

Description

Title of Invention:

PRODUCTION METHOD FOR CATALYST, PRODUCTION METHOD FOR

5 UNSATURATED CARBOXYLIC ACID, PRODUCTION METHOD FOR UNSATURATED
ALDEHYDE AND UNSATURATED CARBOXYLIC ACID, AND PRODUCTION METHOD
FOR UNSATURATED CARBOXYLIC ACID ESTER

Technical Field

10 [0001]

The present invention relates to a production method for a catalyst, a production method for an unsaturated carboxylic acid, a production method for an unsaturated aldehyde and an unsaturated carboxylic acid, and a production method for an unsaturated carboxylic acid ester.

15 Background Art

[0002]

Numerous examinations have been made on a production method for a catalyst. In general, a catalyst is produced by preparing a raw material liquid such as an aqueous solution or an aqueous slurry containing elements constituting the catalyst, drying the raw material liquid, and
20 calcining the resultant.

[0003]

For the calcination described above, Patent Literatures 1 to 3 describe calcination using a gas containing ammonia or water vapor, Patent Literature 4 describes calcination using a non-oxidizing gas, and Patent Literature 5 describes calcination using a gas containing an oxygen-
25 containing organic compound. In addition, Patent Literature 6 describes a calcination method including a plurality of steps in which different gases and calcination temperatures are used. Moreover, Patent Literature 7 describes the flow rate of a gas to a catalyst precursor.

Citation List

30 Patent Literature

[0004]

Patent Literature 1: JP58-61833A

Patent Literature 2: JP58-67643A

Patent Literature 3: JP58-79545A

Patent Literature 4: JP59-66349A

Patent Literature 5: JP59-69148A

Patent Literature 6: JP2012-245432A

Patent Literature 7: JP2009-213969A

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Summary of Invention

Technical Problem

[0005]

10 However, when catalysts produced by any of methods described in Patent Literatures 1 to 7 are used for a reaction in which an unsaturated aldehyde is subjected to gas phase catalytic oxidation with molecular oxygen to produce an unsaturated carboxylic acid, or for a reaction in which at least one selected from the group consisting of propylene, isobutylene, primary butyl alcohol, tertiary butyl alcohol and methyl tertiary butyl ether is subjected to gas phase catalytic oxidation with molecular oxygen to produce an unsaturated aldehyde and an unsaturated
15 carboxylic acid corresponding thereto, there has been a problem that the selectivity for a target product is not sufficient. As such, it has been desired to develop a production method for a catalyst that can produce a target product with a higher selectivity. The present invention has been established in view of such circumstances, and an object thereof is to provide a catalyst that can produce a target product with a high selectivity.

20

Solution to Problem

[0006]

The problem described above is solved by the following [1] to [16] according to the present invention.

25 [0007]

[1] A production method for a catalyst containing at least molybdenum and phosphorus that is used when an unsaturated aldehyde is subjected to gas phase catalytic oxidation with molecular oxygen to produce an unsaturated carboxylic acid, the production method including: a step of calcining a catalyst precursor containing a nitrogen-containing component
30 while exposing the catalyst precursor to a pressure above the atmospheric pressure.

[0008]

[2] A production method for a catalyst containing at least molybdenum and bismuth that is used when at least one selected from the group consisting of propylene, isobutylene, primary butyl alcohol, tertiary butyl alcohol and methyl tertiary butyl ether is subjected to gas phase

catalytic oxidation with molecular oxygen to produce an unsaturated aldehyde and an unsaturated carboxylic acid corresponding thereto, the production method including: a step of calcining a catalyst precursor containing a nitrogen-containing component while exposing the catalyst precursor to a pressure above the atmospheric pressure.

5 [0009]

[3] The production method for a catalyst according to [1] or [2], wherein the unsaturated aldehyde is acrolein or methacrolein.

[0010]

10 [4] The production method for a catalyst according to any of [1] to [3], wherein the calcination is carried out under a flow of at least one gas selected from an oxygen-containing gas and an inert gas when the catalyst precursor is calcined.

[0011]

[5] The production method for a catalyst according to any of [1] to [4], wherein the pressure is 10 kPa (G) or more and 100 kPa (G) or less.

15 [0012]

[6] The production method for a catalyst according to [5], wherein the pressure is 20 kPa (G) or more and 80 kPa (G) or less.

[0013]

20 [7] The production method for a catalyst according to any of [1] to [6], wherein a highest value of the temperature during the calcination is 300°C or higher and 700°C or lower.

[0014]

[8] The production method for a catalyst according to [7], wherein a highest value of the temperature during the calcination is 350°C or higher and 400°C or lower.

[0015]

25 [9] The production method for a catalyst according to any of [1] to [8], wherein the nitrogen-containing component is at least one selected from the group consisting of an ammonium species and a nitric species.

[0016]

30 [10] The production method for a catalyst according to [1], wherein the catalyst precursor includes a heteropolyacid structure.

[0017]

[11] The production method for a catalyst according to [10], wherein the heteropolyacid structure is a Keggin-type heteropolyacid structure.

[12] A production method for an unsaturated carboxylic acid, wherein an unsaturated

aldehyde is subjected to gas phase catalytic oxidation with molecular oxygen in the presence of a catalyst produced by the method according to [1] to produce an unsaturated carboxylic acid.

[0018]

5 [13] A production method for an unsaturated carboxylic acid, wherein a catalyst is produced by the method according to [1], and an unsaturated aldehyde is subjected to gas phase catalytic oxidation with molecular oxygen in the presence of the catalyst to produce an unsaturated carboxylic acid.

10 [14] A production method for an unsaturated aldehyde and an unsaturated carboxylic acid, wherein at least one selected from the group consisting of propylene, isobutylene, primary butyl alcohol, tertiary butyl alcohol and methyl tertiary butyl ether is subjected to gas phase catalytic oxidation with molecular oxygen in the presence of a catalyst produced by the method according to [2] to produce an unsaturated aldehyde and an unsaturated carboxylic acid corresponding thereto.

[0019]

15 [15] A production method for an unsaturated aldehyde and an unsaturated carboxylic acid, wherein a catalyst is produced by the method according to [2], and at least one selected from the group consisting of propylene, isobutylene, primary butyl alcohol, tertiary butyl alcohol and methyl tertiary butyl ether is subjected to gas phase catalytic oxidation with molecular oxygen in the presence of the catalyst to produce an unsaturated aldehyde and an unsaturated carboxylic acid
20 corresponding thereto.

[0020]

[16] A production method for an unsaturated carboxylic acid ester, wherein an unsaturated carboxylic acid produced by the method according to any of [12] to [15] is esterified.

25 Advantageous Effect of Invention

[0021]

According to the present invention, a catalyst that can produce a target product with a high selectivity can be provided.

30 Description of Embodiments

[0022]

[Production Method for Catalyst]

The first embodiment of a production method for a catalyst according to the present invention is a production method for a catalyst containing at least molybdenum and phosphorus

that is used when an unsaturated aldehyde is subjected to gas phase catalytic oxidation with molecular oxygen to produce an unsaturated carboxylic acid. Such a method includes a step of calcining a catalyst precursor containing a nitrogen-containing component while exposing the catalyst precursor to a pressure above the atmospheric pressure.

5 [0023]

In addition, the second embodiment of a production method for a catalyst according to the present invention is a production method for a catalyst containing at least molybdenum and bismuth that is used when at least one selected from the group consisting of propylene, isobutylene, primary butyl alcohol, tertiary butyl alcohol and methyl tertiary butyl ether is subjected to gas phase catalytic oxidation with molecular oxygen to produce an unsaturated aldehyde and an unsaturated carboxylic acid corresponding thereto. Such a method includes a step of calcining a catalyst precursor containing a nitrogen-containing component while exposing the catalyst precursor to a pressure above the atmospheric pressure.

[0024]

15 In the method according to the present invention, the pressure during calcination of a catalyst precursor is focused, and a catalyst that can produce a target product with a high selectivity can be obtained by calcining a catalyst precursor containing a nitrogen-containing component while exposing the catalyst precursor to a pressure above the atmospheric pressure. The reason for this can be deduced as follows. That is, the structure of the catalyst precursor is changed in the course of the nitrogen-containing component being eliminated during the calcination, and a catalytic site that is preferable for a target reaction is formed. Upon this, if the catalyst precursor is exposed to a pressure higher than the atmospheric pressure, the elimination of the nitrogen-containing component is suppressed. As a result, structural change of the catalyst occurs at a slower speed compared to the case where the calcination is carried out at a pressure lower than or equal to the atmospheric pressure, and it is assumed that a more homogeneous active-site structure is formed on the surface of the catalyst. Note that detailed examinations have not been made on the effects of the pressure during calcination in the related art.

[0025]

30 The method according to the present invention is used for production of a catalyst containing at least molybdenum and phosphorus that is used when an unsaturated aldehyde is subjected to gas phase catalytic oxidation with molecular oxygen to produce an unsaturated carboxylic acid (hereinafter, also referred to as a catalyst for producing an unsaturated carboxylic acid). By conducting a reaction using the above catalyst, an unsaturated carboxylic acid can be produced with a higher selectivity. It is preferable that the unsaturated aldehyde be acrolein or

methacrolein because acrylic acid or methacrylic acid can be produced with a higher selectivity. In addition, it is preferable that the catalyst include a heteropolyacid structure, in particular, a Keggin-type heteropolyacid structure because an unsaturated carboxylic acid can be produced with a higher selectivity.

5 [0026]

In addition, the method according to the present invention is used for production of a catalyst containing at least molybdenum and bismuth that is used when at least one selected from the group consisting of propylene, isobutylene, primary butyl alcohol, tertiary butyl alcohol and methyl tertiary butyl ether is subjected to gas phase catalytic oxidation with molecular oxygen to
10 produce an unsaturated aldehyde and an unsaturated carboxylic acid corresponding thereto (hereinafter, also referred to as a catalyst for producing an unsaturated aldehyde and an unsaturated carboxylic acid). By conducting a reaction using the above catalyst, an unsaturated aldehyde and an unsaturated carboxylic acid can be produced with a higher selectivity. It is preferable that the unsaturated aldehyde be acrolein or methacrolein and the unsaturated carboxylic acid be acrylic
15 acid or methacrylic acid from the viewpoint of selectivity.

[0027]

The composition of a catalyst obtained by the method according to the present invention is not particularly limited, and when the catalyst is a catalyst for producing an unsaturated carboxylic acid described above, the catalyst preferably has a composition shown by the following
20 formula (1) from the viewpoint of being capable of producing an unsaturated carboxylic acid with a higher selectivity.

[0028]

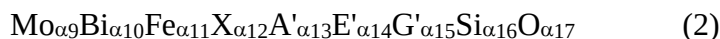


In the formula (1), P, Mo, V, Cu and O are symbols of elements indicating phosphorus,
25 molybdenum, vanadium, copper and oxygen, respectively. A indicates at least one element selected from the group consisting of antimony, bismuth, arsenic, germanium, zirconium, tellurium, silver, selenium, silicon, tungsten and boron. E indicates at least one element selected from the group consisting of potassium, rubidium, cesium, thallium, magnesium and barium. G indicates at least one element selected from the group consisting of iron, zinc, chromium, calcium, strontium,
30 tantalum, cobalt, nickel, manganese, titanium, tin, lead, niobium, indium, sulfur, palladium, gallium, cerium and lanthanum. $\alpha 1$ to $\alpha 8$ represent the atomic ratio of the respective elements, and when $\alpha 2$ is 12, $\alpha 1 = 0.5$ to 3, $\alpha 3 = 0.01$ to 3, $\alpha 4 = 0.01$ to 2, $\alpha 5 = 0$ to 3, preferably 0.01 to 3, $\alpha 6 = 0.01$ to 3, $\alpha 7 = 0$ to 4, and $\alpha 8$ is the atomic ratio of oxygen necessary for satisfying valences of the elements described above.

[0029]

In addition, when a catalyst obtained by the method according to the present invention is the catalyst for producing an unsaturated aldehyde and an unsaturated carboxylic acid described above, the catalyst preferably has a composition shown by the following formula (2) from the viewpoint of being capable of producing an unsaturated aldehyde and an unsaturated carboxylic acid with a higher selectivity.

[0030]



In the formula (2), Mo, Bi, Fe, Si and O are symbols of elements indicating molybdenum, bismuth, iron, silicon and oxygen, respectively. X indicates at least one element selected from the group consisting of cobalt and nickel. A' indicates at least one element selected from the group consisting of chromium, lead, manganese, calcium, magnesium, niobium, silver, barium, tin, tantalum and zinc. E' indicates at least one element selected from the group consisting of phosphorus, boron, sulfur, selenium, tellurium, cerium, tungsten, antimony and titanium. G' indicates at least one element selected from the group consisting of lithium, sodium, potassium, rubidium, cesium and thallium. $\alpha 9$ to $\alpha 17$ represent the atomic ratio of the respective elements, and when $\alpha 9$ is 12, $\alpha 10 = 0.01$ to 3, $\alpha 11 = 0.01$ to 5, $\alpha 12 = 1$ to 12, $\alpha 13 = 0$ to 8, $\alpha 14 = 0$ to 5, $\alpha 15 = 0.001$ to 2, $\alpha 16 = 0$ to 20, and $\alpha 17$ is the atomic ratio of oxygen necessary for satisfying valences of the elements described above.

[0031]

The production method for a catalyst according to the present invention is not particularly limited as long as it includes a step of calcining a catalyst precursor containing a nitrogen-containing component while exposing the catalyst precursor to a pressure above the atmospheric pressure (hereinafter, also referred to as a calcination step). However, such a method preferably includes a step of preparing a raw material liquid containing elements constituting the catalyst (hereinafter, also referred to as a raw material liquid preparation step), a step of drying the raw material liquid to obtain the catalyst precursor (hereinafter, also referred to as a drying step), and the calcination step from the viewpoint of being capable of obtaining a catalyst that can produce a target product with a higher selectivity. In addition, such a method may include a step of molding the catalyst precursor (hereinafter, also referred to as a molding step) between the drying step and the calcination step, as needed.

[0032]

(Raw Material Liquid Preparation step)

In the raw material liquid preparation step, the raw material liquid containing elements

constituting the catalyst is prepared. For producing the catalyst for producing an unsaturated carboxylic acid described above, the raw material liquid contains at least molybdenum and phosphorus. In addition, for producing the catalyst for producing an unsaturated aldehyde and an unsaturated carboxylic acid described above, the raw material liquid contains at least molybdenum and bismuth. When the raw material liquid contains these elements, a catalyst for producing an unsaturated carboxylic acid or a catalyst for producing an unsaturated aldehyde and an unsaturated carboxylic acid with a high selectivity for a target product can be produced. When the catalyst is a catalyst for producing an unsaturated carboxylic acid, the types and the ratio of elements constituting the catalyst may be, for example, the elements and the atomic ratio indicated in the formula (1) described above. In addition, when the catalyst is a catalyst for producing an unsaturated aldehyde and an unsaturated carboxylic acid, the types and the ratio of elements constituting the catalyst may be, for example, the elements and the atomic ratio indicated in the formula (2) described above.

[0033]

A preparation method for the raw material liquid is not particularly limited, and preferable is a method in which raw materials for the elements are charged in water, and the resultant mixture is heated to 30 to 100°C and stirred to prepare a slurry-like raw material liquid. The amount of water used is preferably 200 to 1000 parts by mass per 100 parts by mass of the total of raw materials for the elements.

[0034]

Raw materials for the elements are not particularly limited, and an oxide, a nitrate, a carbonate, an ammonium salt and the like of the elements can be appropriately selected and used. For example, for the raw material for molybdenum, molybdic acid, molybdenum trioxide, ammonium paramolybdate and the like can be used, and molybdic acid and molybdenum trioxide are preferable. For the raw material for phosphorus, orthophosphoric acid, phosphorus pentoxide, ammonium phosphate and the like can be used. For the raw material for vanadium, ammonium metavanadate, divanadium pentoxide and the like can be used. In addition, for the raw material for copper, copper nitrate, copper sulfate, copper carbonate and the like can be used. Moreover, for the raw material for bismuth, bismuth nitrate, bismuth oxide, bismuth acetate, bismuth hydroxide and the like can be used. One of these raw materials may be used singly, or two or more raw materials may be used in combination.

[0035]

In the method according to the present invention, the catalyst precursor contains a nitrogen-containing component, and therefore, the raw material liquid preferably contains the

nitrogen-containing component. Examples of the nitrogen-containing component include an ammonium species, a nitric species, nitrogen-containing heterocycles and the like, but preferable is at least one selected from the group consisting of an ammonium species and a nitric species from the viewpoint of selectivity of the target product. Herein, the ammonium species in the present invention is a generic name for ammonium included in ammonia (NH_3) and ammonium-containing compounds such as ammonium salts, which can be ammonium ion (NH_4^+). Examples of the ammonium-containing compound include, for example, ammonium carbonate, ammonium bicarbonate, ammonium nitrate, ammonium acetate, ammonium vanadate, ammonium salts of the catalyst-constituting elements, and the like. In addition, the nitric species in the present invention is a generic name for nitrogen oxide ions such as nitrate ion (NO_3^-) and nitrite ion (NO_2^-). Examples of the nitric species include, for example, a nitrate ion included in a nitrate salt of the catalyst-constituting elements. One of these nitric species may be used singly, or two or more nitric species may be used in combination. Note that it may be possible to have a nitrogen-containing component contained in the raw material liquid by using an ammonium salt or a nitrate salt of the elements as the raw materials for the elements.

[0036]

The preparation scale for the raw material liquid is not particularly limited, and the lower limit of the amount of the raw material for the principal element is preferably 100 g or more and more preferably 1 kg or more. In addition, the upper limit thereof is preferably 10 t or less and more preferably 1 t or less. When the scale is in such a range, a satisfactory raw material liquid can be stably prepared.

[0037]

(Drying Step)

In the drying step, the raw material liquid obtained in the raw material liquid preparation step described above is dried to obtain a catalyst precursor. A drying method of the raw material liquid is not particularly limited, and examples thereof include, for example, an evaporation drying method, a spray drying method, a drum drying method and a flush drying method. The type and model of a dryer used for the drying, the temperature and atmosphere during the drying, and the like are not particularly limited, and for example, mention may be made of drying conditions in an air atmosphere at 100 to 180°C for 0.1 to 20 hours. By changing drying conditions, physical properties such as flowability and moldability of the catalyst precursor can be controlled, and therefore, it is preferable to set conditions depending on the purpose.

[0038]

When the method according to the present invention is used for production of the catalyst

for producing an unsaturated carboxylic acid described above, a catalyst precursor to be obtained preferably includes a heteropolyacid structure and more preferably includes a Keggin-type heteropolyacid structure from the viewpoint of being capable of producing an unsaturated carboxylic acid with a higher selectivity. Note that whether the catalyst precursor includes a heteropolyacid structure (a Keggin-type heteropolyacid structure) or not can be confirmed by measuring the catalyst precursor with infrared absorption analysis. For example, when the catalyst precursor includes a Keggin-type heteropolyacid structure, the infrared absorption spectrum to be obtained has characteristic peaks in the vicinity of 1060, 960, 870 and 780 cm^{-1} .

[0039]

The amount of the nitrogen-containing component contained in the catalyst precursor to be obtained is not particularly limited, and it may be, for example, 0.5 to 7.0% by mass.

[0040]

(Molding Step)

In the molding step, the catalyst precursor obtained in the drying step described above is molded. A molding method is not particularly limited, and known dry and wet molding methods can be applied. For example, examples thereof include tablet molding, press molding, extrusion molding and granulation molding. The shape of the molded article is not particularly limited, either, and examples of the shape include, for example, cylindrical, ring-like and spherical shapes. In addition, upon the molding, it is preferable to mold the catalyst precursor alone without adding a carrier or the like to the catalyst precursor, but known additives, such as graphite or talc, may be added, as needed.

[0041]

(Calcination Step)

In the calcination step, the obtained catalyst precursor containing a nitrogen-containing component is calcined while exposing the catalyst precursor to a pressure above the atmospheric pressure. The pressure to which the catalyst precursor is exposed is preferably 10 kPa (G) or more, more preferably 20 kPa (G) or more, and further preferably 30 kPa (G) or more. In addition, such a pressure is preferably 100 kPa (G) or less, more preferably 80 kPa (G) or less, and further preferably 70 kPa (G) or less. When the pressure is 10 kPa (G) or more, elimination of the nitrogen-containing component is suppressed and a more homogeneous active-site structure is formed on the surface of the catalyst. In addition, when the pressure is 100 kPa (G) or less, the elimination of the nitrogen-containing component from the catalyst precursor is not hindered unduly, and decline in the reaction speed of the catalyst can be suppressed. Note that "kPa (G)" indicates a gauge pressure, and the actual pressure is obtained by summing up the atmospheric

pressure and a gauge pressure.

[0042]

Note that the pressure described above is a pressure from a temperature elevation process to a constant temperature-retaining process in the calcination step. In addition, the value of such a pressure is, when the calcination is carried out in a vessel with no spatial distribution of the pressure, a value measured at one arbitrary point in the vessel, and when the calcination is carried out in a system with spatial distribution of the pressure, such as a tubular calcining vessel under a flow of a gas, the value of such a pressure is the lowest value inside the system, such as a pressure at the outlet of a calcination gas. Moreover, inside of the system here means the range from the inlet of the calcination gas to the outlet of the calcination gas in the calcining vessel. There is no particular limitation on a method of measuring the pressure inside the system, and for example, the measurement can be carried out by installing a pressure gauge at a position upstream the outlet of the calcination gas and as close as possible to the outlet of the calcination gas. In addition, there is no particular limitation on a method of increasing the pressure described above, and when the calcination is carried out under a flow of a gas as mentioned later, this can be achieved by, for example, methods in which a piping at the outlet of the gas is extended, a pressure control valve is installed at the outlet of the gas and the valve is narrowed, or the outlet of the gas is connected to a trap tank filled with water or the like.

[0043]

There is no particular limitation on the type of an atmosphere gas at the time of calcining the catalyst precursor, and an oxygen-containing gas such as air or an inert gas is preferable. The inert gas here refers to a gas that does not decrease the catalytic activity, and examples thereof include nitrogen, carbon dioxide gas, helium and argon. As the gas described above, air, nitrogen, a mixed gas of oxygen and air, or a mixed gas thereof is more preferable, and air is further preferable. In addition, the gas described above may include water vapor. The water vapor is preferably included in an amount of 0.01 to 5% by volume based on the entire gas that is allowed to flow, and in particular, it is more preferable that the lower limit be 0.05% by volume or more and the upper limit be 2% by volume or less. There is no particular limitation on how to supply the atmosphere gas at the time of the calcination, and the calcination may be carried out after filling the inside of a calcining vessel with the atmosphere gas and sealing the vessel, or the calcination may be carried out under a flow of the gas while constantly supplying the atmosphere gas to the inside of the calcining vessel. However, it is preferable that the calcination be carried out under a flow of the gas from the viewpoint of catalytic activity.

[0044]

The lower limit of the highest value of temperature during the calcination described above is preferably 300°C or higher, more preferably 320°C or higher, further preferably 350°C or higher, and particularly preferably 370°C or higher. In addition, the upper limit of the highest value of temperature is preferably 700°C or lower, more preferably 450°C or lower, further preferably 400°C or lower, and particularly preferably 390°C or lower. When the calcination temperature is 300°C or higher, elimination of the nitrogen-containing component is promoted, and when the calcination temperature is 700°C or lower, thermal decomposition of the catalyst or decline of the specific surface area due to sintering can be suppressed. Here, the highest value of temperature described above refers to the highest temperature at a part among the internal wall surface of the calcining vessel that is in contact with the catalyst precursor. A measuring method for temperature is not particularly limited, and a method of using a thermocouple is preferable.

[0045]

The residual amount of the nitrogen-containing component in the catalyst to be obtained may be preferably in the range of, for example, 0.001 to 1 mmol/g based on the unit mass of the catalyst although it depends on how to use the catalyst and the like.

[0046]

There is no particular limitation on the shape of the calcining vessel, and it may be in the form of a box or tubular. However, it is particularly preferable to use a tubular calcining vessel with a cross section of 2 to 100 cm². When the cross section is 2 cm² or more, industrial productivity is improved. In addition, when the cross section is 100 cm² or less, temperature control becomes easy and occurrence of a hot spot can be suppressed.

[0047]

[Production Method for Unsaturated Carboxylic Acid]

In the presence of a catalyst produced by the method according to the present invention, an unsaturated aldehyde is subjected to gas phase catalytic oxidation with molecular oxygen. That is, the production method for an unsaturated carboxylic acid according to the present invention includes a step of producing a catalyst by the method according to the present invention, and a step of subjecting an unsaturated aldehyde to gas phase catalytic oxidation with molecular oxygen in the presence of the catalyst. By using a catalyst produced by the method according to the present invention, an unsaturated carboxylic acid can be produced with a higher selectivity compared to a conventional manner. For the unsaturated aldehyde, acrolein or methacrolein is preferable, and methacrolein is more preferable. Hereinafter, the case where methacrolein is used as the unsaturated aldehyde will be described. In such a method, for example, methacrolein is subjected to gas phase catalytic oxidation with molecular oxygen by bringing a raw material gas

including methacrolein and molecular oxygen into contact with the catalyst, and methacrylic acid is obtained.

[0048]

There is no limitation on the concentration of the raw material compound in the raw material gas and an arbitrary concentration can be set. However, it is preferably 1 to 20% by volume, and it is more preferable that the lower limit be 3% by volume or more and the upper limit be 10% by volume or less. The concentration of molecular oxygen in the raw material gas is preferably 0.5 to 4.0 mol per mol of the raw material compound, and in particular, it is more preferable that the lower limit be 1.0 mol or more and the upper limit be 3.0 mol or less. In addition, to the raw material gas, an inert gas such as nitrogen and carbon dioxide gas may be added for dilution, or water vapor may be added. The reaction pressure can be set within the range from the atmospheric pressure to several hundred kPa (G). The reaction temperature is preferably 230 to 450°C from the viewpoint of the yield of a target product, and in particular, it is more preferable that the lower limit be 250°C or higher and the upper limit be 400°C or lower.

[0049]

[Production Method for Unsaturated Aldehyde and Unsaturated Carboxylic Acid]

In the presence of a catalyst produced by the method according to the present invention, at least one selected from the group consisting of propylene, isobutylene, primary butyl alcohol, tertiary butyl alcohol and methyl tertiary butyl ether is subjected to gas phase catalytic oxidation with molecular oxygen. That is, the production method for an unsaturated aldehyde and an unsaturated carboxylic acid according to the present invention includes a step of producing a catalyst by the method according to the present invention, and a step of subjecting at least one selected from the group consisting of propylene, isobutylene, primary butyl alcohol, tertiary butyl alcohol and methyl tertiary butyl ether to gas phase catalytic oxidation with molecular oxygen in the presence of the catalyst. By using a catalyst produced by the method according to the present invention, an unsaturated aldehyde and an unsaturated carboxylic acid can be produced with a higher selectivity compared to a conventional manner. For the unsaturated aldehyde, acrolein or methacrolein is preferable, and methacrolein is more preferable. For the unsaturated carboxylic acid, acrylic acid or methacrylic acid is preferable, and methacrylic acid is more preferable. Conditions of the gas phase catalytic oxidation reaction can be the same as those in the production method for an unsaturated carboxylic acid.

[0050]

[Production Method for Unsaturated Carboxylic Acid Ester]

In a production method for an unsaturated carboxylic acid ester according to the present

invention, an unsaturated carboxylic acid obtained by the method according to the present invention is esterified. According to such a method, by using an unsaturated carboxylic acid obtained by subjecting an unsaturated aldehyde to gas phase catalytic oxidation or by subjecting at least one selected from the group consisting of propylene, isobutylene, primary butyl alcohol, tertiary butyl alcohol and methyl tertiary butyl ether to gas phase catalytic oxidation, an unsaturated carboxylic acid ester can be obtained. Examples of the alcohol that is allowed to react with the unsaturated carboxylic acid include methanol, ethanol, isopropanol, n-butanol and isobutanol. Examples of the unsaturated carboxylic acid ester to be obtained include, for example, methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, and butyl (meth)acrylate. The reaction can be carried out in the presence of an acid catalyst such as a sulfonic acid type cation exchange resin. The reaction temperature is preferably 50 to 200°C.

Examples

[0051]

Hereinafter, the present invention will be described in detail with reference to Examples and Comparative Examples, but the present invention is not limited to these Examples. "Part(s)" in Examples and Comparative Examples means a part by mass. The molar ratio in the catalyst composition was calculated by analyzing a component obtained by dissolving a catalyst in aqueous ammonia with ICP emission spectrometry.

[0052]

Analysis of a raw material gas and a product was carried out using gas chromatography in the production of methacrylic acid. From the results of gas chromatography, the reaction rate of methacrolein and the selectivity for methacrylic acid were determined in accordance with the following formulas.

[0053]

$$\text{Reaction rate of methacrolein (\%)} = (R/F) \times 100$$

$$\text{Selectivity for methacrylic acid (\%)} = (P/R) \times 100$$

In the above formulas, F is the mol number of methacrolein that was supplied per unit time, R is the mol number of methacrolein that reacted per unit time, and P is the mol number of methacrylic acid that was generated per unit time.

[0054]

Note that the selectivity for methacrylic acid varies depending on the reaction rate of methacrolein. As such, it is preferable to compare the selectivity for methacrylic acid in the gas phase catalytic oxidation reaction using each catalyst, matching the reaction rate of methacrolein

at the same value. Accordingly, in the following Examples and Comparative Examples, results are shown, matching the reaction rate of methacrolein at approximately 40% by changing the contact time through appropriately adjusting the amount of the catalyst used for the reaction under a constant flow rate of the reaction gas.

5 [0055]

[Example 1]

(1) Raw Material Liquid Preparation step

To 400 parts of pure water, 100 parts of molybdenum trioxide, 4.06 parts of ammonium metavanadate, 6.67 parts of 85 mass% phosphoric acid, 0.84 part of diantimony trioxide and 2.80
10 parts of copper nitrate were added. The resultant mixture was stirred to obtain a slurry, and the obtained slurry was heated at 90°C for 3 hours. In the state of retaining the slurry at 90°C, a solution obtained by dissolving 11.3 parts of cesium carbonate in 40.3 parts of pure water was added and retained for 30 minutes. Next, a solution obtained by dissolving 8.34 parts of ammonium carbonate in 37.5 parts of pure water was added. Then, the resultant mixture was
15 retained at 90°C for 30 minutes to obtain a raw material liquid.

[0056]

(2) Drying Step

The obtained raw material liquid was heated at 101°C, and evaporated to dryness under stirring. Thereafter, the obtained solid was dried at 90°C for 16 hours to obtain a catalyst
20 precursor. The obtained catalyst precursor included a Keggin-type heteropolyacid structure. In addition, the composition of the catalyst precursor excluding oxygen was $\text{Mo}_{12}\text{V}_{0.6}\text{P}_{1.0}\text{Sb}_{0.1}\text{Cu}_{0.2}\text{Cs}_{1.2}(\text{NH}_4)_{3.0}$.

[0057]

(3) Molding Step

25 The obtained catalyst precursor was molded into a ring-like shape with an outer diameter of 5 mm, an inner diameter of 2 mm and a length of 5 mm, using a tablet molding machine.

[0058]

(4) Calcination Step

A molded article of the obtained catalyst precursor was filled in a stainless pipe with an
30 inner diameter of 27.5 mm and a length of 6 m, and the catalyst precursor was calcined at 380°C under a flow of air at a space velocity of 370 h^{-1} to obtain a catalyst. Upon this, the outlet of the calcination gas was connected to a trap tank for an exhaust gas component filled with water to set the pressure during the calcination step at 64 kPa (G). In addition, the retention time at 380°C during the calcination was set to be 16 hours. In the calcination, the highest value of temperature

was 380°C. From the obtained catalyst, 0.001 to 1.0 mmol/g of a nitrogen-containing component was detected per unit mass of the catalyst.

[0059]

The obtained catalyst was filled into a reaction tube and a reaction gas was introduced.

- 5 Production of methacrylic acid was carried out by gas phase catalytic oxidation under the following reaction conditions. Results are shown in Table 1.

[0060]

(Reaction Conditions)

- 10 Reaction gas: a mixed gas composed of 4% by volume of methacrolein, 10% by volume of oxygen, 15% by volume of water vapor, and 71% by volume of nitrogen

Reaction temperature: 310°C

Reaction pressure: 101 kPa (G)

Contact time: 1.8 seconds.

[0061]

- 15 [Comparative Example 1]

- A catalyst was produced in the same manner as in Example 1 except that the pressure during the calcination step was set to be 0 kPa (G) by reducing the amount of water in the trap tank for an exhaust gas component connected to the outlet of the calcination gas compared to Example 1 and that the catalyst precursor was calcined at 380°C for 12 hours. In addition, the
20 obtained catalyst was used to carry out the reaction in the same manner as in Example 1 except that the contact time was changed to 1.5 seconds. Results are shown in Table 1.

[0062]

[Comparative Example 2]

- 25 A catalyst was produced in the same manner as in Example 1 except that the pressure during the calcination step was set to be 0 kPa (G) by reducing the amount of water in the trap tank for an exhaust gas component connected to the outlet of the calcination gas compared to Example 1. In addition, the obtained catalyst was used to carry out the reaction in the same manner as in Example 1 except that the contact time was changed to 1.2 seconds. Results are shown in Table 1.

- 30 [0063]

[Example 2]

A catalyst was produced in the same manner as in Example 1 except that the pressure during the calcination step was set to be 64 kPa (G) by installing a pressure control valve at the outlet of the calcination gas and that the catalyst precursor was calcined at 382°C for 16 hours.

In addition, the obtained catalyst was used to carry out the reaction in the same manner as in Example 1 except that the contact time was changed to 1.7 seconds. Results are shown in Table 1.

[0064]

5 [Example 3]

A catalyst was produced in the same manner as in Example 1 except that the pressure during the calcination step was set to be 54 kPa (G) by reducing the amount of water in the trap tank for an exhaust gas component connected to the outlet of the calcination gas compared to Example 1 and that the catalyst precursor was calcined at 382°C for 14 hours. In addition, the
10 obtained catalyst was used to carry out the reaction in the same manner as in Example 1 except that the contact time was changed to 1.7 seconds. Results are shown in Table 1.

[0065]

[Example 4]

A catalyst was produced in the same manner as in Example 2 except that the pressure
15 during the calcination step was set to be 10 kPa (G) by a pressure control valve and that the catalyst precursor was calcined at 380°C for 16 hours. In addition, the obtained catalyst was used to carry out the reaction in the same manner as in Example 1 except that the contact time was changed to 1.4 seconds. Results are shown in Table 1.

[0066]

20 [Example 5]

A catalyst was produced in the same manner as in Example 4 except that the pressure during the calcination step was set to be 30 kPa (G) by a pressure control valve. In addition, the obtained catalyst was used to carry out the reaction in the same manner as in Example 1 except that the contact time was changed to 1.5 seconds. Results are shown in Table 1.

25

[0067]

[Table 1]

Examples and Comparative Examples	Conditions to which catalyst precursor molded article is exposed			Conversion rate of methacrolein [%]	Selectivity for methacrylic acid [%]
	Pressure [kPa (G)]	Temperature and retention time	Highest temperature [°C]		
Example 1	64	at 380°C for 16 hours	380	40.3	92.1
Comparative Example 1	0	at 380°C for 12 hours	380	39.1	89.6
Comparative Example 2	0	at 380°C for 16 hours	380	41.1	89.3
Example 2	64	at 382°C for 16 hours	382	40.5	91.9
Example 3	54	at 382°C for 14 hours	382	41.9	93.0
Example 4	10	at 380°C for 16 hours	380	41.0	89.9
Example 5	30	at 380°C for 16 hours	380	40.5	91.5

[0068]

As shown in Table 1, Examples 1 to 5 in which catalysts were produced by the method according to the present invention were capable of producing methacrylic acid with a higher selectivity compared to Comparative Examples 1 and 2.

Claims

[Claim 1]

5 A production method for a catalyst containing at least molybdenum and phosphorus that is used when an unsaturated aldehyde is subjected to gas phase catalytic oxidation with molecular oxygen to produce an unsaturated carboxylic acid, the production method comprising:

a step of calcining a catalyst precursor containing a nitrogen-containing component while exposing the catalyst precursor to a pressure above the atmospheric pressure.

[Claim 2]

10 A production method for a catalyst containing at least molybdenum and bismuth that is used when at least one selected from the group consisting of propylene, isobutylene, primary butyl alcohol, tertiary butyl alcohol and methyl tertiary butyl ether is subjected to gas phase catalytic oxidation with molecular oxygen to produce an unsaturated aldehyde and an unsaturated carboxylic acid corresponding thereto, the production method comprising:

15 a step of calcining a catalyst precursor containing a nitrogen-containing component while exposing the catalyst precursor to a pressure above the atmospheric pressure.

[Claim 3]

The production method for a catalyst according to claim 1 or 2, wherein the unsaturated aldehyde is acrolein or methacrolein.

20 [Claim 4]

The production method for a catalyst according to any one of claims 1 to 3, wherein the calcination is carried out under a flow of at least one gas selected from an oxygen-containing gas and an inert gas when the catalyst precursor is calcined.

[Claim 5]

25 The production method for a catalyst according to any one of claims 1 to 4, wherein the pressure is 10 kPa (G) or more and 100 kPa (G) or less.

[Claim 6]

The production method for a catalyst according to claim 5, wherein the pressure is 20 kPa (G) or more and 80 kPa (G) or less.

30 [Claim 7]

The production method for a catalyst according to any one of claims 1 to 6, wherein a highest value of the temperature during the calcination is 300°C or higher and 700°C or lower.

[Claim 8]

The production method for a catalyst according to claim 7, wherein a highest value of the

temperature during the calcination is 350°C or higher and 400°C or lower.

[Claim 9]

The production method for a catalyst according to any one of claims 1 to 8, wherein the nitrogen-containing component is at least one selected from an ammonium species and a nitric species.

[Claim 10]

The production method for a catalyst according to claim 1, wherein the catalyst precursor comprises a heteropolyacid structure.

[Claim 11]

The production method for a catalyst according to claim 10, wherein the heteropolyacid structure is a Keggin-type heteropolyacid structure.

[Claim 12]

A production method for an unsaturated carboxylic acid, wherein an unsaturated aldehyde is subjected to gas phase catalytic oxidation with molecular oxygen in the presence of a catalyst produced by the method according to claim 1 to produce an unsaturated carboxylic acid.

[Claim 13]

A production method for an unsaturated carboxylic acid, wherein a catalyst is produced by the method according to claim 1, and an unsaturated aldehyde is subjected to gas phase catalytic oxidation with molecular oxygen in the presence of the catalyst to produce an unsaturated carboxylic acid.

[Claim 14]

A production method for an unsaturated aldehyde and an unsaturated carboxylic acid, wherein at least one selected from the group consisting of propylene, isobutylene, primary butyl alcohol, tertiary butyl alcohol and methyl tertiary butyl ether is subjected to gas phase catalytic oxidation with molecular oxygen in the presence of a catalyst produced by the method according to claim 2 to produce an unsaturated aldehyde and an unsaturated carboxylic acid corresponding thereto.

[Claim 15]

A production method for an unsaturated aldehyde and an unsaturated carboxylic acid, wherein a catalyst is produced by the method according to claim 2, and at least one selected from the group consisting of propylene, isobutylene, primary butyl alcohol, tertiary butyl alcohol and methyl tertiary butyl ether is subjected to gas phase catalytic oxidation with molecular oxygen in the presence of the catalyst to produce an unsaturated aldehyde and an unsaturated carboxylic acid corresponding thereto.

[Claim 16]

A production method for an unsaturated carboxylic acid ester, wherein an unsaturated carboxylic acid produced by the method according to any one of claims 12 to 15 is esterified.