

DESCRIPTION

Title of Invention:

CATALYST FOR PRODUCTION OF METHACRYLIC ACID, CATALYST PRECURSOR FOR PRODUCTION OF METHACRYLIC ACID, METHOD FOR PRODUCING SAID CATALYST AND CATALYST PRECURSOR, METHOD FOR PRODUCING METHACRYLIC ACID, AND METHOD FOR PRODUCING METHACRYLATE ESTER

Technical Field

[0001]

The present invention relates to a methacrylic acid production catalyst, a methacrylic acid production catalyst precursor, production methods therefor, a method for producing methacrylic acid, and a method for producing a methacrylic acid ester.

Background Art

[0002]

As a methacrylic acid production catalyst (hereinafter, referred to as simply a "catalyst") for use in producing methacrylic acid by a gas-phase catalytic oxidation of methacrolein with molecular oxygen, for example, there is a heteropolyacid-based catalyst containing the molybdenum element and the phosphorus element. As the heteropolyacid-based catalyst, there are a proton-type heteropolyacid in which counter cations are protons and a heteropolyacid salt in which some of the protons are replaced with cations other than the proton (hereinafter, they are referred to as simply a "heteropolyacid" and a "heteropolyacid salt", and the two are collectively referred to as a "heteropolyacid (salt)" also).

[0003]

As for the structure of the heteropolyacid (salt), Non-Patent Literature 1 describes that the heteropolyacid (salt) has a heteroelement at its center (hereinafter, referred to as a center element) and has a mononuclear or dinuclear complex ion formed by sharing oxygen and condensing a condensed acid group, that a multiple kinds of condensation forms are known, and that phosphorus, arsenic, silicon, germanium, titanium or the like can be the center element.

[0004]

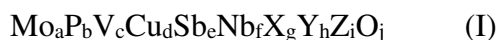
Further, Non-Patent Literature 2 describes that there are various structures such as a Keggin, a defective Keggin, a Dawson and a defective Dawson as the structure of the heteropolyacid (salt) and these structures can be selectively made by controlling the pH during

preparation process, and that the Keggin-type heteropolyacid (salt) can be prepared by controlling the pH during preparation process to 6 or lower.

[0005]

Patent Literature 1 discloses a catalyst represented by the following Formula (I), as a catalyst having a high selectivity of methacrylic acid when methacrylic acid is produced from methacrolein using the heteropolyacid-based catalyst.

[0006]



(in Formula (I), Mo, P, V, Cu, Sb, Nb and O represent molybdenum, phosphorus, vanadium, copper, antimony, niobium and oxygen, respectively, X represents at least one element selected from the group consisting of iron, cobalt, nickel and zinc, Y represents at least one element selected from the group consisting of magnesium, calcium, strontium, barium, titanium, chromium, tungsten, manganese, silver, boron, silicon, tin, lead, arsenic, bismuth, indium, sulfur, selenium, tellurium, lanthanum and cerium, and Z represents at least one element selected from the group consisting of sodium, potassium, rubidium, cesium and thallium. Here, a, b, c, d, e, f, g, h and i represent atomic proportions of the elements, and when $a = 12$, $0.1 \leq b \leq 3$, $0.01 \leq c \leq 3$, $0.01 \leq d \leq 2$, $0.01 \leq e \leq 3$, $0.01 \leq f \leq 3$, $0.01 \leq g \leq 3$, $0 \leq h \leq 3$, and $0.01 \leq i \leq 3$ are satisfied, and j is an atomic proportion of oxygen necessary to satisfy the atomic proportions of the components).

Citation List

Patent Literature

[0007]

Patent Literature 1: JP11-228487A

Non-Patent Literature

[0008]

Non-Patent Literature 1: Masayuki Otake, Takeru Onoda, Catalysts and Catalysis, vol. 18, No. 6 (1976)

Non-Patent Literature 2: Lege Pattersson, Ingerarb Andersson, Lars-Olof Ohman, Inorganic Chemistry, vol. 25, 4726-4733 (1986)

Summary of Invention

Technical Problem

[0009]

However, even when methacrylic acid is produced using the catalyst, the selectivity of methacrylic acid remains insufficient, and a further improvement is demanded from an industrial standpoint.

[0010]

The present invention has an object to provide a catalyst and a catalyst precursor that make it possible to produce methacrylic acid at a high selectivity by a gas-phase catalytic oxidation of methacrolein, production method therefor, a method for producing methacrylic acid that uses the catalyst, and a method for producing a methacrylic acid ester.

Solution to Problem

[0011]

The present invention relates to the following [1] to [11]:

[0012]

[1] A methacrylic acid production catalyst for use in producing methacrylic acid by a gas-phase catalytic oxidation of methacrolein with molecular oxygen, the catalyst having a composition represented by the following Formula (1).

[0013]



(in Formula (1), 'P', 'Mo', 'V', 'Nb', 'Cu', 'NH₄' and 'O' represent phosphorus, molybdenum, vanadium, niobium, copper, ammonium species and oxygen, respectively. 'A' represents at least one element selected from the group consisting of silicon, germanium, arsenic and antimony. 'E' represents at least one element selected from the group consisting of bismuth, zirconium, tellurium, silver, selenium, tungsten, boron, iron, zinc, chromium, magnesium, calcium, strontium, tantalum, cobalt, nickel, manganese, barium, titanium, tin, lead, indium, sulfur, palladium, gallium, cerium and lanthanum. 'G' represents at least one element selected from the group consisting of lithium, sodium, potassium, rubidium, cesium and thallium. 'a' to 'j' represent mole ratios of the components, and when $b = 12$, $0.5 \leq a + f \leq 2.1$, $0.01 \leq c + d \leq 3$, $0.5 \leq a$, $0 \leq c$, $0.01 \leq d \leq 3$, $0.005 \leq e \leq 3$, $0 \leq f$, $0 \leq g \leq 3$, $0.01 \leq h \leq 3$ and $0 \leq i \leq 5$ are satisfied, and 'j' is a mole ratio of oxygen necessary to satisfy valences of the components).

[0014]

[2] A methacrylic acid production catalyst precursor that is a precursor of a catalyst for use in producing methacrylic acid by a gas-phase catalytic oxidation of methacrolein with molecular oxygen, the methacrylic acid production catalyst precursor having a Keggin-type

structure and having a composition represented by the following Formula (2).

[0015]



(in Formula (2), 'P', 'Mo', 'V', 'Nb', 'Cu', 'NH₄' and 'O' represent phosphorus, molybdenum, vanadium, niobium, copper, ammonium species and oxygen, respectively. 'A' represents at least one element selected from the group consisting of silicon, germanium, arsenic and antimony. 'E' represents at least one element selected from the group consisting of bismuth, zirconium, tellurium, silver, selenium, tungsten, boron, iron, zinc, chromium, magnesium, calcium, strontium, tantalum, cobalt, nickel, manganese, barium, titanium, tin, lead, indium, sulfur, palladium, gallium, cerium and lanthanum. 'G' represents at least one element selected from the group consisting of lithium, sodium, potassium, rubidium, cesium and thallium. 'a' to 'j' represent mole ratios of the components, and when $b = 12$, $0.5 \leq a + f \leq 2.4$, $0.01 \leq c + d \leq 3$, $0.5 \leq a$, $0 \leq c$, $0.01 \leq d \leq 3$, $0.005 \leq e \leq 3$, $0 \leq f$, $0 \leq g \leq 3$, $0.01 \leq h \leq 3$ and $0.1 \leq i \leq 20$ are satisfied, and 'j' is a mole ratio of oxygen necessary to satisfy valences of the components).

[0016]

[3] The methacrylic acid production catalyst according to [1], in which in Formula (1), $0.35 \leq d / (c + d) \leq 1$ is satisfied.

[0017]

[4] The methacrylic acid production catalyst precursor according to [2], in which in Formula (2), $0.35 \leq d / (c + d) \leq 1$ is satisfied.

[0018]

[5] A method for producing the methacrylic acid production catalyst precursor according to [2] or [4], the method including:

(i) a step of preparing a slurry (I) or a solution (I) containing at least a source material of molybdenum;

(ii) a step of adding an ammonium compound to the slurry (I) or the solution (I) to prepare a slurry (II) containing an ammonium salt; and

(iii) a step of drying the slurry (II) to obtain the methacrylic acid production catalyst precursor having the Keggin-type structure, in which

in steps (i) and (ii), each pH of the slurry (I), the solution (I) and the slurry (II) is maintained in a range of 0.1 to 6.5.

[0019]

[6] A method for producing a methacrylic acid production catalyst, including a step of calcining the methacrylic acid production catalyst precursor produced by the method according

to [5].

[0020]

[7] A method for producing methacrylic acid, in which methacrylic acid is produced by a gas-phase catalytic oxidation of methacrolein with molecular oxygen using the methacrylic acid production catalyst according to [1] or [3].

[0021]

[8] A method for producing methacrylic acid, in which a methacrylic acid production catalyst is produced by the method according to [6], and methacrylic acid is produced by a gas-phase catalytic oxidation of methacrolein with molecular oxygen using the methacrylic acid production catalyst.

[0022]

[9] A method for producing methacrylic acid, in which methacrylic acid is produced by a gas-phase catalytic oxidation of methacrolein with molecular oxygen using the methacrylic acid production catalyst produced by the method according to [6].

[0023]

[10] A method for producing a methacrylic acid ester, in which the methacrylic acid produced by the method according to any one of [7] to [9] is esterified.

[0024]

[11] A method for producing a methacrylic acid ester, in which methacrylic acid is produced by the method according to any one of [7] to [9], and the methacrylic acid is esterified.

Advantageous Effects of Invention

[0025]

According to the present invention, it is possible to provide a catalyst and a catalyst precursor that make it possible to produce methacrylic acid at a high selectivity by a gas-phase catalytic oxidation of methacrolein, production methods therefor, a method for producing methacrylic acid that uses the catalyst, and a method for producing a methacrylic acid ester.

Description of Embodiments

[0026]

[Methacrylic Acid Production Catalyst]

A methacrylic acid production catalyst according to the present invention is used in the production of methacrylic acid by a gas-phase catalytic oxidation of methacrolein with molecular oxygen, and has a composition represented by the following Formula (1).

[0027]



In Formula (1), 'P', 'Mo', 'V', 'Nb', 'Cu', 'NH₄' and 'O' represent phosphorus, molybdenum, vanadium, niobium, copper, ammonium species and oxygen, respectively. 'A' represents at least one element selected from the group consisting of silicon, germanium, arsenic and antimony. 'E' represents at least one element selected from the group consisting of bismuth, zirconium, tellurium, silver, selenium, tungsten, boron, iron, zinc, chromium, magnesium, calcium, strontium, tantalum, cobalt, nickel, manganese, barium, titanium, tin, lead, indium, sulfur, palladium, gallium, cerium and lanthanum. 'G' represents at least one element selected from the group consisting of lithium, sodium, potassium, rubidium, cesium and thallium. 'a' to 'j' represent mole ratios of the components, and when $b = 12$, $0.5 \leq a + f \leq 2.1$, $0.01 \leq c + d \leq 3$, $0.5 \leq a$, $0 \leq c$, $0.01 \leq d \leq 3$, $0.005 \leq e \leq 3$, $0 \leq f$, $0 \leq g \leq 3$, $0.01 \leq h \leq 3$ and $0 \leq i \leq 5$ are satisfied, and 'j' is a mole ratio of oxygen necessary to satisfy valences of the components.

[0028]

In the present invention, the "ammonium species" is a generic term of ammonia (NH₃) that can become ammonium ion (NH₄⁺), and ammonium that is contained in ammonium-containing compounds such as ammonium salts.

[0029]

The mole ratios of the elements are values that are evaluated by analyzing components when the catalyst or the catalyst precursor is dissolved in an ammonia water, by an ICP atomic emission spectroscopy. Further, the mole ratio of the ammonium species is a value that is evaluated by analyzing the catalyst or the catalyst precursor by a Kjeldahl method.

[0030]

According to the present invention, the selectivity of methacrylic acid is increased by using the catalyst having the composition represented by Formula (1). Typically, after methacrolein is oxidized to become methacrylic acid, the oxidation reaction further continues, causing a successive oxidation reaction that generates carbon monoxide, carbon dioxide and the like. However, it is thought that the catalyst according to the present invention inhibits the successive oxidation reaction and thereby increases the selectivity of methacrylic acid.

[0031]

In the methacrylic acid production catalyst, when the mole ratios of the components fall outside the ranges specified by Formula (1), the selectivity of methacrylic acid as a target product decreases. In Formula (1), when $b = 12$, $a + f$, which is the total amount of phosphorus and 'A', satisfies $0.5 \leq a + f \leq 2.1$. Particularly, if $2.1 < a + f$, the selectivity of methacrylic acid

considerably decreases. The lower limit of $a + f$ is preferably 0.6 or more, more preferably 0.8 or more, further preferably 0.9 or more, and most preferably 1.3 or more. Further, the upper limit of $a + f$ is preferably 2.0 or less, more preferably 1.9 or less, and further preferably 1.8 or less. 'a' satisfies $0.5 \leq a$. The lower limit of 'a' is preferably 0.6 or more, and more preferably 0.7 or more. The upper limit of 'a' is preferably 1.9 or less, and more preferably 1.8 or less. 'f' satisfies $0 \leq f$. The lower limit of 'f' is preferably 0.01 or more, and more preferably 0.1 or more. The upper limit of 'f' is preferably 1.0 or less, and more preferably 0.9 or less.

[0032]

Further, $c + d$, which is the total amount of 'V' and 'Nb', satisfies $0.01 \leq c + d \leq 3$. Here, the catalyst contains at least 'Nb', and satisfies $0 \leq c$ and $0.01 \leq d \leq 3$. The lower limit of $c + d$ is preferably 0.1 or more, more preferably 0.15 or more, and further preferably 0.2 or more. Further, the upper limit of $c + d$ is preferably 2.5 or less, more preferably 2 or less, and further preferably 1 or less. The lower limit of 'd' is preferably 0.1 or more, more preferably 0.15 or more, and further preferably 0.2 or more. Further, the upper limit of 'd' is preferably 2.5 or less, more preferably 2 or less, and further preferably 1 or less. It is preferable that $d / (c + d)$ satisfies $0.35 \leq d / (c + d) \leq 1$. Thereby, the selectivity of methacrylic acid further increases. The lower limit of $d / (c + d)$ is more preferably 0.5 or more, further preferably 0.75 or more, and particularly preferably 0.9 or more.

[0033]

'e' satisfies $0.005 \leq e \leq 3$. Particularly, if $e < 0.005$, the reaction rate of methacrolein decreases. The lower limit of 'e' is preferably 0.01 or more, more preferably 0.03 or more, and further preferably 0.05 or more. Further, the upper limit of 'e' is preferably 2 or less, more preferably 1 or less, and further preferably 0.5 or less.

[0034]

'g' satisfies $0 \leq g \leq 3$. 'h' satisfies $0.01 \leq h \leq 3$. The lower limit of 'h' is preferably 0.1 or more, more preferably 0.3 or more, and further preferably 0.5 or more. Further, the upper limit of 'h' is preferably 2.5 or less, more preferably 2 or less, and further preferably 1.5 or less. 'i' satisfies $0 \leq i \leq 5$. The upper limit of 'i' is preferably 3 or less, and more preferably 2 or less.

[0035]

[Methacrylic Acid Production Catalyst Precursor]

A methacrylic acid production catalyst precursor (hereinafter, referred to as a catalyst precursor also) according to the present invention is a precursor of a catalyst for use in producing methacrylic acid by a gas-phase catalytic oxidation of methacrolein with molecular oxygen, has a Keggin-type structure, and has a composition represented by the following Formula (2).

[0036]



In Formula (2), 'P', 'Mo', 'V', 'Nb', 'Cu', 'NH₄' and 'O' represent phosphorus, molybdenum, vanadium, niobium, copper, ammonium species and oxygen, respectively. 'A' represents at least one element selected from the group consisting of silicon, germanium, arsenic and antimony. 'E' represents at least one element selected from the group consisting of bismuth, zirconium, tellurium, silver, selenium, tungsten, boron, iron, zinc, chromium, magnesium, calcium, strontium, tantalum, cobalt, nickel, manganese, barium, titanium, tin, lead, indium, sulfur, palladium, gallium, cerium and lanthanum. 'G' represents at least one element selected from the group consisting of lithium, sodium, potassium, rubidium, cesium and thallium. 'a' to 'j' represent mole ratios of the components, and when $b = 12$, $0.5 \leq a + f \leq 2.4$, $0.01 \leq c + d \leq 3$, $0.5 \leq a$, $0 \leq c$, $0.01 \leq d \leq 3$, $0.005 \leq e \leq 3$, $0 \leq f$, $0 \leq g \leq 3$, $0.01 \leq h \leq 3$ and $0.1 \leq i \leq 20$ are satisfied, and 'j' is a mole ratio of oxygen necessary to satisfy valences of the components.

[0037]

According to the present invention, the selectivity of methacrylic acid is increased by using a catalyst that is obtained from the catalyst precursor having the composition represented by Formula (2). Typically, after methacrolein is oxidized to become methacrylic acid, the oxidation reaction further continues, causing a successive oxidation reaction that generates carbon monoxide, carbon dioxide and the like. However, it is thought that the catalyst that is obtained from the catalyst precursor according to the present invention inhibits the successive oxidation reaction and thereby increases the selectivity of methacrylic acid.

[0038]

In the methacrylic acid production catalyst precursor, when the mole ratios of the components fall outside the ranges specified by Formula (2), the selectivity of methacrylic acid as the target product decreases. In Formula (2), when $b = 12$, $a + f$, which is the total amount of phosphorus and 'A', satisfies $0.5 \leq a + f \leq 2.4$. Particularly, if $2.4 < a + f$, the selectivity of methacrylic acid considerably decreases. The lower limit of $a + f$ is preferably 0.6 or more, more preferably 0.8 or more, further preferably 0.9 or more, and most preferably 1.3 or more. Further, the upper limit of $a + f$ is preferably 2.2 or less, more preferably 2.0 or less, and further preferably 1.8 or less. 'a' satisfies $0.5 \leq a$. The lower limit of 'a' is preferably 0.6 or more, and more preferably 0.7 or more. The upper limit of 'a' is preferably 1.9 or less, and more preferably 1.8 or less. 'f' satisfies $0 \leq f$. The lower limit of 'f' is preferably 0.01 or more, and more preferably 0.1 or more. The upper limit of 'f' is preferably 1.0 or less, and more preferably 0.9 or less.

[0039]

Further, $c + d$, which is the total amount of 'V' and 'Nb', satisfies $0.01 \leq c + d \leq 3$. Here, the catalyst precursor contains at least 'Nb', and satisfies $0 \leq c$ and $0.01 \leq d \leq 3$. The lower limit of $c + d$ is preferably 0.1 or more, more preferably 0.15 or more, and further preferably 0.2 or more. Further, the upper limit of $c + d$ is preferably 2.5 or less, more preferably 2 or less, and further preferably 1 or less. The lower limit of 'd' is preferably 0.1 or more, more preferably 0.15 or more, and further preferably 0.2 or more. Further, the upper limit of 'd' is preferably 2.5 or less, more preferably 2 or less, and further preferably 1 or less. It is preferable that $d / (c + d)$ satisfies $0.35 \leq d / (c + d) \leq 1$. Thereby, the selectivity of methacrylic acid further increases. The lower limit of $d / (c + d)$ is more preferably 0.5 or more, further preferably 0.75 or more, and particularly preferably 0.9 or more.

[0040]

'e' satisfies $0.005 \leq e \leq 3$. If $e < 0.005$, the reaction rate of methacrolein decreases. The lower limit of 'e' is preferably 0.01 or more, more preferably 0.03 or more, and further preferably 0.05 or more. Further, the upper limit of 'e' is preferably 2 or less, more preferably 1 or less, and further preferably 0.5 or less.

[0041]

'g' satisfies $0 \leq g \leq 3$. 'h' satisfies $0.01 \leq h \leq 3$. The lower limit of 'h' is preferably 0.1 or more, more preferably 0.3 or more, and further preferably 0.5 or more. Further, the upper limit of 'h' is preferably 2.5 or less, more preferably 2 or less, and further preferably 1.5 or less. 'i' satisfies $0.1 \leq i \leq 20$. The lower limit of 'i' is preferably 0.5 or more, and more preferably 1 or more. The upper limit of 'i' is preferably 18 or less, and more preferably 16 or less.

[0042]

The methacrylic acid production catalyst precursor according to the present invention has a Keggin-type structure. Thereby, a high activity is exhibited when methacrylic acid is produced by the gas-phase catalytic oxidation of methacrolein with molecular oxygen. The structure of the catalyst precursor can be judged by an infrared absorption analysis measurement. In the case where the catalyst precursor has the Keggin-type structure, the infrared absorption spectrum obtained has specific peaks around 1060, 960, 870 and 780 cm^{-1} .

[0043]

In the case where the methacrylic acid production catalyst according to the present invention has a composition represented by the following Formula (3), it is preferable that the following atomic ratios are satisfied.

[0044]



In Formula (3), 'P', 'Mo', 'V', 'Nb', 'Cu', 'Sb' and 'O' represent phosphorus, molybdenum, vanadium, niobium, copper, antimony and oxygen, respectively. 'X' represents at least one element selected from the group consisting of silicon, titanium, germanium, arsenic, tellurium and selenium. 'Z' represents at least one element selected from the group consisting of potassium, rubidium and cesium. 'a' to 'h' represent atomic ratios of the elements, $0.5 \leq a \leq 3$, $0.01 \leq c + d \leq 3$, $0.01 \leq d \leq 3$, $0.01 \leq e \leq 2$, $0 \leq f < 0.01$, $0.01 \leq g \leq 3$ and $0.01 \leq h \leq 3$ are satisfied, and 'i' is an atomic ratio of oxygen necessary to satisfy valences of the elements.

[0045]

In Formula (3), when $b = 12$, a satisfies $0.5 \leq a \leq 3$, should preferably satisfy $0.6 \leq a \leq 2.5$, should more preferably satisfy $0.8 \leq a \leq 2$, and should further preferably satisfy $0.9 \leq a \leq 1.3$. $c + d$ satisfies $0.01 \leq c + d \leq 3$, should preferably satisfy $0.1 \leq c + d \leq 2.5$, should more preferably satisfy $0.15 \leq c + d \leq 2$, and should further preferably satisfy $0.2 \leq c + d \leq 1$. d satisfies $0.01 \leq d \leq 3$, should preferably satisfy $0.1 \leq d \leq 2.5$, should more preferably satisfy $0.15 \leq d \leq 2$, and should further preferably satisfy $0.2 \leq d \leq 1$. 'e' satisfies $0.01 \leq e \leq 2$, should preferably satisfy $0.03 \leq e \leq 1.5$, should more preferably satisfy $0.04 \leq e \leq 1$, and should further preferably satisfy $0.05 \leq e \leq 0.5$. 'f' satisfies $0 \leq f < 0.01$, should preferably satisfy $0 \leq f \leq 0.005$, should more preferably satisfy $0 \leq f \leq 0.001$, and should further preferably satisfy $f = 0$. 'g' satisfies $0.01 \leq g \leq 3$, should preferably satisfy $0.1 \leq g \leq 2.5$, should more preferably satisfy $0.3 \leq g \leq 2$, and should further preferably satisfy $0.5 \leq g \leq 1$. 'h' satisfies $0.01 \leq h \leq 3$, should preferably satisfy $0.1 \leq h \leq 2.5$, should more preferably satisfy $0.3 \leq h \leq 2$, and should further preferably satisfy $0.5 \leq h \leq 1.5$.

[0046]

When the atomic ratios of the elements fall outside the ranges specified by Formula (3), the selectivity of methacrylic acid as the target product sometimes decreases. Particularly, from the standpoint of the increase in the selectivity of methacrylic acid, it is preferable to contain no antimony, that is, to be $f = 0$. If $3 < d$, the reaction rate of methacrolein decreases.

[0047]

Further, the value of $d / (c + d)$ should preferably satisfy $0.5 \leq d / (c + d) \leq 1$, should more preferably $0.75 \leq d / (c + d) \leq 1$, and should further preferably satisfy $0.9 \leq d / (c + d) \leq 1$. By satisfying $0.5 \leq d / (c + d) \leq 1$, the selectivity of methacrylic acid further increases.

[0048]

[Method for Producing Methacrylic Acid Production Catalyst Precursor]

A method for producing the methacrylic acid production catalyst precursor according to the present invention includes the following steps (i) to (iii), and in steps (i) and (ii), each pH of the slurry (I), the solution (I) and the slurry (II) is maintained in a range of 0.1 to 6.5.

(i) a step of preparing a slurry (I) or a solution (I) containing at least a source material of molybdenum

(ii) a step of adding an ammonium compound to the slurry (I) or the solution (I) to prepare a slurry (II) containing an ammonium salt

(iii) a step of drying the slurry (II) to obtain the methacrylic acid production catalyst precursor having the Keggin-type structure

[0049]

Further, the method for producing the methacrylic acid production catalyst precursor according to the present invention may further include a forming step described later. According to this method, it is possible to suitably produce the methacrylic acid production catalyst precursor according to the present invention.

[0050]

(Step (i))

In step (i), the slurry (I) or solution (I) containing at least the source material of molybdenum is prepared. Either the slurry (I) or the solution (I) may be adopted. For example, the slurry (I) can be prepared by suspending a source material compound of the catalyst component in a solvent using a preparation container, and the solution (I) can be prepared by dissolving the source material compound in the solvent. The slurry (I) or the solution (I) contains at least the source material of molybdenum, can contain the components that are contained in the composition represented by Formula (2), and should preferably contain a source material of niobium.

[0051]

The source material compound to be used, without being particularly limited, includes nitrates, carbonates, acetates, ammonium salts, oxides, halogenides, oxoacids, oxoacid salts and the like of the elements, and combinations of them may be used. Examples of the molybdenum source material include ammonium paramolybdate, molybdenum trioxide, molybdic acid, and molybdenum chloride. Examples of the phosphorus source material include orthophosphoric acid, phosphorus pentoxide, and phosphates such as ammonium phosphate and cesium phosphate. Examples of the copper source material include copper sulfate, copper nitrate, copper oxide, copper carbonate, copper acetate, and copper chloride. Examples of the vanadium source material include phospho vanado-molybdic acid, ammonium metavanadate, vanadium pentoxide,

and vanadium chloride. Here, in the case where phospho vanado-molybdic acid is used as the vanadium source material, since phospho vanado-molybdic acid concurrently contains the molybdenum element and the phosphorus element, the amounts of the molybdenum source material and the phosphorus source material added are adjusted such that a targeted catalyst precursor composition is obtained, depending on the amount of phospho vanado-molybdic acid added. Examples of niobium source material include niobic acid, niobium pentoxide, niobium chloride, niobium hydrogen-oxalate, and ammonium niobate oxalate. In the case of using water as the solvent at the time of the preparation of the catalyst precursor, it is preferable to use water-soluble source materials such as niobium hydrogen-oxalate and ammonium niobate oxalate, as the niobium source material. Meanwhile, in the case of using a water-insoluble source material such as niobium pentoxide, for example, it is preferable to select a preparation method by which the niobium source material is dissolved in water, as exemplified by the addition of oxalic acid or hydrogen peroxide to water. Thereby, it is possible to obtain a catalyst precursor having a preferred structure in step (iii) described later.

[0052]

The slurry (I) or the solution (I) can be obtained by adding and mixing source materials containing the elements constituting the catalyst precursor in a solvent. As the solvent, water, an organic solvent or the like can be used. From an industrial standpoint, it is preferable to use water. Further, as necessary, heating treatment of the slurry (I) or the solution (I) may be performed. The order of addition of the source materials at the time of the preparation is not particularly limited. In step (i), the preparation is performed while the pH of the slurry (I) or the solution (I) is maintained at 0.1 to 6.5. Thereby, the selectivity of methacrylic acid increases. The lower limit of the pH is preferably 0.5 or higher, and more preferably 1.0 or higher. Further, the upper limit of the pH is preferably 6 or lower. The pH of the slurry (I) or the solution (I) can be measured, for example, by D-72 (trade name), which is a portable-type pH meter manufactured by HORIBA, Ltd. As a method for controlling the pH of the slurry (I) or the solution (I), there is a method of appropriately selecting source materials of the components constituting the catalyst precursor, the amount of the ammonium species added, and the like, and appropriately adding nitric acid, oxalic acid or the like.

[0053]

(Step (ii))

In step (ii), the slurry (II) containing an ammonium salt is prepared by adding an ammonium compound to the slurry (I) or the solution (I). The ammonium compound includes ammonium hydrogen carbonate, ammonium carbonate, ammonium nitrate, ammonia water and

the like. One of these ammonium compounds can be used, or two or more thereof can be used in combination. In step (ii), it is preferable to add a metal cation-containing compound, in addition to the ammonium compound. As the metal cation-containing compound, it is preferable to use a compound containing at least one element (corresponding to G in Formula (2)) selected from the group consisting of lithium, sodium, potassium, rubidium, cesium and thallium.

[0054]

Further, it is preferable to perform heating treatment of the slurry (II). The temperature of the heating treatment is not particularly limited, but it is preferable to perform the heating to a temperature at which a compound containing molybdenum, niobium, copper, phosphorus and as necessary, another metallic element can be dissolved or can react with another compound. Specifically, 75 to 130°C is preferable, and 95 to 130°C is more preferable. Depending on the vapor pressure of the solvent to be used, condensation or reflux may be performed at the time of the heating, or the heating treatment may be performed under a pressurized condition by an operation in a closed container. The temperature rise rate is not particularly limited, but 0.8 to 15°C/minute is preferable. When the temperature rise rate is 0.8°C/minute or higher, it is possible to shorten the slurry preparation time. Further, when the temperature rise rate is 15°C/minute or lower, it is possible to perform temperature rise using a usual temperature rise apparatus.

[0055]

In step (ii), the preparation is performed while the pH of the slurry (II) is maintained at 0.1 to 6.5. Thereby, the selectivity of methacrylic acid increases. The lower limit of the pH is preferably 0.5 or higher, and more preferably 1.0 or higher. Further, the upper limit is preferably 6.0 or lower. In the case where the heating treatment is performed in step (ii), it is preferable that the pH of the slurry (II) to be obtained after the heating treatment be 0.1 to 3.0, and it is more preferable that the lower limit be 1.0 or higher and the upper limit be 2.5 or lower. The pH of the slurry (II) can be measured, for example, by D-72 (trade name), which is a portable-type pH meter manufactured by HORIBA, Ltd. As a method for controlling the pH of the slurry (II), there is a method of appropriately selecting source materials of the components constituting the catalyst precursor, the amount of the ammonium species added, and the like, and appropriately adding nitric acid, oxalic acid or the like. Thereby, it is possible to obtain a catalyst precursor having a preferred structure in step (iii) described later.

[0056]

(Step (iii))

In step (iii), the slurry (II) is dried, and the methacrylic acid production catalyst precursor having the Keggin-type structure is obtained. The drying method, without being particularly restricted, includes drum drying, freeze drying, spray drying, evaporation to dryness and the like. Among them, in the method according to the present invention, the drum drying, the spray drying or the evaporation to dryness is preferable.

[0057]

As a method for obtaining the catalyst precursor having the Keggin-type structure in step (iii), there is a method of adjusting the pH of the slurry (II) to be obtained after the heating treatment in step (ii), to 3 or lower, preferably 2.5 or lower. The structure of the catalyst precursor can be judged by an infrared absorption analysis measurement. In the case where the catalyst precursor has the Keggin-type structure, the infrared absorption spectrum obtained has characteristic peaks around 1060, 960, 870 and 780 cm^{-1} .

[0058]

(Forming Step)

In the forming step, the catalyst precursor or the catalyst after calcining that is obtained in a calcining step described later is formed. For the catalyst that is produced by the method according to the present invention, either a fixed-bed reactor or a fluidized-bed reactor can be used, and therefore, the shape of the catalyst can be appropriately selected from shapes suitable for the forms of the respective reactions. For example, the forming method for the catalyst to be used in the fixed-bed reactor can be appropriately selected from known methods, without being particularly limited, but it is preferable to perform the forming into a shape allowing the pressure loss at the time of the reaction not to become large. The forming method includes tableting, wet forming, pressure forming, tumbling granulation and the like, and a suitable size and shape can be adopted depending on use condition. For example, in the case of the production of the catalyst to be used in the fluidized-bed reactor, it is preferable to perform the wet forming of a catalyst precursor composed of fine powders by spray drying.

[0059]

[Method for Producing Methacrylic Acid Production Catalyst]

The method for producing the methacrylic acid production catalyst according to the present invention includes a step (hereinafter, referred to as a calcining step also) of calcining the catalyst precursor obtained in step (iii) or the formed product of the catalyst precursor obtained in the forming step (hereinafter, collectively referred to as the catalyst precursor also).

[0060]

(Calcining Step)

In the calcining step, the catalyst precursor is calcined, and the methacrylic acid production catalyst is obtained. The calcining method is not particularly limited, and a suitable method can be appropriately selected from stationary calcining, flow calcining and the like. As the stationary calcining, there is a method of performing the calcining, for example, using a box-shaped electric furnace, a circular calcining furnace or the like. As the flow calcining, there is a method of performing the calcining, for example, using a flow calcining furnace, a rotary kiln or the like. The calcining gas can be appropriately selected from air, nitrogen and the like. As long as a desired calcining gas atmosphere can be maintained, the calcining gas may be circulated or not circulated. From the standpoint of obtaining a catalyst having a high activity and selectivity for methacrylic acid, it is preferable that the calcining temperature be 200 to 500°C, and it is more preferable that the lower limit be 300°C or higher and the upper limit be 450°C or lower. The calcining time is preferably 0.5 to 40 hours, more preferably 1 to 40 hours, and further preferably 2 to 40 hours.

[0061]

The catalyst to be obtained can be used by itself, but it may be used by supporting onto an inert carrier such as silica, alumina, silica-alumina and silicon carbide, or may be used by mixing with these carrier. Further, the catalyst may be used by mixing with a catalyst produced by a method other than the production method according to the present invention.

[0062]

[Method for Producing Methacrylic Acid]

In a method for producing methacrylic acid according to the present invention, methacrylic acid is produced by a gas-phase catalytic oxidation of methacrolein with molecular oxygen using the methacrylic acid production catalyst according to the present invention. Further, in a method for producing methacrylic acid according to the present invention, a methacrylic acid production catalyst is produced by the method according to the present invention, and methacrylic acid is produced by a gas-phase catalytic oxidation of methacrolein with molecular oxygen using the methacrylic acid production catalyst. Further, in a method for producing methacrylic acid according to the present invention, methacrylic acid is produced by a gas-phase catalytic oxidation of methacrolein with molecular oxygen using the methacrylic acid production catalyst produced by the method according to the present invention. According to these methods, it is possible to produce methacrylic acid at a high selectivity.

[0063]

The method can be performed by the contact of the methacrylic acid production catalyst with a source gas containing methacrolein and molecular oxygen. The concentration of

methacrolein in the source gas is not particularly limited, but is preferably 1 to 20 vol%, and more preferably 3 to 10 vol%. Methacrolein as a source material may contain small amounts of impurities that have no substantial influence on the reaction, as exemplified by water and lower saturated aldehydes.

[0064]

The concentration of molecular oxygen in the source gas is preferably 0.4 to 4 moles, and more preferably 0.5 to 3 moles, with respect to 1 mole of methacrolein. As a source of the molecular oxygen, air is preferable from an economic standpoint. As necessary, pure oxygen may be added to air, and a molecular oxygen-enriched gas may be used.

[0065]

The source gas may be a gas in which methacrolein and molecular oxygen are diluted with an inert gas such as nitrogen and carbon dioxide gas. Furthermore, steam may be added to the source gas. By the reaction in the existence with water, it is possible to obtain methacrylic acid at a higher selectivity and a higher yield. The concentration of steam in the source gas is preferably 0.1 to 50 vol%, and more preferably 1 to 40 vol%.

[0066]

The time of the contact between the source gas and the methacrylic acid production catalyst is preferably 1.5 to 15 seconds, and more preferably 2 to 10 seconds. The reaction pressure is preferably 0.1 to 1 MPa (G). Here, (G) means gauge pressure. The reaction temperature is preferably 200 to 450°C, and more preferably 250 to 400°C.

[0067]

[Method for Producing Methacrylic Acid Ester]

In a method for producing a methacrylic acid ester according to the present invention, the methacrylic acid produced by the method according to the present invention is esterified. Further, in a method for producing a methacrylic acid ester according to the present invention, methacrylic acid is produced by the method according to the present invention, and the methacrylic acid is esterified. According to these methods, it is possible to obtain the methacrylic acid ester using the methacrylic acid obtained by the gas-phase catalytic oxidation of methacrolein. The alcohol to be reacted with methacrylic acid, without being particularly limited, includes methanol, ethanol, isopropanol, n-butanol, isobutanol and the like. Examples of the methacrylic acid ester to be obtained include methyl methacrylate, ethyl methacrylate, propyl methacrylate, and butyl methacrylate. The reaction can be performed in the existence with an acid catalyst such as a sulfone acid-type cation exchange resin. The reaction temperature is preferably 50 to 200°C.

Examples

[0068]

The present invention will be described below in detail, with Examples and Comparative Examples. The present invention is not limited to these Examples. The "part" in the Examples and the Comparative Examples means part by mass.

[0069]

The composition ratio of each element in the catalyst precursor and the catalyst was evaluated by analyzing components when the catalyst or the catalyst precursor was dissolved in an ammonia water, by an ICP atomic emission spectroscopy. Further, the mole ratio of the ammonium species was evaluated by analyzing the catalyst or the catalyst precursor by the Kjeldahl method. Further, each pH of the slurry and the solution was measured using by D-72 (product name), which is a portable-type pH meter manufactured by HORIBA, Ltd.

[0070]

The analysis of the source gas and the product was performed using a gas chromatography. From results of the gas chromatography, the reaction rate of methacrolein and the selectivity of methacrylic acid were evaluated by the following formulas.

[0071]

Reaction Rate (%) of Methacrylic Acid = Number of Moles of Reacted Methacrolein / Number of Moles of Supplied Methacrolein $\times$ 100

Selectivity (%) of Methacrylic Acid = Number of Moles of Methacrylic Acid Generated / Number of Moles of Reacted Methacrolein $\times$ 100

[0072]

[Example 1]

The slurry (I) was prepared by mixing 1200 parts of pure water at room temperature with a dilution in which 300 parts of molybdenum trioxide, 21 parts of ammonium niobate oxalate and 20.1 parts of 85 mass% aqueous solution of phosphoric acid are diluted in 18 parts of pure water, a dilution in which 24.6 parts of 60 mass% aqueous solution of arsenic acid were diluted in 18 parts of pure water, and a dissolution in which 4.2 parts of copper nitrate (II) trihydrate were dissolved in 9.0 parts of pure water. The slurry (II) was obtained by dropping a dissolution in which 23.5 parts of cesium bicarbonate and 5.2 parts of potassium bicarbonate were dissolved in 60 parts of pure water at room temperature and a dissolution in which 27.5 parts of ammonium carbonate were dissolved in 73 parts of pure water at room temperature while stirring the slurry (I) at room temperature. Thus obtained slurry (II), after the temperature

rise at 2°C/minute, was heated and stirred at 95°C for 2 hours. In the preparation of the slurry (I) and the slurry (II), each pH of the slurry (I) and the slurry (II) changed in a range of 1.4 to 5.5, and the pH of the slurry (II) obtained after the heating and stirring was in a range of 1.4 to 2.5. The slurry (II) was heated and evaporated to dryness to obtain a catalyst precursor. The composition ratio of the obtained catalyst precursor excluding oxygen is shown in Table 1. Further, the catalyst precursor had the Keggin-type structure.

[0073]

A catalyst was produced by performing the pressure molding of the obtained catalyst precursor and crushing, performing the classification using a sieve such that the particle diameter is in a range of 710 μm to 2.36 mm, and calcining the resultant at 380°C for 5 hours in air flow. The composition ratio of the obtained catalyst excluding oxygen is shown in Table 2. The mole ratio of the ammonium species in the catalyst was $0 \leq i \leq 1$.

[0074]

The catalyst was filled into a reactor, a source gas composed of 5 vol% methacrolein, 10 vol% oxygen, 30 vol% steam and 55 vol% nitrogen was introduced into the reactor, and the reaction evaluation was performed at a reaction temperature of 285°C. The amount of catalyst charged was adjusted such that the reaction rate of methacrolein was in a range of 13 to 27%. The gas after the reaction was collected and analyzed with a gas chromatography, and the methacrolein reaction rate and the selectivity for methacrylic acid were calculated. The result is shown in Table 2.

[0075]

[Example 2]

A catalyst precursor was produced by the same method as Example 1, except that the amount of ammonium niobate oxalate charged was changed to 17 parts and the amount of 60 mass% aqueous solution of arsenic acid charged was changed to 20.5 parts in Example 1. In the preparation of the slurry (I) and the slurry (II), each pH of the slurry (I) and the slurry (II) changed in a range of 1.4 to 5.6, and the pH of the slurry (II) obtained after the heating and stirring was in a range of 1.4 to 2.5. The composition ratio of the obtained catalyst precursor excluding oxygen is shown in Table 1. Further, the catalyst precursor had the Keggin-type structure.

[0076]

A catalyst was produced by forming and calcining the obtained catalyst precursor by the same method as Example 1, and the reaction evaluation was performed using the catalyst, by the same method as Example 1. The composition ratio of the catalyst excluding oxygen and the

result of the reaction evaluation are shown in Table 2. The mole ratio of the ammonium species in the catalyst was $0 \leq i \leq 1$.

[0077]

[Example 3]

The slurry (I) was prepared by mixing 1200 parts of pure water at room temperature with a dilution in which 300 parts of molybdenum trioxide, 0.22 parts of ammonium metavanadate, 13 parts of ammonium niobate oxalate and 20.1 parts of 85 mass% aqueous solution of phosphoric acid were diluted in 18 parts of pure water, a dilution in which 24.6 parts of 60 mass% aqueous solution of arsenic acid were diluted in 18 parts of pure water, and a dissolution in which 4.2 parts of copper nitrate (II) trihydrate were dissolved in 9.0 parts of pure water. The slurry (II) was obtained by dropping a dissolution in which 33.6 parts of cesium bicarbonate were dissolved in 60 parts of pure water at room temperature and a dissolution in which 27.5 parts of ammonium carbonate were dissolved in 73 parts of pure water at room temperature while stirring the slurry (I) at room temperature. The obtained slurry (II), after the temperature rise at 2°C/minute, was heated and stirred at 95°C for 2 hours. In the preparation of the slurry (I) and the slurry (II), each pH of the slurry (I) and the slurry (II) changed in a range of 1.4 to 5.6, and the pH of the slurry (II) obtained after the heating and stirring was in a range of 1.4 to 2.5. The slurry (II) was heated and evaporated to dryness to obtain a catalyst precursor. The composition ratio of the obtained catalyst precursor excluding oxygen is shown in Table 1. Further, the catalyst precursor had the Keggin-type structure.

[0078]

A catalyst was produced by forming and calcining the obtained catalyst precursor by the same method as Example 1, and the reaction evaluation was performed using the catalyst, by the same method as Example 1. The composition ratio of the catalyst excluding oxygen and the result of the reaction evaluation are shown in Table 2. The mole ratio of the ammonium species in the catalyst was $0 \leq i \leq 1$.

[0079]

[Example 4]

A catalyst precursor was produced by the same method as Example 3, except that the amount of ammonium metavanadate charged was changed to 2 parts in Example 3. In the preparation of the slurry (I) and the slurry (II), each pH of the slurry (I) and the slurry (II) changed in a range of 1.5 to 5.7, and the pH of the slurry (II) obtained after the heating and stirring was in a range of 1.5 to 2.5. The composition ratio of the obtained catalyst precursor excluding oxygen is shown in Table 1. Further, the catalyst precursor had the Keggin-type

structure.

[0080]

A catalyst was produced by forming and calcining the obtained catalyst precursor by the same method as Example 1, and the reaction evaluation was performed using the catalyst, by the same method as Example 1. The composition ratio of the catalyst excluding oxygen and the result of the reaction evaluation are shown in Table 2. The mole ratio of the ammonium species in the catalyst was $0 \leq i \leq 1$.

[0081]

[Example 5]

The slurry (I) was prepared by mixing 1200 parts of pure water at room temperature with a dilution in which 300 parts of molybdenum trioxide, 4.1 parts of ammonium metavanadate, 10.5 parts of ammonium niobate oxalate and 20.1 parts of 85 mass% aqueous solution of phosphoric acid were diluted in 18 parts of pure water, a dilution in which 24.6 parts of 60 mass% aqueous solution of arsenic acid were diluted in 18 parts of pure water, and a dissolution in which 4.2 parts of copper nitrate (II) trihydrate were dissolved in 9.0 parts of pure water. The slurry (II) was obtained by dropping a dissolution in which 30.3 parts of cesium bicarbonate and 1.7 parts of potassium bicarbonate were dissolved in 60 parts of pure water at room temperature and a dissolution in which 27.5 parts of ammonium carbonate were dissolved in 73 parts of pure water at room temperature while stirring the slurry (I) at room temperature. The obtained slurry (II), after the temperature rise at 2°C/minute, was heated and stirred at 95°C for 2 hours. In the preparation of the slurry (I) and the slurry (II), each pH of the slurry (I) and the slurry (II) changed in a range of 1.5 to 5.7, and the pH of the slurry (II) obtained after the heating and stirring was in a range of 1.5 to 2.5. The slurry (II) was heated and evaporated to dryness to obtain a catalyst precursor. The composition ratio of the obtained catalyst precursor excluding oxygen is shown in Table 1. Further, the catalyst precursor had the Keggin-type structure.

[0082]

A catalyst was produced by forming and calcining the obtained catalyst precursor by the same method as Example 1, and the reaction evaluation was performed using the catalyst, by the same method as Example 1. The composition ratio of the catalyst excluding oxygen and the result of the reaction evaluation are shown in Table 2. The mole ratio of the ammonium species in the catalyst was $0 \leq i \leq 1$.

[0083]

[Comparative Example 1]

A catalyst precursor was produced by the same method as Example 5, except that the amount of ammonium metavanadate charged was changed to 8.2 parts, the amount of the cesium bicarbonate charged was changed to 23.5 parts, the amount of potassium bicarbonate charged was changed to 5.2 parts and ammonium niobate oxalate was not used in Example 5. In the preparation of the slurry (I) and the slurry (II), each pH of the slurry (I) and the slurry (II) changed in a range of 1.5 to 5.7, and the pH of the slurry (II) obtained after the heating and stirring was in a range of 1.5 to 2.5. The composition ratio of the obtained catalyst precursor excluding oxygen is shown in Table 1. Further, the catalyst precursor had the Keggin-type structure.

[0084]

A catalyst was produced by forming and calcining the obtained catalyst precursor by the same method as Example 1, and the reaction evaluation was performed using the catalyst, by the same method as Example 1. The composition ratio of the catalyst excluding oxygen and the result of the reaction evaluation are shown in Table 2. The mole ratio of the ammonium species in the catalyst was $0 \leq i \leq 1$.

[0085]

[Comparative Example 2]

The slurry (I) was obtained by mixing 1200 parts of pure water with a dilution in which 300 parts of molybdenum trioxide, 4.1 parts of ammonium metavanadate, 10.5 parts of ammonium niobate oxalate, 22.8 parts of antimony pentoxide and 20.1 parts of 85 mass% aqueous solution of phosphoric acid were diluted in 18 parts of pure water, a dilution in which 24.6 parts of 60 mass% aqueous solution of arsenic acid were diluted in 18 parts of pure water, and a dissolution in which 4.2 parts of copper nitrate (II) trihydrate were dissolved in 9.0 parts of pure water. The slurry (II) was obtained by dropping a dissolution in which 30.3 parts of cesium bicarbonate and 1.7 parts of potassium bicarbonate were dissolved in 60 parts of pure water at room temperature and a dissolution in which 27.5 parts of ammonium carbonate were dissolved in 73 parts of pure water at room temperature while stirring the slurry (I) at room temperature. The obtained slurry (II), after the temperature rise at 2°C/minute, was heated and stirred at 95°C for 2 hours. In the preparation of the slurry (I) and the slurry (II), each pH of the slurry (I) and the slurry (II) changed in a range of 1.5 to 5.7, and the pH of the slurry (II) obtained after the heating and stirring was in a range of 1.5 to 2.5. The slurry (II) was heated and evaporated to dryness to obtain a catalyst precursor. The composition ratio of the obtained catalyst precursor excluding oxygen is shown in Table 1. Further, the catalyst precursor had the Keggin-type structure.

[0086]

A catalyst was produced by forming and calcining the obtained catalyst precursor by the same method as Example 1, and the reaction evaluation was performed using the catalyst, by the same method as Example 1. The composition ratio of the catalyst excluding oxygen and the result of the reaction evaluation are shown in Table 2. The mole ratio of the ammonium species in the catalyst was $0 \leq i \leq 1$.

[0087]

[Table 1]

	Composition of Catalyst Precursor												
	Mo	P	V	Nb	Cu	A		G		NH ₄	a+f	c+d	d/(c+d)
						As	Sb	K	Cs				
Example 1	12	1		0.40	0.1	0.6		0.3	0.7	3.7	1.6	0.4	1.00
Example 2	12	1		0.32	0.1	0.5		0.3	0.7	3.6	1.5	0.3	1.00
Example 3	12	1	0.01	0.25	0.1	0.6			1.0	3.6	1.6	0.3	0.96
Example 4	12	1	0.10	0.25	0.1	0.6			1.0	3.6	1.6	0.3	0.72
Example 5	12	1	0.20	0.20	0.1	0.6		0.1	0.9	3.7	1.6	0.4	0.50
Comparative Example 1	12	1	0.40		0.1	0.6		0.3	0.7	3.7	1.6	0.4	0.00
Comparative Example 2	12	1	0.20	0.20	0.1	0.6	0.9	0.1	0.9	3.7	2.5	0.4	0.50

[0088]

[Table 2]

	Composition of Catalyst											Methacrolein		Selectivity for
	Mo	P	V	Nb	Cu	A		G		a+f	c+d	d/(c+d)	Reaction Rate (%)	Methacrylic Acid (%)
						As	Sb	K	Cs					
Example 1	12	1		0.40	0.1	0.6		0.3	0.7	1.6	0.4	1.00	26.2	94.7
Example 2	12	1		0.32	0.1	0.5		0.3	0.7	1.5	0.3	1.00	20.9	94.2
Example 3	12	1	0.01	0.25	0.1	0.6			1.0	1.6	0.3	0.96	20.0	95.1
Example 4	12	1	0.10	0.25	0.1	0.6			1.0	1.6	0.3	0.72	22.2	92.6
Example 5	12	1	0.20	0.20	0.1	0.6		0.1	0.9	1.6	0.4	0.50	21.7	92.3
Comparative Example 1	12	1	0.40		0.1	0.6		0.3	0.7	1.6	0.4	0.00	22.4	91.6
Comparative Example 2	12	1	0.20	0.20	0.1	0.6	0.9	0.1	0.9	2.5	0.4	0.50	16.5	79.1

[0089]

As shown in Tables 1 and 2, it was confirmed that in Examples 1 to 5, the composition ratios of the catalyst precursors and the catalysts were in the range of the present invention and the catalysts had a high selectivity for methacrylic acid. On the other hand, in Comparative Example 1 in which the niobium composition ratio was out of the range of the present invention and Comparative Example 2 in which the value of a + f is out of the range of the present

invention, the selectivity for methacrylic acid was lower than in Examples 1 to 5.

[0090]

By esterifying each methacrylic acid obtained in the examples, it is possible to obtain methacrylic acid ester.

[0091]

This application claims priority based on Japanese Patent Application No. 2017-028174 filed on February 17, 2017, and all of the disclosure thereof are incorporated herein.

[0092]

Thus, the invention in the present application has been described with reference to the embodiment and the examples, but the invention in the present application is not limited to the above embodiment and examples. For configurations and details of the invention in the present application, various modifications that can be understood by those in the art can be made within the scope of the invention in the present application.

Industrial Applicability

[0093]

The methacrylic acid production catalyst according to the present invention makes it possible to produce methacrylic acid at a high selectivity, and therefore, is useful when methacrylic acid is industrially produced.

CLAIMS

[Claim 1]

A methacrylic acid production catalyst for use in producing methacrylic acid by a gas-phase catalytic oxidation of methacrolein with molecular oxygen, the catalyst having a composition represented by the following Formula (1),



wherein in Formula (1), 'P', 'Mo', 'V', 'Nb', 'Cu', 'NH₄' and 'O' represent phosphorus, molybdenum, vanadium, niobium, copper, ammonium species and oxygen, respectively. 'A' represents at least one element selected from the group consisting of silicon, germanium, arsenic and antimony. 'E' represents at least one element selected from the group consisting of bismuth, zirconium, tellurium, silver, selenium, tungsten, boron, iron, zinc, chromium, magnesium, calcium, strontium, tantalum, cobalt, nickel, manganese, barium, titanium, tin, lead, indium, sulfur, palladium, gallium, cerium and lanthanum. 'G' represents at least one element selected from the group consisting of lithium, sodium, potassium, rubidium, cesium and thallium. 'a' to 'j' represent mole ratios of the components, and when $b = 12$, $0.5 \leq a + f \leq 2.1$, $0.01 \leq c + d \leq 3$, $0.5 \leq a$, $0 \leq c$, $0.01 \leq d \leq 3$, $0.005 \leq e \leq 3$, $0 \leq f$, $0 \leq g \leq 3$, $0.01 \leq h \leq 3$ and $0 \leq i \leq 5$ are satisfied, and 'j' is a mole ratio of oxygen necessary to satisfy valences of the components.

[Claim 2]

A methacrylic acid production catalyst precursor that is a precursor of a catalyst for use in producing methacrylic acid by a gas-phase catalytic oxidation of methacrolein with molecular oxygen, the methacrylic acid production catalyst precursor having a Keggin-type structure and having a composition represented by the following Formula (2),



in Formula (2), 'P', 'Mo', 'V', 'Nb', 'Cu', 'NH₄' and 'O' represent phosphorus, molybdenum, vanadium, niobium, copper, ammonium species and oxygen, respectively. 'A' represents at least one element selected from the group consisting of silicon, germanium, arsenic and antimony. 'E' represents at least one element selected from the group consisting of bismuth, zirconium, tellurium, silver, selenium, tungsten, boron, iron, zinc, chromium, magnesium, calcium, strontium, tantalum, cobalt, nickel, manganese, barium, titanium, tin, lead, indium, sulfur, palladium, gallium, cerium and lanthanum. 'G' represents at least one element selected from the group consisting of lithium, sodium, potassium, rubidium, cesium and thallium. 'a' to 'j' represent mole ratios of the components, and when $b = 12$, $0.5 \leq a + f \leq 2.4$, $0.01 \leq c + d \leq 3$, $0.5 \leq a$, $0 \leq c$, $0.01 \leq d \leq 3$, $0.005 \leq e \leq 3$, $0 \leq f$, $0 \leq g \leq 3$, $0.01 \leq h \leq 3$ and $0.1 \leq i \leq 20$ are

satisfied, and 'j' is a mole ratio of oxygen necessary to satisfy valences of the components.

[Claim 3]

The methacrylic acid production catalyst according to claim 1, wherein in Formula (1), $0.35 \leq d / (c + d) \leq 1$ is satisfied.

[Claim 4]

The methacrylic acid production catalyst precursor according to claim 2, wherein in Formula (2), $0.35 \leq d / (c + d) \leq 1$ is satisfied.

[Claim 5]

A method for producing the methacrylic acid production catalyst precursor according to claim 2 or 4, the method comprising:

(i) a step of preparing a slurry (I) or a solution (I) containing at least a source material of molybdenum;

(ii) a step of adding an ammonium compound to the slurry (I) or the solution (I) to prepare a slurry (II) containing an ammonium salt; and

(iii) a step of drying the slurry (II) to obtain the methacrylic acid production catalyst precursor having the Keggin-type structure, wherein

in steps (i) and (ii), each pH of the slurry (I), the solution (I) and the slurry (II) is maintained in a range of 0.1 to 6.5.

[Claim 6]

A method for producing a methacrylic acid production catalyst, comprising a step of calcining the methacrylic acid production catalyst precursor produced by the method according to claim 5.

[Claim 7]

A method for producing methacrylic acid, wherein methacrylic acid is produced by a gas-phase catalytic oxidation of methacrolein with molecular oxygen using the methacrylic acid production catalyst according to claim 1 or 3.

[Claim 8]

A method for producing methacrylic acid, wherein a methacrylic acid production catalyst is produced by the method according to claim 6, and methacrylic acid is produced by a gas-phase catalytic oxidation of methacrolein with molecular oxygen using the methacrylic acid production catalyst.

[Claim 9]

A method for producing methacrylic acid, wherein methacrylic acid is produced by a gas-phase catalytic oxidation of methacrolein with molecular oxygen using the methacrylic acid

production catalyst produced by the method according to claim 6.

[Claim 10]

A method for producing a methacrylic acid ester, wherein the methacrylic acid produced by the method according to any one of claims 7 to 9 is esterified.

[Claim 11]

A method for producing a methacrylic acid ester, wherein methacrylic acid is produced by the method according to any one of claims 7 to 9, and the methacrylic acid is esterified.