thus the present invention is industrially useful.

CLAIMS

1. A method for producing a catalyst precursor for production of α,β -unsaturated carboxylic acid, wherein the catalyst precursor is a precursor of a catalyst for use in production of α,β -unsaturated carboxylic acid through gas-phase catalytic oxidation of α,β -unsaturated aldehyde with molecular oxygen, the precursor contains an ammonium species, and the method includes:

- (i) a step of providing an aqueous slurry or aqueous solution (I) containing molybdenum-containing heteropolyacid;
- (ii) a step of adding an ammonium compound to the aqueous slurry or aqueous solution (I) to obtain a slurry (II) including a precipitated ammonium salt of heteropolyacid; and
- (iii) a step of drying the slurry (II) including the precipitated ammonium salt of heteropolyacid to obtain the precursor, wherein

the ammonium compound used in the step (ii) is an ammonium compound containing 30% by mass or more of ammonium carbamate.

2. A method for producing a catalyst precursor for production of α,β -unsaturated carboxylic acid, wherein the catalyst precursor is a precursor of a catalyst for use in production of α,β -unsaturated carboxylic acid through gas-phase catalytic oxidation of α,β -unsaturated aldehyde with molecular oxygen, the precursor contains an ammonium species, and the method includes:

- (i) a step of providing an aqueous slurry or aqueous solution (I) containing molybdenum-containing heteropolyacid;
- (ii) a step of adding an ammonium compound to the aqueous slurry or aqueous solution (I) to obtain a slurry (II) including a precipitated ammonium salt of heteropolyacid; and
- (iii) a step of drying the slurry (II) including the precipitated ammonium salt of heteropolyacid to obtain the precursor, wherein

the ammonium compound used in the step (ii) satisfies the following expression (1):

$$0.048 \leq W1/W2 \leq 0.2 \quad (1)$$

wherein W1 represents the mass of ammonium carbamate in the ammonium compound, and W2 represents the mass of molybdenum element contained in the aqueous slurry or aqueous solution (I).

3. The method for producing a catalyst precursor for production of α,β -unsaturated

carboxylic acid according to claim 1, wherein the ammonium compound in the step (ii) satisfies the following expression (1):

$$0.048 \leq W1/W2 \leq 0.2 \quad (1)$$

wherein W1 represents the mass of ammonium carbamate in the ammonium compound, and W2 represents the mass of molybdenum element contained in the aqueous slurry or aqueous solution (I).

4. The method for producing a catalyst precursor for production of α,β -unsaturated carboxylic acid according to any one of claims 1 to 3, wherein the catalyst precursor has a composition represented by the following formula (2):



wherein 'P', 'Mo', 'V', 'Cu', 'NH₄', and 'O' represent phosphorus, molybdenum, vanadium, copper, an ammonium ion, 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; 'G' represents at least one element selected from the group consisting of potassium, rubidium, cesium, thallium, magnesium, and barium; 'a' to 'h' each represent a mole ratio of the corresponding component, provided that if $b = 12$, then $a = 0.5$ 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 $h = 0.1$ to 20 ; and 'i' represents a mole ratio of oxygen required to satisfy the valences of the components.

5. The method for producing a catalyst precursor for production of α,β -unsaturated carboxylic acid according to any one of claims 1 to 4, wherein the ammonium compound is added to the aqueous slurry or aqueous solution (I) heated to a temperature of higher than 90°C and 105°C or lower in the step (ii).

6. The method for producing a catalyst precursor for production of α,β -unsaturated carboxylic acid according to any one of claims 1 to 5, wherein the ammonium compound in the step (ii) is a mixture of ammonium carbamate and ammonium bicarbonate.

7. The method for producing a catalyst precursor for production of α,β -unsaturated carboxylic acid according to any one of claims 1 to 6, wherein the α,β -unsaturated aldehyde is

(meth)acrolein and the α,β -unsaturated carboxylic acid is (meth)acrylic acid.

8. A method for producing a catalyst for production of α,β -unsaturated carboxylic acid, comprising a step of heat treatment of a catalyst precursor for production of α,β -unsaturated carboxylic acid, wherein the catalyst precursor is produced by using the method according to any one of claims 1 to 7.

9. The method for producing a catalyst for production of α,β -unsaturated carboxylic acid according to claim 8, wherein temperature in the heat treatment is 200 to 500°C.

10. A method for producing α,β -unsaturated carboxylic acid, wherein α,β -unsaturated aldehyde is subjected to gas-phase catalytic oxidation with molecular oxygen in the presence of a catalyst for production of α,β -unsaturated carboxylic acid, and the catalyst is produced by using the method according to claim 8 or 9.

11. A method for producing α,β -unsaturated carboxylic acid, wherein a catalyst for production of α,β -unsaturated carboxylic acid is produced by using the method according to claim 8 or 9, and α,β -unsaturated aldehyde is subjected to gas-phase catalytic oxidation with molecular oxygen with use of the catalyst.

12. A method for producing α,β -unsaturated carboxylic acid ester, wherein α,β -unsaturated carboxylic acid produced by using the method according to claim 10 or 11 is esterified.

13. A method for producing α,β -unsaturated carboxylic acid ester, wherein α,β -unsaturated carboxylic acid is produced by using the method according to claim 10 or 11, and the α,β -unsaturated carboxylic acid is esterified.