

DESCRIPTION

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

TECHNICAL FIELD

[0001]

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

BACKGROUND ART

[0002]

As a catalyst used in producing an α,β -unsaturated carboxylic acid by gas phase catalytic oxidation of an α,β -unsaturated aldehyde with molecular oxygen, a catalyst mainly containing a heteropolyacid or a salt thereof such as phosphomolybdic acid or phosphomolybdate is known. This catalyst is usually produced by first preparing an aqueous solution or an aqueous slurry containing each element constituting a catalyst, and then drying the aqueous slurry and calcining the dried material.

[0003]

As an example of an examination of a method for producing a catalyst, for example, Patent Document 1 discloses that a catalyst having a high methacrylic acid production yield is obtained by cooling the prepared aqueous slurry at a rate of 1.5° C or more per minute. Patent Document 2 discloses that a catalyst having a high methacrylic acid production yield can be obtained by adding an alkali metal raw material at a rate of 0.1 to 3.0 moles/s per 12 moles of Mo element. In addition, Patent Document 3 discloses that a catalyst having a high methacrylic acid production yield can be obtained by adding an alkali metal compound to an aqueous slurry while stirring at a stirring power per unit volume required of 0.01 to 4.00

kW/m³. In addition, Patent Document 4 discloses that a catalyst having a high methacrylic acid production yield can be obtained by regulating the addition temperature and the stirring time of the raw material to the aqueous slurry.

[0004]

However, further high yield is desired for the catalyst for producing α,β -unsaturated carboxylic acid.

PRIOR-ART DOCUMENT

PATENT DOCUMENT

[0005]

Patent Document 1: JP 2013-192988 A

Patent Document 2: JP 2013-192989 A

Patent Document 3: WO 2013/172414 A1

Patent Document 4: JP 2005-230720 A

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0006]

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

MEANS FOR SOLVING THE PROBLEMS

[0007]

The present invention includes the following [1] to [12].

[1] A method for producing a catalyst for producing an α,β -unsaturated carboxylic acid, which is used in producing an α,β -unsaturated carboxylic acid by catalytic oxidation of an α,β -unsaturated aldehyde in a gas phase with molecular oxygen,

wherein the method includes:

(i) a step for obtaining an aqueous slurry (S2) including a heteropolyacid salt containing at least molybdenum and phosphorus;

(ii) a step for holding the aqueous slurry (S2) with stirring at less than 50° C for 2.5 to 24.5 hours to obtain an aqueous slurry (S3); and

(iii) a step for spray-drying the aqueous slurry (S3).

[2] The method for producing a catalyst for producing an α,β -unsaturated carboxylic acid according to [1], wherein the heteropolyacid salt in step (i) is at least one selected from the group consisting of metal cation salts and ammonium salts.

[3] The method for producing a catalyst for producing an α,β -unsaturated carboxylic acid according to [1] or [2], wherein in step (i), an aqueous slurry or aqueous solution (S1) containing at least molybdenum and phosphorus is held at 70 to 130° C and is mixed with a base-containing compound to obtain the aqueous slurry (S2).

[4] The method for producing a catalyst for producing an α,β -unsaturated carboxylic acid according to any one of [1] to [3], wherein the heteropolyacid salt in step (i) has a Keggin-type structure.

[5] The method for producing a catalyst for producing an α,β -unsaturated carboxylic acid according to any one of [1] to [4], wherein the holding of the aqueous slurry (S2) with stirring is carried out for 3.4 hours or more and less than 15 hours in the step (ii).

[6] The method for producing a catalyst for producing an α,β -unsaturated carboxylic acid according to any one of [1] to [5], wherein the holding of the aqueous slurry (S2) with stirring is carried out at a temperature higher than 30° C and lower than 50° C in the step (ii).

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



(In the above formula (1), P, Mo, V, Cu, NH_4 and O represent phosphorus, molybdenum, vanadium, copper, ammonium species and oxygen, respectively; A represents at least one element selected from the group consisting of antimony, bismuth, arsenic, germanium, zirconium, tellurium, silver, selenium, silicon, tungsten and boron; E represents at least one element selected from the group consisting of iron, zinc, chromium, magnesium, calcium, strontium, tantalum, cobalt, nickel,

manganese, barium, titanium, tin, thallium, 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 and cesium; and a to i represent the molar ratio of each component, and when $b = 12$, $a = 0.5-3$, $c = 0.01-3$, $d = 0.01-2$, $e = 0-3$, $f = 0-3$, $g = 0.01-3$, $h = 0-30$, i is the molar ratio of oxygen required to satisfy the valence of each said component).

[8] A method for producing an α,β -unsaturated carboxylic acid, wherein an α,β -unsaturated aldehyde is subjected to gas phase catalytic oxidation with molecular oxygen in the presence of a catalyst produced by the method according to any one of [1] to [7].

[9] A method for producing an α,β -unsaturated carboxylic acid, wherein a catalyst is produced by the method according to any one of [1] to [7], and the catalyst is used to catalytically oxidize an α,β -unsaturated aldehyde with molecular oxygen in a gas phase.

[10] A method for producing an α,β -unsaturated carboxylic acid ester, in which an α,β -unsaturated carboxylic acid produced by the method of [8] or [9] is esterified.

[11] A method for producing an α,β -unsaturated carboxylic acid ester including producing an α,β -unsaturated carboxylic acid by the method of [8] or [9], and esterifying the α,β -unsaturated carboxylic acid.

EFFECT OF INVENTION

[0008]

According to the present invention, it is possible to provide a catalyst for producing an α,β -unsaturated carboxylic acid capable of producing an α,β -unsaturated carboxylic acid in high yield. Further, according to the present invention, it is possible to obtain α,β -unsaturated carboxylic acid and α,β -unsaturated carboxylic acid ester in high yield.

DETAILED DESCRIPTION OF THE INVENTION

[0009]

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

The catalyst obtained in the method for producing a catalyst for producing an α,β -unsaturated carboxylic acid according to the present invention is used in producing an α,β -unsaturated carboxylic acid by gas phase catalytic oxidation of an α,β -unsaturated aldehyde with molecular oxygen to produce an α,β -unsaturated carboxylic acid. The present invention is a process for the preparation of the catalyst including the following steps (i) to (iii):

- (i) A step for obtaining an aqueous slurry (S2) including a heteropolyacid salt containing at least molybdenum and phosphorus.
- (ii) A step for holding the aqueous slurry (S2) with stirring at less than 50° C for 2.5 to 24.5 hours to obtain an aqueous slurry (S3).
- (iii) A step for spray-drying the aqueous slurry (S3).

[0010]

It is considered that the method for producing a catalyst according to the present invention includes the steps (i) to (iii), whereby the precipitation reaction of the dissolved element in the aqueous slurry proceeds, and the specific surface area of the obtained catalyst is improved by suppressing the dissolving element from blocking the fine pores on the surface of the catalyst during spray-drying. Thus, the catalytic activity is improved, and when an α,β -unsaturated carboxylic acid is produced by a gas phase catalytic oxidation of the α,β -unsaturated aldehyde with molecular oxygen, the yield of the α,β -unsaturated carboxylic acid can be improved.

[0011]

The catalyst for producing an α,β -unsaturated carboxylic acid that is produced by the method according to the present invention contains at least molybdenum and phosphorus. Most especially, the catalyst preferably has a composition represented by the following formula (1) from the viewpoint of producing an α,β -unsaturated carboxylic acid in high yield in the production of an α,β -unsaturated carboxylic acid. Note that the molar ratio of each element in the catalyst is a value determined by analyzing a component in which the catalyst is dissolved in aqueous ammonia by an ICP atomic emission spectroscopy. Note that the molar ratio of ammonium species is a value obtained by analyzing the catalyst component by the Kjeldahl method.

[0012]



In formula (1), P, Mo, V, Cu, NH_4 and O represent phosphorus, molybdenum, vanadium, copper, ammonium species and oxygen, respectively. A represents at least one element selected from the group consisting of antimony, bismuth, arsenic, germanium, zirconium, tellurium, silver, selenium, silicon, tungsten and boron. E represents at least one element selected from the group consisting of iron, zinc, chromium, magnesium, calcium, strontium, tantalum, cobalt, nickel, manganese, barium, titanium, tin, thallium, 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 and cesium. a to i represent the molar proportions of each component, and when $b = 12$, $a = 0.5-3$, $c = 0.01-3$, $d = 0.01-2$, $e = 0-3$, $f = 0-3$, $g = 0.01-3$, $h = 0-30$, i is the molar ratio of oxygen required to satisfy the valence of each said component.

The term "ammonium species" as used herein is a generic term for ammonium, that can be ammonium ions (NH_4^+), contained in ammonia (NH_3) and an ammonium-containing compound such as an ammonium salt.

[0013]

(Step (i))

In step (i), an aqueous slurry (S2) including at least a heteropolyacid salt containing molybdenum and phosphorus is prepared. The heteropolyacid salt consists of a heteropolyacid and a base. The base is not particularly limited, and examples thereof include cations of metals such as alkali metals and ammonium ions. From the viewpoint of activity and thermal stability of the catalyst, the heteropolyacid salt is preferably at least one selected from the group consisting of a metal cation salt and an ammonium salt. Note that a composite salt of a plurality of different metal cations and a composite salt of a metal cation and an ammonium are also included in this heteropolyacid salt. In addition, when a catalyst having a composition represented by the above formula (1) is produced, it is preferable to prepare an aqueous slurry (S2) including elements contained in the composition represented by the above formula (1).

[0014]

The catalyst raw material to be used is not particularly limited, and nitrates, carbonates, acetates, ammonium salts, oxides, halides, oxoacids, oxoacid salts, and the like of each element can be used alone or in combination of 2 or more thereof. Examples of the raw material for molybdenum include ammonium paramolybdate, molybdenum trioxide, molybdic acid, and molybdenum chloride. Examples of the raw material for phosphorus include normal phosphoric acid, phosphorous pentoxide, or phosphate such as cesium phosphate. Examples of the raw material for copper include copper sulfate, copper nitrate, copper oxide, copper carbonate, copper acetate, and copper chloride. Examples of the raw material for vanadium include ammonium metavanadate, vanadium pentoxide, and vanadium chloride. These may be used singly, or in combination of two or more thereof.

[0015]

As raw materials for molybdenum, phosphorus, and vanadium, heteropolyacid containing at least one element selected from molybdenum, phosphorus, and vanadium may be used. Examples of the heteropolyacid include phosphomolybdic acid, phosphovanadomolybdic acid, silicomolybdic acid. These may be used singly, or in combination of two or more thereof.

[0016]

It is preferable that the aqueous slurry (S2) is prepared by holding an aqueous slurry or aqueous solution (S1) containing at least molybdenum and phosphorus at 70 to 130° C, and mixing it with a base-containing compound.

Although there is no particular limitation on the method for preparing the aqueous slurry or aqueous solution (S1), it is simple and preferable to perform the preparation by a method in which a part or all of a raw material of each element constituting a catalyst is added to water and heated and stirred. An aqueous solution, an aqueous slurry or an aqueous sol of a raw material of each element constituting a catalyst may also be added to water. The number of moles of molybdenum added to 100 g of water is preferably 0.01 to 1 mole, the lower limit and the upper limit are more preferably 0.05 mole or more, and 0.5 mole or less, respectively.

The aqueous slurry or aqueous solution (S1) may be any of aqueous slurry and aqueous solutions depending on conditions such as components and a temperature, and either of them may be used.

[0017]

The temperature of the aqueous slurry or aqueous solution (S1) during the preparation is preferably 80 to 130° C, more preferably 90 to 130° C. By setting the temperature of the aqueous slurry or aqueous solution (S1) to 80° C or higher, it is possible to sufficiently increase the production rate of the heteropolyacid. In the meantime, by setting the temperature of the aqueous slurry or aqueous solution (S1) to 130° C or less, it is possible to suppress the formation of by-products other than the heteropolyacid and the evaporation of water in the aqueous slurry or aqueous solution (S1). The pH of the aqueous slurry or aqueous solution (S1) is preferably 4 or less, more preferably 2 or less. By lowering the pH of the aqueous slurry or aqueous solution sufficiently, a heteropolyacid having a Keggin-type structure can be stably formed. Note that the pH of the aqueous slurry or aqueous solution can be measured by a portable pH meter D-21 (trade name) made of HORIBA or the like.

[0018]

The aqueous slurry or aqueous solution (S1) is then mixed with a base-containing compound in the state keeping at 70 to 130°C. This produces heteropolyacid salts. Preferably, the base-containing compound is added to the aqueous slurry or aqueous solution (S1).

The base-containing compound may be any compound containing a base forming a salt with a heteropolyacid, and is not particularly limited, but preferably contains a metal cation or an ammonium ion as a base. By mixing the aqueous slurry or aqueous solution (S1) with at least one selected from the group consisting of a metal cation-containing compound and an ammonium-containing compound, an aqueous slurry (S2) containing a metal salt or an ammonium salt of a heteropolyacid can be obtained.

The temperature of the aqueous slurry or aqueous solution (S1) when mixed with the base-containing compound is preferably adjusted to be in the range of 70 to 130° C. Thus, when the obtained catalyst is used for producing an α,β -unsaturated carboxylic acid, hot spot generation of the catalyst layer is easily suppressed. More preferably, the lower limit of the temperature of the aqueous slurry or aqueous solution (S1) is 80° C or higher, and the upper limit is 100° C or less.

As the metal cation-containing compound, a compound containing an alkali metal is preferably used, and a compound containing at least one element selected from the group consisting of lithium, sodium, potassium, rubidium and cesium (corresponding to G of the above formula (1)) is more preferably used. By adding the metal cation-containing compound, the thermal stability of the catalyst is improved, and the thermal deterioration thereof can be suppressed. Examples of the ammonium-containing compound include ammonium hydrogen carbonate, ammonium carbonate, ammonium nitrate, and aqueous ammonia. These base-containing compounds may be used singly, or in combination of a plurality of kinds thereof. By adding the ammonium-containing compound, a crystal structure suitable for gas-phase catalytic oxidation of α,β -unsaturated aldehydes with molecular oxygen is formed. Note that, by using a plurality of kinds of metal cation-containing compounds or a plurality of kinds of ammonium-containing compounds in combination, or by using a metal cation-containing compound and an ammonium-containing compound in combination, each of them exhibits excellent performance because the respective preferable characteristics appear.

The base-containing compound is preferably dissolved or suspended in a solvent and mixed. Examples of the solvent include water, ethyl alcohol, and acetone, and water is preferably used as a solvent. After mixing the base-containing compound, it is preferable to hold with stirring at 70 to 130° C for 5 to 60 minutes. Note that, the "hold(ing) with stirring" means that it is held in a state of being stirred. More preferably, the lower limit of the time for holding with stirring is 10 minutes or more, and the upper limit is 30 minutes or less. By setting the time for holding with stirring to 5 minutes or more, a salt of a heteropolyacid can be sufficiently formed. In the meantime, by setting the time for holding with stirring to 60 minutes or less, side reactions other than the formation of the target heteropolyacid salt can be suppressed.

[0019]

The obtained heteropolyacid salt preferably has a Keggin-type structure from the viewpoint of yield of α,β -unsaturated carboxylic acid. As a method for precipitating a heteropolyacid salt having a Keggin-type structure, for example, a method in which the pH of the aqueous slurry (S2) is adjusted to 4 or less, preferably

3 or less, by appropriately selecting the addition amount of a raw material compound, ammonium, or the like, and adding nitric acid, oxalic acid, or the like as appropriate, can be mentioned. Note that the structure of the obtained heteropolyacid salt can be considered from infrared absorption spectrometry using a NICOLET 6700 FT-IR (product name, manufactured by Thermo Electron Co., Ltd.). If the heteropolyacid salt has a Keggin-type structure, the resulting infrared absorption spectra have characteristic peaks around 1060, 960, 870 and 780 cm^{-1} .

[0020]

(Step (ii))

In step (ii), the aqueous slurry (S2) obtained in step (i) is cooled and held with stirring for 2.5 to 24.5 hours at less than 50° C, thereby obtaining an aqueous slurry (S3). For cooling, the aqueous slurry (S2) may be cooled by contacting it with a refrigerant to lower the temperature, or the aqueous slurry (S2) may be placed at room temperature to lower the temperature. Cooling is preferably carried out while stirring the aqueous slurry (S2). The precipitated heteropolyacid salt or the like is uniformly dispersed by stirring, and a homogeneous dried product stable in properties is easily obtained by spray-drying in step (iii) described later. From the viewpoint of promoting precipitation of the heteropolyacid salt, the temperature lowering rate is preferably 0.1° C or more per minute, more preferably 0.3° C or more per minute. However, the temperature lowering rate is usually 10° C or less per minute.

By setting the holding temperature of the aqueous slurry (S2) to less than 50° C, and the time for holding with stirring to be 2.5 hours or more, it is possible to sufficiently precipitate elements contained in the aqueous slurry (S2), so that the specific surface area of the catalyst obtained after drying is improved and the yield is improved in the production of the α,β -unsaturated carboxylic acid. Further, by setting the holding temperature of the aqueous slurry to less than 50° C, excessive volatilization of the volatile compound contained in the aqueous slurry (S2) can be suppressed, which is advantageous from the viewpoint of α,β -unsaturated carboxylic acid yield. Further, by setting the holding time of the aqueous slurry (S2) to 24.5 hours or less, it is possible to suppress the decrease in the bulk density of the catalyst obtained in step (iii) and to maintain largely an amount of the catalyst which can be

filled in the reactor, which is advantageous from the viewpoint of continuously using the catalyst for a long time. The temperature at which the aqueous slurry (S2) is held with stirring is equal to or higher than a temperature at which the aqueous slurry (S2) can be stirred using an impeller, a stirring blade, or the like (e.g., the temperature more than a freezing point of the aqueous slurry (S2)), and is preferably 10° C or more from the viewpoint of α,β -unsaturated carboxylic acid yield, and more preferably a temperature higher than 30° C. Further, the lower limit of the time for holding with stirring is preferably 3.4 hours or more, and the upper limit is preferably less than 15 hours.

In the present invention, the time for holding with stirring refers to a time in which the temperature of the aqueous slurry (S2) is less than 50° C, and the aqueous slurry (S2) is stirred using an impeller, a stirring blade, or the like to give fluidity. Stirring of the aqueous slurry (S2) may be carried out continuously for 2.5 to 24.5 hours, or stirring may be intermittently carried out, and the total time thereof may be 2.5 to 24.5 hours. By stirring, the precipitated heteropolyacid salt or the like is uniformly dispersed, and a homogeneous dried product stable in properties is easily obtained during spray-drying of step (iii) described later. In step (ii), in this way, an aqueous slurry (S3) in which elements in the liquid are sufficiently precipitated is obtained.

[0021]

(Step (iii))

In step (iii), the aqueous slurry (S3) obtained by the step (ii) is spray-dried. Drying of the aqueous slurry (S3) is performed following step (ii). Preferably, from the start of holding of the aqueous slurry (S2) with stirring at less than 50° C to the end of drying of the aqueous slurry (S3) is performed at 2.5 to 24.5 hours. Further, the spray-drying may be performed by gradually supplying a portion of the aqueous slurry, while holding with stirring to the spray dryer after a lapse of 2.5 hours or more, instead of drying at once. The drying temperature is preferably 120 to 500° C, the lower limit is more preferably 140° C or more, and the upper limit is more preferably 350° C or less. The drying is preferably carried out so that the moisture content of the obtained dried product is 0.1 to 4.5% by mass. Note that these

conditions can be appropriately selected depending on the shape and size of the desired catalyst.

The dried product obtained in step (iii) exhibits catalytic performance, and this can be used as a catalyst for producing an α,β -unsaturated carboxylic acid, but is further preferred to perform molding or calcination described later because the performance as a catalyst is improved. In the present invention, these molded and calcined products are collectively referred to as a catalyst.

[0022]

(Molding step)

In the molding step, the dried product obtained in the step (iii) is pulverized if necessary and molded. Incidentally, the molding may be performed after the calcination step described later. The molding method is not particularly limited, and known dry or wet molding methods can be applied. For example, tablet molding, extrusion molding, pressing, rolling granulation, and the like can be mentioned. The shape of the molded product 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. When the shape of the catalyst after molding is spherical granular, it is preferable that the diameter is 0.1 mm or more and 10 mm or less. By having a diameter of 0.1 mm or more, the pressure loss in the reaction tube can be reduced. In the meantime, when the diameter is 10 mm or less, the catalytic activity is further improved. When molding, it may be supported on a carrier, and other additives may be mixed.

[0023]

(Calcination step)

It is preferable from the viewpoint of yield of α,β -unsaturated carboxylic acid to calcine the catalyst obtained in the step (iii) or the molding step. The calcination condition is not particularly limited, for example, it can be carried out under the flow of at least one of an oxygen-containing gas such as air, and/or an inert gas. The calcination is preferably performed under the flow of an oxygen-containing gas such as air. The "inert gas" refers to a gas which does not reduce the catalyst activity, and includes, for example, nitrogen, carbon dioxide, helium, argon, and the like. These may be used singly, or two or more kinds thereof may be mixed and

used. From the viewpoint of yield of α,β -unsaturated carboxylic acid, the calcination temperature is preferably 200 to 500° C, more preferably, the lower limit is 300° C or more, and the upper limit is 450° C or less. Further, the lower limit of the calcination time is preferably 0.5 to 40 hours, more preferably 1 to 40 hours.

[0024]

[Method for Producing α,β -Unsaturated Carboxylic Acid]

In the method for producing an α,β -unsaturated carboxylic acid according to the present invention, an α,β -unsaturated aldehyde is subjected to gas phase catalytic oxidation with molecular oxygen in the presence of a catalyst produced by the method according to the present invention. Alternatively, in the method for producing an α,β -unsaturated carboxylic acid according to the present invention, a catalyst is produced by the method according to the present invention, and an α,β -unsaturated aldehyde is subjected to gas phase catalytic oxidation with molecular oxygen by using the catalyst to produce an α,β -unsaturated carboxylic acid. According to these methods, α,β -unsaturated carboxylic acids can be produced in high yields.

[0025]

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 them, it is preferably (meth)acrolein, and more preferably methacrolein, from the viewpoint of yield of the target product. The α,β -unsaturated carboxylic acid produced is an α,β -unsaturated carboxylic acid in which an aldehyde group of the α,β -unsaturated aldehyde is changed to a carboxyl group. Specifically, when the α,β -unsaturated aldehyde is (meth)acrolein, (meth)acrylic acid is obtained. Note that "(meth)acrolein" indicates acrolein and methacrolein, and "(meth)acrylic acid" indicates acrylic acid and methacrylic acid.

[0026]

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

[0027]

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

[0028]

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

[0029]

The concentration of molecular oxygen in the source gas is preferably 0.4 to 4 moles, and the lower limit is more preferably 0.5 moles or more and the upper limit is more preferably 3 moles or less, based on 1 mole of methacrolein. Note that air is preferred as the molecular oxygen source from the viewpoint of economic efficiency. If necessary, a gas obtained by enriching molecular oxygen by adding pure oxygen to air may be used.

[0030]

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

[0031]

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

[0032]

[Method for Producing α,β -Unsaturated Carboxylic Acid Esters]

Examples of the method for producing an α,β -unsaturated carboxylic ester according to the present invention include those which esterify an α,β -unsaturated carboxylic acid produced by the method according to the present invention. Alternatively, examples of the method for producing an α,β -unsaturated carboxylic acid ester according to the present invention include those in which an α,β -unsaturated carboxylic acid is produced by the method according to the present invention and the α,β -unsaturated carboxylic acid is esterified. According to these methods, α,β -unsaturated carboxylic acids obtained by gas phase catalytic oxidation of α,β -unsaturated aldehydes can be used to obtain α,β -unsaturated carboxylic acid esters. The alcohol to be reacted with the α,β -unsaturated carboxylic acid is not particularly limited, and examples thereof include methanol, ethanol, isopropanol, n-butanol, and isobutanol. Examples of the obtained α,β -unsaturated carboxylic acid ester include methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, and butyl (meth)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.

EXAMPLES

[0033]

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.

[0034]

The molar ratio of each element in the catalyst was calculated by analyzing the component in which the catalyst was dissolved in aqueous ammonia by ICP atomic emission spectrometry.

[0035]

Analyses of the source gas and the product were performed using gas chromatography (instrument: GC-2014 manufactured by Shimadzu Corporation, column: DB-FFAP manufactured by J&W Co., Ltd., 30 m × 0.32 mm, film thickness 1.0 μm). From the results of gas chromatography, methacrylic acid yield was determined by the following formula:

$$\text{Methacrylic acid yield (\%)} = (\text{number of moles of methacrylic acid produced} / \text{number of moles of methacrolein fed to the reactor}) \times 100$$

[0036]

(Example 1)

To 400 parts of pure water, 100 parts of molybdenum trioxide, 3.4 parts of ammonium metavanadate, 9.4 parts of an 85% by mass aqueous phosphoric acid solution diluted with 6.0 parts of pure water, and 2.1 parts of copper (II) nitrate trihydrate dissolved in 4.5 parts of pure water were added. The resulting aqueous slurry was heated from 25° C to 95° C while stirring, and stirred for 2 hours while keeping the liquid temperature at 95° C, to obtain an aqueous slurry (S1). Further, while holding the liquid temperature at 95° C with stirring, 13.5 parts of cesium bicarbonate dissolved in 24 parts of pure water and 9.2 parts of ammonium carbonate dissolved in 26 parts of pure water were added dropwise and stirred to precipitate a cesium salt and an ammonium salt of heteropolyacid. The precipitated heteropolyacid salt had a Keggin-type structure. The resulting aqueous slurry (S2) was cooled with stirring from 95° C to 40° C. At that time, the time until the aqueous slurry (S2) becomes 40° C from below 50° C was 0.4 hours. Subsequently, the aqueous slurry (S2) was held at 40° C with stirring for 3.0 hours. Thereafter, the aqueous slurry (S3) after holding with stirring was spray-dried. The obtained dried product was subjected to pressing, pulverized, and calcined at 380° C for 5 hours under air flow. The compositions of the resulting catalysts excluding ammonium species and oxygen were $\text{P}_{1.4}\text{Mo}_{12}\text{V}_{0.5}\text{Cu}_{0.15}\text{Cs}_{1.2}$.

[0037]

This catalyst was filled into a reaction tube, and a source gas including 5% by volume of methacrolein, 10% by volume of oxygen, 30% by volume of water vapor, and 55% by volume of nitrogen was passed through at a reaction temperature of 285° C, and a contact time of the source gas with the catalyst of 2.4 seconds. The product obtained from the reactor was collected and analyzed by gas chromatography to calculate the yield of methacrylic acid. The production conditions and evaluation results of the catalyst, and the reaction results are shown in Table 1. In the table, the holding time T of the aqueous slurry (S2) with stirring is the total of the time until the aqueous slurry (S2) becomes the holding temperature R with stirring from less than 50° C, and the holding time at the holding temperature R with stirring.

[0038]

(Examples 2-10)

Each catalyst was produced in the same manner as in Example 1, except that the holding time after cooling the aqueous slurry (S2) from 95° C to 40° C was changed, and the yield of methacrylic acid was calculated. The respective holding times T with stirring and evaluation results, and the reaction results are shown in Table 1.

[0039]

(Example 11)

An aqueous slurry (S2) obtained in the same manner as in Example 1 was cooled while stirring from 95° C to 20° C. At that time, the time until the aqueous slurry (S2) becomes 20° C from less than 50° C was 0.5 hours. Subsequently, a catalyst was produced in the same manner as in Example 1, except that the aqueous slurry (S2) was held at 20° C with stirring for 3.0 hours, and the yield of methacrylic acid was calculated. The conditions for producing the catalyst and the reaction results are shown in Table 2.

(Example 12)

A catalyst was produced in the same manner as in Example 11, except that the holding time after cooling the aqueous slurry (S2) from 95° C to 20° C was changed to 16.0 hours, and the yield of methacrylic acid was calculated. The holding time T with stirring and the reaction result are shown in Table 2.

(Example 13)

To 400 parts of pure water, 100 parts of molybdenum trioxide, 3.4 parts of ammonium metavanadate, 9.4 parts of an 85% by mass aqueous phosphoric acid solution diluted with 6.0 parts of pure water, and 2.1 parts of copper (II) nitrate trihydrate dissolved in 4.5 parts of pure water were added. This aqueous slurry was heated from 25° C to 95° C while stirring, and held for 2 hours the liquid temperature at 95° C with stirring, to obtain an aqueous slurry (S1). Further, while holding the liquid temperature at 95° C with stirring, 13.5 parts of cesium nitrate dissolved in 28.3 parts of pure water and 40.0 parts of 30% by mass aqueous ammonia were added dropwise and stirred to precipitate a cesium salt and an ammonium salt of heteropolyacid. The precipitated heteropolyacid salt had a Dawson-type structure. The resulting aqueous slurry (S2) was cooled with stirring from 95° C to 40° C. At that time, the time until the aqueous slurry (S2) becomes 40° C from less than 50° C was 0.4 hours. Subsequently, the aqueous slurry (S2) was held at 40° C with stirring for 3.0 hours. Thereafter, the aqueous slurry (S3) after holding with stirring was spray-dried. The obtained dried product was subjected to pressing, pulverized, and calcined at 380° C for 5 hours under air flow. The compositions of the resulting catalysts excluding oxygen were $P_{1.4}Mo_{12}V_{0.5}Cu_{0.15}Cs_{1.2}$.

For the catalyst, the yield of methacrylic acid was calculated in the same manner as in Example 1. The conditions for producing the catalyst and the reaction results are shown in Table 2.

[0040]

(Comparative Examples 1 and 2)

Each catalyst was produced in the same manner as in Example 1, except that the holding time after cooling the aqueous slurry (S2) from 95 ° C. to 40 ° C was changed to 1.0 hour and 2.0 hours, respectively, and the yields of methacrylic acid were calculated. Reaction results are given in Table 2.

[0041]

(Comparative Example 3)

A catalyst was produced in the same manner as in Example 1, except that the aqueous slurry (S2) was cooled from 95° C to 70° C and held at 70° C for 0.3 hours with stirring, and the yield of methacrylic acid was calculated. Reaction results are given in Table 2.

(Comparative Example 4)

A catalyst was produced in the same manner as in Example 1, except that the aqueous slurry (S2) was cooled from 95° C to 55° C and held at 55° C for 3.0 hours with stirring, and the yield of methacrylic acid was calculated. Reaction results are given in Table 2.

(Comparative Example 5)

A catalyst was produced in the same manner as in Example 13, except that the holding time after cooling the aqueous slurry (S2) from 95° C to 40° C was changed to 2.0 hours, and the yield of methacrylic acid was calculated. Evaluation results are given in Table 2.

(Comparative Example 6)

A catalyst was produced in the same manner as in Example 1, except that the slurry (S3) after holding with stirring was dried by evaporation-to-dryness, and the yield of methacrylic acid was calculated. Reaction results are given in Table 2.

(Comparative Example 7)

A catalyst was produced in the same manner as in Comparative Example 6, except that the holding time after cooling the aqueous slurry (S2) from 95° C to 40° C was changed to 2.0 hours, and the yield of methacrylic acid was calculated. Reaction results are given in Table 2.

(Comparative Example 8)

A catalyst was produced in the same manner as in Example 1, except that the slurry (S3) after holding with stirring was dried by vacuum concentration, and the yield of methacrylic acid was calculated. Reaction results are given in Table 2.

(Comparative Example 9)

A catalyst was produced in the same manner as in Comparative Example 8, except that the holding time after cooling the aqueous slurry (S2) from 95° C to 40° C was changed to 2.0 hours, and the yield of methacrylic acid was calculated. Reaction results are given in Table 2.

[0042]

Table 1

	Structure of heteropolyacid salt of Step (i)	Holding temperature R of aqueous slurry (S2) with stirring [°C]	Holding time T of aqueous slurry (S2) with stirring [Hour]	Drying method	Bulk density of dried product [kg/L]	Yield of methacrylic acid [%]
Example 1	Keggin-type	40	3.4	Spray-drying	1.38	27.7
Example 2	Keggin-type	40	5.3	Spray-drying	1.33	27.9
Example 3	Keggin-type	40	6.8	Spray-drying	1.36	28.8
Example 4	Keggin-type	40	7.4	Spray-drying	1.36	29.6
Example 5	Keggin-type	40	8.7	Spray-drying	1.34	30.5
Example 6	Keggin-type	40	9.4	Spray-drying	1.36	31.3
Example 7	Keggin-type	40	10.1	Spray-drying	1.32	32.1
Example 8	Keggin-type	40	10.6	Spray-drying	1.33	32.5
Example 9	Keggin-type	40	16.1	Spray-drying	1.30	32.9
Example 10	Keggin-type	40	22.5	Spray-drying	1.29	34.0

Table 2

	Structure of heteropolyacid salt of Step (i)	Holding temperature R of aqueous slurry (S2) with stirring [°C]	Holding time T of aqueous slurry (S2) with stirring [Hour]	Drying method	Yield of methacrylic acid [%]
Example 11	Keggin-type	20	3.5	Spray-drying	27.1
Example 12	Keggin-type	20	16.5	Spray-drying	29.8
Example 13	Dawson-type	40	3.4	Spray-drying	26.4
Comparative Example 1	Keggin-type	40	1.4	Spray-drying	24.7
Comparative Example 2	Keggin-type	40	2.4	Spray-drying	25.9
Comparative Example 3	Keggin-type	70	0.3	Spray-drying	14.0
Comparative Example 4	Keggin-type	55	3.0	Spray-drying	21.1
Comparative Example 5	Dawson-type	40	2.4	Spray-drying	25.8
Comparative Example 6	Keggin-type	40	3.4	Evaporation-to-dryness	27.6
Comparative Example 7	Keggin-type	40	2.4	Evaporation-to-dryness	27.4
Comparative Example 8	Keggin-type	40	3.4	Vacuum concentration	27.9
Comparative Example 9	Keggin-type	40	2.4	Vacuum concentration	27.7

As shown in Table 1, it was confirmed that the method for producing the catalyst of Examples 1 to 12 has a temperature and a time at which the aqueous slurry (S2) is held with stirring within the range of the present invention, and a catalyst having a high yield of methacrylic acid can be obtained. On the other hand, in Comparative Examples 1 and 2, in which the time for holding the aqueous slurry (S2) with stirring is outside the range of the present invention, catalysts having a yield of methacrylic acid lower than in Examples 1 to 12 were obtained. Comparative Example 3 in which both the temperature and time for holding the aqueous slurry with stirring are outside the scope of the present invention, and Comparative Example 4 in which the temperature for holding the aqueous slurry with stirring is outside the scope of the present invention, catalysts having a much lower yield of methacrylic acid were also obtained. Further, in Examples 1 and 9, temperature for holding the aqueous slurry (S2) with stirring is higher than 30° C, as compared with Examples 11 and 12 that are holding with stirring for the same degree of time, the yields of methacrylic acid resulted in high, respectively. In addition, Examples 1 to 8 in which the time for holding the aqueous slurry (S2) with stirring was less than 15 hours were superior from the viewpoint that the decrease in the bulk density of the catalyst was suppressed and that the catalyst can be continuously used for a long time as compared with Examples 9 and 10.

[0045]

When the heteropolyacid salt in step (i) has a Dawson type structure, Example 13 in which the temperature and time at which the aqueous slurry (S2) is held with stirring are within the scope of the present invention confirmed that a catalyst having a high yield of methacrylic acid is obtained. On the other hand, in Comparative Example 5 in which the time for holding the aqueous slurry (S2) with stirring was outside the range of the present invention, a catalyst having a lower yield of methacrylic acid was obtained as compared with Example 13.

On the other hand, in Comparative Examples 6 and 7 in which are dried by evaporation-to-dryness the aqueous slurry (S3) after holding with stirring, and in Comparative Examples 8 and 9 in which are dried by vacuum concentration, even if the temperature and time for holding the aqueous slurry (S2) with stirring are within

the scope of the present invention, the yields of methacrylic acid were hardly improved.

Note that, by esterifying the methacrylic acid obtained in the present examples, a methacrylic acid ester can be obtained.

[0046]

This application claims priority to Japanese Patent Application No. 2018-031564, filed February 26, 2018, the entire disclosure of which is incorporated herein by reference.

While the present invention has been described with reference to the embodiments and examples, the present invention is not limited to the above embodiments and examples. Various changes that can be understood by those skilled in the art within the scope of the present invention can be made in the configuration and details of the present invention.

INDUSTRIAL APPLICABILITY

[0047]

According to the present invention, it is possible to provide a catalyst for producing an α,β -unsaturated carboxylic acid capable of producing an α,β -unsaturated carboxylic acid in high yield from an α,β -unsaturated aldehyde, and is industrially useful.

CLAIMS

1. A method for producing a catalyst for producing an α,β -unsaturated carboxylic acid, which is used in producing an α,β -unsaturated carboxylic acid by catalytic oxidation of an α,β -unsaturated aldehyde in a gas phase with molecular oxygen,
wherein the method comprises:
 - (i) a step for obtaining an aqueous slurry (S2) comprising a heteropolyacid salt containing at least molybdenum and phosphorus;
 - (ii) a step for holding the aqueous slurry (S2) with stirring at less than 50° C for 2.5 to 24.5 hours to obtain an aqueous slurry (S3); and
 - (iii) a step for spray-drying the aqueous slurry (S3).
2. The method for producing a catalyst for producing an α,β -unsaturated carboxylic acid according to claim 1, wherein the heteropolyacid salt in step (i) is at least one selected from the group consisting of metal cation salts and ammonium salts.
3. The method for producing a catalyst for producing an α,β -unsaturated carboxylic acid according to claim 1 or 2, wherein in step (i), an aqueous slurry or aqueous solution (S1) containing at least molybdenum and phosphorus is held at 70 to 130° C and is mixed with a base-containing compound to obtain the aqueous slurry (S2).
4. The method for producing a catalyst for producing an α,β -unsaturated carboxylic acid according to any one of claims 1 to 3, wherein the heteropolyacid salt in step (i) has a Keggin-type structure.
5. The method for producing a catalyst for producing an α,β -unsaturated carboxylic acid according to any one of claims 1 to 4, wherein the holding of the aqueous slurry (S2) with stirring is carried out for 3.4 hours or more and less than 15 hours in the step (ii).

6. The method for producing a catalyst for producing an α,β -unsaturated carboxylic acid according to any one of claims 1 to 5, wherein the holding of the aqueous slurry (S2) with stirring is carried out at a temperature higher than 30° C and lower than 50° C in the step (ii).

7. The method for producing a catalyst for producing an α,β -unsaturated carboxylic acid according to any one of claims 1 to 6, wherein the catalyst has a composition represented by the following formula (1)



(In the above formula (1), P, Mo, V, Cu, NH_4 and O represent phosphorus, molybdenum, vanadium, copper, ammonium species and oxygen, respectively; A represents at least one element selected from the group consisting of antimony, bismuth, arsenic, germanium, zirconium, tellurium, silver, selenium, silicon, tungsten and boron; E represents at least one element selected from the group consisting of iron, zinc, chromium, magnesium, calcium, strontium, tantalum, cobalt, nickel, manganese, barium, titanium, tin, thallium, 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 and cesium; and a to i represent the molar proportions of each component, and when $b = 12$, $a = 0.5-3$, $c = 0.01-3$, $d = 0.01-2$, $e = 0-3$, $f = 0-3$, $g = 0.01-3$, $h = 0-30$, i is the molar ratio of oxygen required to satisfy the valence of each said component).

8. A method for producing an α,β -unsaturated carboxylic acid, wherein an α,β -unsaturated aldehyde is subjected to gas phase catalytic oxidation with molecular oxygen in the presence of a catalyst produced by the method according to any one of claims 1 to 7.

9. A method for producing an α,β -unsaturated carboxylic acid, wherein a catalyst is produced by the method according to any one of claims 1 to 7, and the catalyst is used to catalytically oxidize an α,β -unsaturated aldehyde with molecular oxygen in a gas phase.

10. A method for producing an α,β -unsaturated carboxylic acid ester, in which an α,β -unsaturated carboxylic acid produced by the method of claim 8 or 9 is esterified.

11. A method for producing an α,β -unsaturated carboxylic acid ester comprising producing an α,β -unsaturated carboxylic acid by the method according to claim 8 or 9, and esterifying the α,β -unsaturated carboxylic acid.