

Method for producing a catalyst for the production of α,β -unsaturated carboxylic acid, method for producing α,β -unsaturated carboxylic acid and method for producing α,β -unsaturated carboxylic acid ester

5 [Technical field]

[0001]

The present invention relates to a method for producing a catalyst for the production of α,β -unsaturated carboxylic acids, a method for producing an α,β -unsaturated carboxylic acids and a method for producing an α,β -unsaturated carboxylic acid esters.

10 [Technical background]

[0002]

As a catalyst used for producing α,β -unsaturated carboxylic acid by gas phase catalytic oxidation of α,β -unsaturated aldehyde with molecular oxygen, a catalyst containing heteropolyacid such as phosphomolybdic acid or phosphomolybdate salt or a salt thereof as a main component is known. Many studies have been conducted on methods for producing the catalyst, and many of them produce a catalyst by preparing an aqueous slurry or aqueous solution containing each element constituting the catalyst at first, then drying and calcining the slurry or aqueous solution.

[0003]

20 The basic performance of such a catalyst depends mainly on the elemental composition, crystal structure, particle size, and the like, and the control thereof requires control of the conditions of the preparation process of the aqueous slurry or aqueous solution. Generally, both water-soluble and water-insoluble raw material materials can be used as raw materials used for the preparation of the aqueous slurry or aqueous solution. However, it is known that the physical properties of the raw material have a large influence on the catalyst performance, particularly when a raw material insoluble in water is used. For example, Patent Document 1 discloses that a molybdenum contain solid catalyst having high catalytic activity and selectivity can be produced by using molybdenum oxide having a compression degree of 60 or less as a raw material. Patent Document 2 discloses a method for producing a catalyst using a molybdenum oxide having a diffraction peak position and a diffraction intensity defined in an X-ray diffraction diagram using CuK α rays as X-rays as a raw material.

30 [Prior-art document]

[Patent Application]

[0004]

[Patent Document 1] JP-A-2007-229561

[Patent Document 2] JP-A-2004-8834

[SUMMARY OF THE INVENTION]

[Problems to be Solved]

5 [0005]

However, in the catalyst produced using molybdenum oxide disclosed in Patent Documents 1 and 2, the yield of α,β -unsaturated carboxylic acid is still insufficient, and further improvement of the catalyst is desired.

[0006]

10 It is an object of the present invention to provide a catalyst capable of producing α,β -unsaturated carboxylic acids in high yield.

[Means for Solving the Problems]

[0007]

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

15 [0008]

[1] A method for producing a catalyst for the production of α,β -unsaturated carboxylic acid using molybdenum oxide as a molybdenum raw material, wherein proportion of particles having a particle diameter of 6 μ m or less is 2 to 55% by volume in a frequency distribution curve obtained by particle size distribution measurement.

20 [0009]

[2] The method for producing a catalyst for the production of α,β -unsaturated carboxylic acid according to [1], comprising the steps of:

- (i) heating an aqueous slurry (I) obtained by mixing water with a catalyst raw material containing at least said molybdenum raw material and phosphorus raw material to a temperature of 90 to 25 150°C to obtain an aqueous slurry or aqueous solution (II) containing a heteropolyacid;
- (ii) adding a metal cation-containing compound to said aqueous slurry or aqueous solution (II) to obtain an aqueous slurry (III) in which a heteropolyacid salt is precipitated;
- (iii) drying said aqueous slurry (III) to obtain a catalyst precursor dried product; and
- (iv) heat treating said catalyst precursor dried product to obtain a catalyst;

30 wherein a duration time in which temperature of said aqueous slurry (I) reaches from 60°C to 90°C in step (i) is 5 to 40 minutes.

[0010]

[3] The method for producing a catalyst for the production of α,β -unsaturated carboxylic acid according to [2], wherein the duration time in which temperature of said aqueous slurry (I) reaches from 60°C to 90°C in step (i) is 7 to 30 minutes.

[0011]

5 [4] The method for producing a catalyst for the production of α,β -unsaturated carboxylic acid according to any one of [1] to [3], wherein the molybdenum raw material is a molybdenum oxide in which the proportion of particles having a particle diameter of 6 μ m or less is 2 to 35% by volume.

[0012]

10 [5] The method for producing a catalyst for the production of α,β -unsaturated carboxylic acid according to [4], wherein the molybdenum raw material is a molybdenum oxide in which the proportion of particles having a particle diameter of 6 μ m or less is 2 to 15% by volume.

[0013]

15 [6] The method for producing a catalyst for the production of α,β -unsaturated carboxylic acid according to any one of [1] to [5], wherein the catalyst has a composition represented by the following formula (1).



(In formula (1), P, Mo, V, Cu, and O are elemental symbols representing phosphorus, molybdenum, vanadium, copper, and oxygen, respectively; A represents at least one element
20 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, magnesium, calcium, strontium, tantalum, cobalt, nickel, manganese, barium, titanium, tin, lead, niobium, indium, sulfur, palladium, gallium, cerium and lanthanum; G represents at least one element selected from the group
25 consisting of lithium, sodium, potassium, rubidium, cesium and thallium; a to h represent atomic ration of each element; when b=12, a=0.5 to 3, c=0.01 to 3, d=0.01 to 2, e=0 to 3, f=0 to 3 and g=0.01 to 3 and h is the atomic ratio of oxygen required to satisfy the valence of each of the above elements).

[0014]

30 [7] The method for producing a catalyst for the production of α,β -unsaturated carboxylic acid according to any one of [1] to [6], wherein 50 mass % or more of molybdenum trioxide is used as the molybdenum raw material.

[0015]

[8] The method for producing a catalyst for the production of α,β -unsaturated carboxylic acid according to [7], wherein 70 mass % or more of molybdenum trioxide is used as the molybdenum raw material.

[0016]

5 [9] The method for producing a catalyst for the production of α,β -unsaturated carboxylic acid according to any one of [1] to [8], wherein the catalyst for the production of α,β -unsaturated carboxylic acid is a catalyst used in the production of α,β -unsaturated carboxylic acid by gas phase catalytic oxidation of α,β -unsaturated aldehyde with molecular oxygen, wherein the α,β -unsaturated aldehyde is (meth)acrolein and the α,β -unsaturated carboxylic acid is (meth)acrylic
10 acid.

[0017]

[10] A method for producing an α,β -unsaturated carboxylic acid, wherein a catalyst for the production of α,β -unsaturated carboxylic acid is produced by the method according to any one of [1] to [9], and an α,β -unsaturated carboxylic acid is produced by gas phase catalytic oxidation of
15 α,β -unsaturated aldehyde with molecular oxygen using the catalyst.

[0018]

[11] A method for producing an α,β -unsaturated carboxylic acids, wherein the α,β -unsaturated carboxylic acid is produced by gas phase catalytic oxidation of α,β -unsaturated aldehyde with molecular oxygen using a catalyst for the production of α,β -unsaturated
20 carboxylic acid produced by the method of any one of [1] to [9].

[0019]

[12] A method for producing an α,β -unsaturated carboxylic acid esters, by esterifying the α,β -unsaturated carboxylic acids produced by the method of [10] or [11].

[0020]

25 [13] A method for producing an α,β -unsaturated carboxylic acid ester, wherein an α,β -unsaturated carboxylic acid is produced by the method of [10] or [11], and said α,β -unsaturated carboxylic acid is esterified.

[Effect of Invention]

[0021]

30 According to the present invention, it is possible to provide a catalyst capable of producing α,β -unsaturated carboxylic acid in high yield.

[BRIEF DESCRIPTION OF THE DRAWINGS]

[0022]

Figure 1 is a diagram showing particle size distributions of molybdenum trioxide in Examples 1 to 4 and Comparative Examples 1 to 3.

[DETAILED DESCRIPTION OF THE PRESENT INVENTION]

[0023]

5 [Catalyst for the Production of α,β -Unsaturated Carboxylic Acids]

The catalyst for the production of α,β -unsaturated carboxylic acid produced by the method according to the present invention contains at least molybdenum, preferably phosphorus and molybdenum, and more preferably has a composition represented by the following formula (1).

This makes it possible to produce α,β -unsaturated carboxylic acids in high yield in the
10 production of α,β -unsaturated carboxylic acids. Note that the elemental composition of the catalyst is a value obtained by analyzing a solution in which the catalyst is dissolved in ammonia water by an ICP luminescence analysis method.



[0024]

15 In formula, P, Mo, V, Cu and O are elemental symbols representing phosphorus, molybdenum, vanadium, copper 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, magnesium, calcium, strontium, tantalum,
20 cobalt, nickel, manganese, barium, titanium, tin, lead, niobium, indium, sulfur, palladium, gallium, cerium and lanthanum; and G represents at least one element selected from the group consisting of lithium, sodium, potassium, rubidium, cesium and thallium. a~h represents the atomic ratio of each element, when b=12, a=0.5~3, c=0.01~3, d=0.01~2, e=0~3, f=0~3, g=0.01~3, h is the atomic ratio of oxygen necessary to satisfy the valence of each element.

25 The catalyst may contain a small amount of an element not described in formula (1).

[0025]

The catalyst for the production of α,β -unsaturated carboxylic acid produced by the method according to the present invention is preferably used when producing α,β -unsaturated carboxylic acid by gas phase catalytic oxidation of α,β -unsaturated aldehyde with molecular oxygen. It is
30 also preferred that the α,β -unsaturated aldehyde is (meth)acrolein and the α,β -unsaturated carboxylic acid is (meth)acrylic acid.

[0026]

[Method for Producing Catalysts for the Production of α,β -Unsaturated Carboxylic Acids]

In the method for producing a catalyst for the production of α,β -unsaturated carboxylic acid according to the present invention, molybdenum oxide in which the proportion of particles having a particle diameter of $6\mu\text{m}$ or less is 2 to 55% by volume in the frequency distribution curve obtained by particle diameter distribution measurement is used as a molybdenum raw material. The particle size distribution of molybdenum oxide is measured by dispersing 0.02 to 0.1g of molybdenum oxide in 500g of pure water and agitating for 30 seconds using a laser diffractive particle size distribution measuring device SALD-7000 (manufactured by Shimadzu Corporation). Further, in the present invention, the frequency distribution curve is obtained by setting the cumulative volume of particles having a particle diameter of $1000\mu\text{m}$ or less as the total particle volume.

[0027]

In the present invention, in the frequency distribution curve obtained by the particle size distribution measurement described above, a catalyst for the production of α,β -unsaturated carboxylic acid is produced by using a molybdenum oxide in which the proportion of particles having a particle diameter of $6\mu\text{m}$ or less in particles having a particle diameter of $1000\mu\text{m}$ or less is 2 to 55% by volume as a molybdenum raw material. Thereby, it is considered that an active point suitable for the obtained catalyst is formed, the catalyst activity is improved, and the yield of α,β -unsaturated carboxylic acid can be improved.

[0028]

The method for producing a catalyst for the production of α,β -unsaturated carboxylic acid according to the present invention is not particularly limited except that the molybdenum oxide is used as a molybdenum raw material, and for example, the method may include a step of mixing the raw material containing the molybdenum oxide and water to obtain an aqueous slurry or an aqueous solution. However, from the viewpoint of further improving the yield of the α,β -unsaturated carboxylic acid, it is preferable that the method has the following steps (i) to (iv).

(i) An aqueous slurry (I) obtained by mixing water with a catalyst raw material containing at least a molybdenum raw material and a phosphorus raw material is heated to 90 to 150°C to obtain an aqueous slurry or an aqueous solution (II) containing heteropolyacid.

(ii) A step of adding a metal cation-containing compound to the aqueous slurry or aqueous solution (II) to obtain an aqueous slurry (III) in which a heteropolyacid salt is precipitated.

(iii) Drying the aqueous slurry (III) to obtain a catalyst precursor dried product.

(iv) A step of heat treating the catalyst precursor dried product to obtain a catalyst.

[0029]

The method for producing a catalyst for the production of an α,β -unsaturated carboxylic acid according to the present invention may further include molding steps described later.

[0030]

(Step (i))

5 In step (i), an aqueous slurry (I) obtained by mixing water with a catalyst raw material containing at least a molybdenum raw material and a phosphorus raw material is heated to 90 to 150° C to obtain an aqueous slurry or an aqueous solution (II) containing a heteropolyacid. After the aqueous slurry (I) is heated, it may become an aqueous slurry or an aqueous solution. Therefore, they are collectively referred to as "aqueous slurry or aqueous solution (II)". When
10 the catalyst has the composition represented by the above formula (1), it is preferable that an element other than G included in the composition represented by the above formula (1) be mixed with water as the catalyst raw material to obtain an aqueous slurry (I).

[0031]

When the aqueous slurry (I) is heated, the molybdenum raw material dissolves in water, and
15 the dissolution rate at this time changes depending on the particle size distribution of the molybdenum raw material. It is speculated that this dissolution rate affects the active point of the resulting catalyst.

[0032]

As the molybdenum raw material, a molybdenum oxide having a proportion of particles
20 having a particle diameter of 6 μ m or less being 2 to 55% by volume in a frequency distribution curve obtained by particle diameter distribution measurement is used. This forms an active point suitable for gas phase catalytic oxidation of α,β -unsaturated aldehydes with molecular oxygen. The lower limit of the proportion is preferably 5% or more by volume, more preferably 10% or more by volume. The upper limit is preferably 35% or less by volume, more preferably 30% or
25 less by volume, still more preferably 25% or less by volume, particularly preferably 20% or less by volume, and most preferably 15% or less by volume.

[0033]

The molybdenum oxide preferably has a proportion of particles having a particle diameter of 30 to 200 μ m being 35 to 90% by volume. The lower limit of the ratio is more preferably 40% or
30 more by volume, more preferably 50% or more by volume, particularly preferably 60% or more by volume, and most preferably 70% or more by volume. The upper limit is more preferably 85% or less by volume, and more preferably 80% or less by volume. This forms an active point which is more suitable for gas phase catalytic oxidation of α,β -unsaturated aldehydes with molecular oxygen.

[0034]

The atomic ratio of molybdenum to oxygen in the molybdenum oxide is not particularly limited, and for example, molybdenum dioxide in which the atomic ratio of molybdenum to oxygen is 1:2, molybdenum trioxide in which the atomic ratio of molybdenum to oxygen is 1:3, or the like can be given. However, from the viewpoint of further improving the yield of the α,β -unsaturated carboxylic acid, it is preferable to use 50 mass % or more of molybdenum trioxide as the molybdenum raw material in which the proportion of particles having a particle diameter of 6 μ m or less is 2 to 55 volume %. The lower limit of the proportion of molybdenum trioxide is more preferably 70% or more by mass, and more preferably 90% or more by mass. The molybdenum oxide may contain trace amounts of impurities such as sodium, potassium, iron, lead, sulfate, nitrate, and ammonium species, but it is preferable the content of these impurities is smaller, and it is particularly preferable not to contain these impurities.

[0035]

As a method for producing the molybdenum oxide according to the present invention, for example, the following method can be cited. The crude molybdenum trioxide obtained by roasting the ore containing molybdenum is dispersed in pure water and then dissolved in ammonia water. After this solution is filtered, the precipitate obtained by adding hydrochloric acid and adjusting the pH is dispersed and washed with pure water, or an aqueous solution containing a small amount of ammonium nitrate, ammonium chloride, or the like. Thereafter, the moisture content is reduced by centrifugal filtration or the like to obtain a precursor precipitate, followed by dried and then calcined to obtain a molybdenum oxide. In addition, a method of calcining ammonium paramolybdate obtained by adding ammonia water to the precursor precipitate and dissolving and crystallizing the precipitate is also mentioned. The latter method can reduce the particle size of the obtained molybdenum oxide compared to the former method. Further, the particle diameter of the molybdenum oxide can be adjusted by the calcinating temperature. The particle diameter of the molybdenum oxide obtained by lowering the calcinating temperature tends to be small, and the particle diameter of the molybdenum oxide obtained by raising the calcinating temperature tends to be large. If necessary, the molybdenum oxide produced by the above method may be grinded or classified so that the ratio of particles having a particle diameter of 6 μ m or less is 2 to 55% by volume, preferably 2 to 35% by volume, more preferably 2 to 15% by volume. The grinding operations include a method of using an apparatus such as a ball mill, a rod mill, an SAG mill, an autogenous grinding mill, a pebble mill, a high-pressure grinding roll, a vertical axis impactor mill and a jet mill. Classification operations include methods using sieving, methods using gravity or centrifugal force (semi-free

vortex classifier, forced vortex classifier), and the like. As the molybdenum oxide according to the present invention, a mixture of a plurality of molybdenum oxides having different particle size distributions produced by the above-described method may be used.

[0036]

5 Phosphorus raw materials include, for example, orthophosphoric acid, phosphorus pentoxide, ammonium phosphate, cesium phosphate, and the like. One of these may be used, or two or more types may be used in combination.

[0037]

10 Types of catalyst raw materials other than molybdenum raw materials and phosphorus raw materials are not particularly limited, for example, sulfates, nitrates, carbonates, bicarbonates, acetates, ammonium salts, oxides, hydroxides, chlorides, halides, oxoacids, oxoacid salts of each element are mentioned. Examples of the copper raw material include copper sulfate, copper nitrate, copper acetate, copper oxide and copper chloride. Examples of the vanadium raw material include ammonium vanadate, ammonium metavanadate, vanadium pentoxide and
15 vanadium chloride. One of these may be used, or two or more types may be used in combination.

[0038]

The preparation of the aqueous slurry or the aqueous solution (II) containing the heteropolyacid is convenient and preferable to be carried out by a method in which the aqueous slurry (I) obtained by adding part or all of the catalyst raw material to water is stirred while being
20 heated. The aqueous slurry (I) may be obtained by adding an aqueous solution, an aqueous slurry or an aqueous sol of the catalyst raw material to water. Preferably, the aqueous slurry (I) is heated to 90 to 150° C to obtain an aqueous slurry or aqueous solution (II). The lower limit of the heating temperature is more preferably 95° C or more and the upper limit is more preferably 130° C or less. By setting the heating temperature to 90° C or more, heteropolyacid is efficiently
25 generated from the catalyst raw material. By setting the heating temperature to 150° C or less, evaporation of water in the aqueous slurry or the aqueous solution can be suppressed.

[0039]

As described above, when proportion of particles having a particle diameter of 6μm or less is 2 to 55% by volume in a frequency distribution curve obtained by particle size distribution
30 measurement as the molybdenum raw material, it is speculated that the dissolution rate of dissolving the molybdenum raw material in water at heating the aqueous slurry (I) affects the active point of the resulting catalyst. At this time, the molybdenum raw material dissolves in water during a period from when the temperature of the aqueous slurry (I) reaches 60° C. to when it reaches 90° C. Therefore, by adjusting this duration time, it is possible to form a more

suitable active point for gas phase catalytic oxidation of α,β -unsaturated aldehyde with molecular oxygen. The duration time from when the temperature of the aqueous slurry (I) reaches 60° C to when it reaches 90° C is preferably 5 to 40 minutes, more preferably 7 to 30 minutes.

[0040]

5 In the aqueous slurry (I), the duration time from the time when the temperature reaches 60° C to the time when the temperature reaches 90° C can be controlled by adjusting the temperature rising rate or the like. The temperature of the aqueous slurry (I) may be monotonously increased, or may be controlled while appropriately changing the temperature increasing rate.

[0041]

10 The pH of the aqueous slurry or the aqueous solution (II) to be prepared is preferably 4 or less, more preferably 2 or less, from the viewpoint of improving the yield of the α,β -unsaturated carboxylic acid. When the pH of the aqueous slurry or the aqueous solution (II) is high, it is preferable to select each raw material so as to contain a large number of nitrate roots and the like.

[0042]

15 Whether or not heteropolyacids are formed in the aqueous slurries or the aqueous solution (II) in the step (i) can be confirmed by infrared absorbing analysis using NICOLET6700FT-IR (product name, manufactured by Thermo electron) or the like and X-ray diffraction analysis using an X-ray diffraction device X'Pert PRO MPD (product name, manufactured by PANalytical) or the like.

20 [0043]

(Step (ii))

In step (ii), a metal cation-contain compound is added to the aqueous slurry or aqueous solution (II) obtained in step (i) to obtain an aqueous slurry (III) in which the heteropolyacid salt is precipitated. As the metal cation-contain compound, it is preferable to use a compound
25 containing at least one element selected from the group consisting of lithium, sodium, potassium, rubidium, cesium and thallium (corresponding to G of the above formula (1)). In the step (ii), it is preferable to add an ammonium compound in addition to the metal cation-contain compound. By adding an ammonium compound, a crystal structure suitable for gas phase catalytic oxidation of α,β -unsaturated aldehyde with molecular oxygen is formed. Examples of the ammonium
30 compound include ammonium bicarbonate, ammonium carbonate, ammonium nitrate, ammonia water, and the like. One or more of these ammonium compounds may be used.

[0044]

The metal cation-contain compound and the ammonium compound are preferably added by dissolving or suspending them in a solvent. Examples of the solvent include water, ethyl alcohol,

acetone, and the like. However, it is preferable to use the same water as the aqueous slurry or the aqueous solution (II) obtained in the step (i) as a solvent. The stirring time of the aqueous slurry or the aqueous solution after the addition of the metal cation-containing compound and the ammonium compound added as necessary is preferably 1 to 300 minutes, the lower limit is more preferably 10 minutes or more, and the upper limit is more preferably 30 minutes or less. The temperature of the aqueous slurry or the aqueous solution at the time of stirring is preferably 50 to 100° C., and the lower limit is more preferably 80° C or more. By setting the stirring time to 1 minute or more and the temperature to 50° C or more, the metal salt and the ammonium salt of the heteropolyacid can be sufficiently formed. On the other hand, by setting the stirring time to 300 minutes or less and the temperature to 100° C or less, it is possible to suppress the formation of compounds other than the metal salt and the ammonium salt of the target heteropolyacid.

[0045]

The heteropolyacid salt to be precipitated (metal salt and ammonium salt of heteropolyacid) may have a keggin type structure or a structure other than a keggin type such as a dawson type structure, but it is preferable to have a keggin type structure from the viewpoint of improving yield of α,β -unsaturated carboxylic acid. As a method of precipitating a heteropolyacid salt having a keggin-type structure, a method of adjusting the pH of the aqueous slurry (III) obtained in step (ii) to 3 or less. The structures of the precipitated heteropolyacid salts can be confirmed by infrared absorbing analysis using NICOLET6700FT-IR (product name, manufactured by Thermo electron) and X-ray diffraction analysis using an X-ray diffraction device X'Pert PRO MPD (product name, manufactured by PANalitical).

[0046]

(Step (iii))

In step (iii), the aqueous slurry (III) obtained in step (ii) is dried to obtain a catalyst precursor dried product. The drying method includes, for example, a drum drying method, an air stream drying method, an evaporation drying method, a spray drying method, and the like. The drying temperature is preferably 120 to 500° C, and the lower limit is more preferably 140° C or more and the upper limit is more preferably 350° C or less. Drying can be carried out until the aqueous slurry (III) has dried. The moisture content of the catalyst precursor dried product is preferably 0.1 to 4.5 mass %. These conditions can be appropriately selected depending on the shape and size of the desired catalyst precursor dried product.

[0047]

(Molding step)

In the molding step, the dried catalyst precursor dried product obtained in step (iii) can be molded. Examples of the device used for molding include a molding machine for powder such as a tablet press, an extruder, a pressure molding machine and a rolling granulator. The shape of the molded article is not particularly limited, and may be any shape such as spherical granules, rings, cylindrical pellets, stars, granules crushed and classified after molding, and the like. At the time of molding, it may be carried on a carrier, and known additives such as graphite and talc, and known binders derived from organic substances and inorganic substances may be added as necessary. In the present invention, the catalyst precursor dried product obtained in the step (iii) and a product obtained by molding the catalyst precursor dried product are collectively referred to as a catalyst precursor dried product.

[0048]

(Step (iv))

In step (iv), the catalyst precursor dried product obtained in step (iii) or in the molding step is heat treated to obtain a catalyst. The heat treatment conditions are not particularly limited, but can be performed under the circulation of at least one of an inert gas and an oxygen-containing gas such as air. The heat treatment temperature is preferably 200 to 500° C, and the lower limit is more preferably 300° C or more and the upper limit is more preferably 450° C or less. The heat treatment time is preferably 0.5 to 40 hours, and the lower limit is more preferably 1 hour or more. When the molding step is not performed after the step (iii), the molding step may be performed on the catalyst after the heat treatment obtained in the step (iv).

[0049]

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

In the present invention, a catalyst for the production of α,β -unsaturated carboxylic acid is produced by the method according to the present invention, and α,β -unsaturated aldehyde is gas phase catalytically oxidized by molecular oxygen using the catalyst to produce α,β -unsaturated carboxylic acid. The method for producing α,β -unsaturated carboxylic acid according to the present invention is a method for producing α,β -unsaturated carboxylic acid by gas phase catalytic oxidation of α,β -unsaturated aldehyde with molecular oxygen using the catalyst for the production of α,β -unsaturated carboxylic acid produced by the method according to the present invention.

[0050]

In the method according to the present invention, examples of the α,β -unsaturated aldehyde include (meth)acrolein, crotonaldehyde (β -methylacrolein), cinnamaldehyde (β -phenylacrolein), and the like. Among these, from the viewpoint of the yield of the target product, (meth)acrolein

is preferable, and methacrolein is more preferable. The α,β -unsaturated carboxylic acid produced is an α,β -unsaturated carboxylic acid in which the aldehyde group of the α,β -unsaturated aldehyde is converted to a carboxyl group. Specifically, when the α,β -unsaturated aldehyde is (meth)acrolein, (meth)acrylic acid is obtained. Note that "(meth)acrolein" represents acrolein and methacrolein, and "(meth)acrylic acid" represents acrylic acid and methacrylic acid.

[0051]

Hereinafter, as a typical example, a method for producing methacrylic acid by gas phase catalytic oxidation of methacrolein with molecular oxygen in the presence of a catalyst for the production of methacrylic acid produced by the method according to the present invention will be described.

[0052]

In this method, methacrylic acid is produced by contacting a raw material gas containing methacrolein and molecular oxygen with a catalyst according to the present invention. In this reaction, a fixed bed reactor can be used. Specifically, the reaction can be carried out by filling a catalyst in a reaction tube and supplying a raw material gas to the reactor. The catalyst layer may be a single layer, or a plurality of catalysts having different activities may be separately filled into a plurality of layers. In order to control the activity, the catalyst for the production of methacrylic acid may be diluted and filled with an inert carrier.

[0053]

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

[0054]

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

[0055]

The raw material gas may be obtained by diluting methacrolein and molecular oxygen with an inert gas such as nitrogen or carbon dioxide. Further, steam may be added to the raw material gas. By carrying out the reaction in the presence of steam, methacrylic acid can be obtained with

high yield. The concentration of steam in the raw material gas is preferably 0.1 to 50% by volume, the lower limit is more preferably 1% or more by volume, and the upper limit is more preferably 40% or less by volume.

[0056]

5 The contact time between the raw material gas and the catalyst for the production of methacrylic acid is preferably 1.5 to 15 seconds. The reaction pressure is preferably 0.1 to 1MPa (G). Here, (G) means gauge pressure. The reaction temperature is preferably 200 to 450° C, and the lower limit is more preferably 250° C or more and the upper limit is more preferably 400° C or less.

10 [0057]

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

The method for producing an α,β -unsaturated carboxylic acid ester according to the present invention is a method for esterifying an α,β -unsaturated carboxylic acid produced by the method according to the present invention. The method for producing an α,β -unsaturated carboxylic acid ester according to the present invention is a method for producing an α,β -unsaturated carboxylic acid by the method according to the present invention and esterifying the α,β -unsaturated carboxylic acid. According to these methods, α,β -unsaturated carboxylic acid esters can be obtained using α,β -unsaturated carboxylic acids obtained by gas phase catalytic oxidation of α,β -unsaturated aldehydes. The alcohol to be reacted with the α,β -unsaturated carboxylic acid is not particularly limited, and for example, methanol, ethanol, isopropanol, n-butanol, isobutanol, and the like can be given. Examples of the obtained α,β -unsaturated carboxylic acid ester include (meth)methyl acrylate, (meth)ethyl acrylate, (meth)propyl acrylate, and (meth)butyl acrylate. 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.

25 [EXAMPLES]

[0058]

Hereinafter, the present invention will be explained in detail by examples and comparative examples, but the present invention is not limited to these examples. In the examples and comparative examples, "parts" means parts by mass. The analysis of the raw material gas and the product was carried out using gas chromatography. The methacrylic acid yield was determined from the results of gas chromatography by the following formula.

[0059]

$$\text{Methacrylic acid yield (\%)} = (B/A) \times 100$$

Where A is the number of moles of methacrolein fed to the reactor and B is the number of moles of methacrylic acid produced.

[0060]

The particle size distribution of molybdenum trioxide was measured by dispersing 0.02 to 0.1g of molybdenum trioxide in 500g of pure water and agitating for 30 seconds using a laser diffractive particle size distribution measuring device SALD-7000 (product name, manufactured by Shimadzu Corporation).

[0061]

(Example 1)

To 400 parts of pure water, 100 parts of molybdenum trioxide (the proportion of particles having a particle diameter of 6 μ m or less: 2.9% by volume) having the particle diameter distribution shown as Example 1 in FIG. 1, 3.4 parts of ammonium metavanadate, a diluted product obtained by diluting 9.4 parts of an 85% by mass phosphoric acid aqueous solution 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 to obtain an aqueous slurry (I). The aqueous slurry (I) was heated from 25° C to 95° C while stirring, and stirred for 2 hours while maintaining the liquid temperature at 95° C to obtain an aqueous slurry (II) containing a heteropolyacid. At this time, the duration time from when the temperature of the aqueous slurry (I) reached 60° C to when it reached 90° C was 15 minutes. Further, while maintaining the liquid temperature at 95° C and stirring, a dissolved substance obtained by dissolving 13.5 parts of cesium bicarbonate in 24 parts of pure water and a dissolved substance obtained by dissolving 9.2 parts of ammonium carbonate in 26 parts of pure water were added dropwise and stirred to precipitate cesium salts and ammonium salts of heteropolyacids. The precipitated cesium salts and ammonium salts of the heteropolyacid had a keggin-type structure. Thereafter, the mixture was stirred for 15 minutes while maintaining the liquid temperature at 95° C. The obtained aqueous slurry (III) was dried by a spray dryer to obtain a catalyst precursor dried product. The obtained catalyst precursor dried product was extruded to form a cylinder having a diameter of 5.5mm and a height of 5.5mm, and heat-treated at 380° C for 10 hours under air flow to produce a catalyst. The compositions other than oxygen of the catalysts were $P_{1.4}Mo_{12}V_{0.5}Cu_{0.15}Cs_{1.2}$.

[0062]

The catalyst was charged into a reaction tube, and a raw material gas containing 5% by volume of methacrolein, 10% by volume of oxygen, 30% by volume of steam, and 55% by volume of nitrogen was passed through the reaction tube at a reaction temperature of 310° C for a contact time of 7.1 seconds between the raw material gas and the catalyst. The product from

the reactor was collected and analyzed by gas chromatography to calculate the methacrylic acid yield. The results are given in Table 1.

[0063]

(Examples 2 to 4, Comparative Examples 1 to 3)

5 In place of 100 parts of molybdenum trioxide used in Example 1, a catalyst was produced in the same manner as in Example 1 except that 100 parts of molybdenum trioxide having a particle size distribution shown in each example and as a comparative example (the proportion of particles having a particle diameter of 6 μ m or less is shown in Table 1) was used, and the methacrylic acid yield was calculated. The results are given in Table 1. In Examples 2 to 4 and
10 Comparative Examples 1 to 3, as in Example 1, the cesium salt and ammonium salt of the heteropolyacid precipitated had a keggin-type structure.

[0064]

(Examples 5 to 8)

15 Except for the duration time from when the temperature of the aqueous slurry (I) reached 60° C to when it reached 90° C was prepared as shown in Table 1, the catalyst was prepared as in Example 1, and the methacrylic yield was calculated. The results are given in Table 1. In Examples 5 to 8 as well, the cesium salt and the ammonium salt of the heteropolyacid precipitated had a keggin-type structure as in Example 1.

[0065]

20 [Table 1]

	Particle proportion of molybdenum oxide [volume %]		Duration time in which temperature of aqueous slurry (I) reaches from 60° C to 90° C [Min]	Methacrylic acid yeild [%]
	6 μ m or less	30~200 μ m		
Example 1	2.9	75.5	15	65.2
Example 2	13.6	74.6	15	67.8
Example 3	31.9	55.0	15	64.8
Example 4	40.0	45.5	15	63.2
Example 5	2.9	75.5	6	61.9
Example 6	2.9	75.5	35	62.6
Example 7	2.9	75.5	4	60.4
Example 8	2.9	75.5	45	61.8
Comparative Example 1	0.0	100.0	15	57.2
Comparative Example 2	0.9	92.7	15	58.4
Comparative Example 3	60.0	29.1	15	37.4

[0066]

As shown in Table 1, methacrylic acid was obtained in high yield in Examples 1 to 8 in which molybdenum oxide was used as the molybdenum raw material in which the proportion of
25 particles having a particle diameter of 6 μ m or less in the particle diameter distribution was 2 to 55% by volume. Among Examples 1 to 8, Examples 1 to 6 in which the duration time from the

time when the temperature of the aqueous slurry (I) reached 60° C to the time when it reached 90° C was in the range of 5 to 40 minutes had higher methacrylic acid yield, and Examples 1 to 4 in which it was in the range of 7 to 30 minutes had particularly high methacrylic acid yield. On the other hand, in Comparative Examples 1 to 3 using molybdenum oxide in which the proportion of particles having a particle diameter of 6 μ m or less in the particle diameter distribution was out of the above range as the molybdenum raw material, the methacrylic acid yield was low as compared with Examples.

[0067]

This application claims priority to Japanese Patent Application No. 2017-203592, filed Oct. 20, 2017, the entire disclosure of which is incorporated herein by reference.

[0068]

Although the present invention has been described above with reference to embodiments and examples, the present invention is not limited to the above embodiments and examples. Various modifications can be made to the structure and details of the present invention which can be understood by a person skilled in the art within the scope of the present invention.

[Industrial Applicability]

[0069]

According to the present invention, it is possible to provide a catalyst for the production of α,β -unsaturated carboxylic acids capable of producing α,β -unsaturated carboxylic acids in high yield from α,β -unsaturated aldehydes, which is industrially useful.

Claims

[Claim 1]

A method for producing a catalyst for the production of α,β -unsaturated carboxylic acid using molybdenum oxide as a molybdenum raw material,

- 5 wherein the molybdenum raw material is a molybdenum oxide in which the proportion of particles having a particle diameter of $6\mu\text{m}$ or less is 2 to 55% by volume in a frequency distribution curve obtained by particle size distribution measurement.

[Claim 2]

- 10 The method for producing a catalyst for the production of α,β -unsaturated carboxylic acid according to claim 1, comprising the steps of:

- (i) heating an aqueous slurry (I) obtained by mixing water with a catalyst raw material containing at least said molybdenum raw material and phosphorus raw material to a temperature of 90 to 150°C to obtain an aqueous slurry or aqueous solution (II) containing a heteropolyacid;
- 15 (ii) adding a metal cation-contain compound to said aqueous slurry or aqueous solution (II) to obtain an aqueous slurry (III) in which a heteropolyacid salt is precipitated;
- (iii) drying said aqueous slurry (III) to obtain a catalyst precursor dried product; and
- (iv) heat treating said catalyst precursor dried product to obtain a catalyst;
- 20 wherein a duration time in which temperature of said aqueous slurry (I) reaches from 60°C to 90°C in step (i) is 5 to 40 minutes.

[Claim 3]

The method for producing a catalyst for the production of α,β -unsaturated carboxylic acid according to claim 2,

- 25 wherein the duration time in which temperature of said aqueous slurry (I) reaches from 60°C to 90°C in step (i) is 7 to 30 minutes.

[Claim 4]

- 30 The method for producing a catalyst for the production of α,β -unsaturated carboxylic acid according to any one of claims 1 to 3,

wherein the molybdenum raw material is a molybdenum oxide in which the proportion of particles having a particle diameter of $6\mu\text{m}$ or less is 2 to 35% by volume.

[Claim 5]

The method for producing a catalyst for the production of α,β -unsaturated carboxylic acid according to claim 4,

wherein the molybdenum raw material is a molybdenum oxide in which the proportion of particles having a particle diameter of 6 μ m or less is 2 to 15% by volume.

5

[Claim 6]

The method for producing a catalyst for the production of α,β -unsaturated carboxylic acid according to any one of claims 1 to 5,

wherein the catalyst has a composition represented by the following formula (1).

10
$$P_a Mo_b V_c Cu_d A_e E_f G_g O_h \quad (1)$$

(In formula (1), P, Mo, V, Cu, and O are elemental symbols representing phosphorus, molybdenum, vanadium, copper, 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
15 from the group consisting of iron, zinc, chromium, magnesium, calcium, strontium, tantalum, cobalt, nickel, manganese, barium, titanium, tin, lead, niobium, indium, sulfur, palladium, gallium, cerium and lanthanum; G represents at least one element selected from the group consisting of lithium, sodium, potassium, rubidium, cesium and thallium; a to h represent atomic ratio of each element; when b=12, a=0.5 to 3, c=0.01 to 3, d=0.01 to 2, e=0 to 3, f=0 to 3 and
20 g=0.01 to 3 and h is the atomic ratio of oxygen required to satisfy the valence of each of the above elements).

[Claim 7]

25 The method for producing a catalyst for the production of α,β -unsaturated carboxylic acid according to any one of claims 1 to 6,

wherein 50 mass % or more of molybdenum trioxide is used as the molybdenum raw material.

[Claim 8]

30 The method for producing a catalyst for the production of α,β -unsaturated carboxylic acid according to claim 7,

wherein 70 mass % or more of molybdenum trioxide is used as the molybdenum raw material.

[Claim 9]

The method for producing a catalyst for the production of α,β -unsaturated carboxylic acid according to any one of claims 1 to 8,

wherein the catalyst for the production of α,β -unsaturated carboxylic acid is a catalyst used in the production of α,β -unsaturated carboxylic acid by gas phase catalytic oxidation of α,β -unsaturated aldehyde with molecular oxygen, wherein the α,β -unsaturated aldehyde is (meth)acrolein and the α,β -unsaturated carboxylic acid is (meth)acrylic acid.

[Claim 10]

A method for producing an α,β -unsaturated carboxylic acid,

wherein a catalyst for the production of α,β -unsaturated carboxylic acid is produced by the method according to any one of claims 1 to 9, and an α,β -unsaturated carboxylic acid is produced by gas phase catalytic oxidation of α,β -unsaturated aldehyde with molecular oxygen using the catalyst.

[Claim 11]

A method for producing an α,β -unsaturated carboxylic acids,

wherein the α,β -unsaturated carboxylic acid is produced by gas phase catalytic oxidation of α,β -unsaturated aldehyde with molecular oxygen using a catalyst for the production of α,β -unsaturated carboxylic acid produced by the method of any one of claims 1 to 9.

[Claim 12]

A method for producing an α,β -unsaturated carboxylic acid esters, by esterifying the α,β -unsaturated carboxylic acids produced by the method of claim 10 or 11.

[Claim 13]

A method for producing an α,β -unsaturated carboxylic acid ester,

wherein an α,β -unsaturated carboxylic acid is produced by the method of claim 10 or 11, and said α,β -unsaturated carboxylic acid is esterified.