DESCRIPTION

TITLE OF THE INVENTION

CATALYST FOR METHACRYLIC ACID PRODUCTION, METHOD FOR PRODUCING SAME, AND METHOD FOR PRODUCING METHACRYLIC ACID AND METHACRYLIC ACID ESTERS USING CATALYST

TECHNICAL FIELD

[0001]

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

BACKGROUND ART

[0002]

There are known as catalysts for methacrylic acid production, for use in the production of methacrylic acid by oxidation of methacrolein (hereinafter, also simply designated as “catalysts”), for example, heteropoly acid-based catalysts each including molybdenum and phosphorus. Heteropoly acid refers to condensed oxyacid with 12 coordinating atoms forming a basic structure of poly acid (hereinafter, designated as “polyatoms”) and oxide of heteroatom. Heteropoly acid-based catalysts include proton-type heteropoly acid with protons as counter cations, and heteropoly acid salts with some protons substituted with cations other than such protons (hereinafter, proton-type heteropoly acid is also simply expressed as “heteropoly acid”, and at least one selected from proton-type heteropoly acid and heteropoly acid salts is also simply expressed as “heteropoly acid (salt)”).

[0003]

NPL 1 describes with respect to structures of heteropoly acid (salt), phosphorus, silicon, arsenic, germanium, titanium, antimony, and the like which can serve

as heteroatoms, and tungsten, molybdenum, vanadium, niobium, tantalum, and the like which can serve as polyatoms of heteropoly acid (salt). Keggin-type, Dawson-type, Preyssler-type, and the like are also described as basic structures of heteropoly acid (salt).

[0004]

PTL 1 discloses, as a catalyst for methacrylic acid production, a catalyst including a Keggin-type heteropoly acid salt having a composition represented by the following formula:

$P_aMo_bV_cX_dY_eO_f$

wherein P, Mo, V and O respectively represent phosphorus, molybdenum, vanadium and oxygen, X represents at least one element selected from potassium, rubidium, cesium and thallium, Y represents at least one element selected from copper, arsenic, antimony, boron, silver, bismuth, iron, cobalt, lanthanum and cerium, a, b, c, d, e and f respectively represent the atomic ratios of P, Mo, V, X, Y and O, and when b = 12 is set, a, c, d and e are each independently a value of more than 0 and 3 or less, and f is a value defined by the oxidation state and the atomic ratio of each element other than oxygen.

[0005]

Examples of known Keggin-type heteropoly acid include $H_3PMo_{12}O_{40}$, $H_4PMo_{11}VO_{40}H_3$, and $PW_{12}O_{40}$, and NPL 1 indicates that the pyrolysis temperature of $PW_{12}O_{40}$ is higher than those of $H_3PMo_{12}O_{40}$ and $H_4PMo_{11}VO_{40}H_3$. In this regard, as described in NPL 2, use of $H_3PMo_{12}O_{40}$ as a catalyst for methacrylic acid production favorably provides methacrylic acid, but use of $PW_{12}O_{40}$ leads to both activity and selectivity which are very low.

RELATED ART DOCUMENTS

PATENT DOCUMENT

[0006]

PTL 1: JP-A 2003-010691

NON PATENT DOCUMENTS

[0007]

NPL 1: Toshio Okuhara, Noritaka Mizuno, Makoto Misono, Advances in Catalysis, volume 41.

NPL 2: Shuhei Yasuda, Atsuki Iwakura, Jun Hirata, Mitsuru Kanno, Wataru Ninomiya, Ryoichi Otomo, Yuichi Kamiya, Catalysis Communications, 125 (2019), 43-47.

SUMMARY OF THE INVENTION

PROBLEM TO BE SOLVED BY THE INVENTION

[0008]

However, known catalysts for methacrylic acid production are low in heat resistance and still insufficient in catalyst life. Therefore, it is demanded for use as an industrial catalyst to develop a catalyst which has high heat resistance and which can allow for production of methacrylic acid at a high yield.

An object of the present invention is to provide a catalyst which has high heat resistance and which can allow for production of methacrylic acid at a high yield. Another object of the present invention is to provide methods for producing methacrylic acid and methacrylic acid ester with the catalyst.

MEANS FOR SOLVING THE PROBLEMS

[0009]

The present inventors have made intensive studies in view of the above problems, and as a result, have found that the above problems can be solved by use of a catalyst having a specified ^{31}P-NMR spectrum, and thus have completed the present invention.

Specifically, the present invention includes the followings.

[1]: A catalyst for use in the production of methacrylic acid by oxidation of methacrolein, wherein

the catalyst contains heteropoly acid including phosphorus, molybdenum and tungsten, and

C/(A + B + C) is 0.015 to 0.085 when the area of a signal observed in a range of -5.2 ppm or more and less than 0 ppm is defined as A, the area of a signal observed in a range of -10 ppm or more and less than -5.2 ppm is defined as B, and the area of a signal observed in a range of -20 ppm or more and less than -10 ppm is defined as C in a ^{31}P-NMR spectrum of the catalyst.

[2]: The catalyst for methacrylic acid production according to [1], wherein B/(A + B + C) in the ^{31}P-NMR spectrum is 0.1 to 0.485.

[3]: The catalyst for methacrylic acid production according to [1] or [2], wherein A/(A + B + C) in the ^{31}P-NMR spectrum is 0.5 to 0.885.

[4]: The catalyst for methacrylic acid production according to any of [1] to [3], wherein C/(A + B + C) in the ^{31}P-NMR spectrum is 0.02 to 0.08.

[5]: The catalyst for methacrylic acid production according to any of [1] to [4], wherein B/(A + B + C) in the ^{31}P-NMR spectrum is 0.2 to 0.45.

[6]: The catalyst for methacrylic acid production according to any of [1] to [5], wherein A/(A + B + C) in the ^{31}P-NMR spectrum is 0.53 to 0.75.

[7]: The catalyst for methacrylic acid production according to any of [1] to [6], having a composition represented by the following formula (I):

$$P_aMo_bW_cV_dCu_eA_fE_gG_hO_i \quad (I)$$

wherein P, Mo, W, V, Cu and O respectively represent phosphorus, molybdenum, tungsten, vanadium, copper and oxygen, A represents at least one element selected from the group

consisting of antimony, bismuth, arsenic, germanium, tellurium, selenium and silicon, E represents at least one element selected from the group consisting of iron, zinc, chromium, tantalum, cobalt, nickel, manganese, titanium and niobium, G represents at least one element selected from the group consisting of potassium, rubidium and cesium, a to i each represent the molar ratio of each component, b + c = 12, a = 0.5 to 3, c = 0.22 to 5, d = 0.01 to 3, e = 0.01 to 2, f = 0 to 3, g = 0 to 3, and h = 0.01 to 3 are satisfied, and i is the molar ratio of oxygen necessary for satisfying the valence of such each component.

[8]: The catalyst for methacrylic acid production according to [7], wherein c = 0.22 to 3 is satisfied in the formula (I).

[9]: A method for producing the catalyst for methacrylic acid production according to any of [1] to [8], the method including

(i) a step of mixing a phosphorus raw material, a molybdenum raw material and a tungsten raw material with a solvent, to prepare a solution or slurry (liquid A) having a pH of 0.1 to 4,

(ii) a step of drying the liquid A, to obtain a dried product, and

(iii) a step of firing the dried product, to obtain a calcination product.

[10]: The method for producing the catalyst for methacrylic acid production according to [9], wherein a tungsten raw material having a solubility at 20°C of 4.1 g/100 mL or more occupies 50% by mass or more of the entire tungsten raw material in step (i).

[11]: The method for producing the catalyst for methacrylic acid production according to [9] or [10], wherein the pH of the liquid A is 0.1 to 3 in step (i).

[12]: A method for producing methacrylic acid, including a step of oxidizing methacrolein with the catalyst for methacrylic acid production according to any of [1] to [8], to produce methacrylic acid.

[13]: A method for producing methacrylic acid, including a step of oxidizing methacrolein with a catalyst for methacrylic acid production, produced by the method according to any one of [9] to [12], to produce methacrylic acid.

[14]: A method for producing methacrylic acid ester, including a step of esterifying methacrylic acid produced by the method according to [12] or [13].

EFFECTS OF THE INVENTION

[0010]

According to the present invention, there can be provided a catalyst which has high heat resistance and which can allow for production of methacrylic acid at a high yield.

MODE FOR CARRYING OUT THE INVENTION

[0011]

Hereinafter, embodiments according to the present invention are described, but the present invention is not limited to the following.

Herein, a numerical value range expressed with “to” means a range including numerical values described before and after “to” respectively as the lower limit value and the upper limit value, and “A to B” means A or more and B or less.

[0012]

[Catalyst for methacrylic acid production]

A catalyst for methacrylic acid production according to the present embodiment is a catalyst for use in the production of methacrylic acid by oxidation of methacrolein, in which the catalyst contains heteropoly acid including phosphorus, molybdenum, and tungsten. The C/(A + B + C) is 0.015 to 0.085 when the area of a signal observed in a range of -5.2 ppm or

more and less than 0 ppm is defined as A, the area of a signal observed in a range of -10 ppm or more and less than -5.2 ppm is defined as B, and the area of a signal observed in a range of -20 ppm or more and less than -10 ppm is defined as C in a ^{31}P-NMR spectrum of the catalyst.

Such a catalyst has high heat resistance and can allow for production of methacrylic acid at a high yield.

[0013]

<^{31}P-NMR spectrum of catalyst>

In a ^{31}P-NMR spectrum of the catalyst, A, B and C each correspond to the area of a signal mainly derived from a Keggin-type heteropoly acid structure. Specifically, A corresponds to the area of a signal mainly derived from a structure having phosphorus as heteroatoms and molybdenum as polyatoms (hereinafter, also designated as “structure A”). B corresponds to the area of a signal mainly derived from a structure having phosphorus as heteroatoms, and atoms such as tungsten and vanadium as 1 to 5 polyatoms and molybdenum as the balance (hereinafter, also designated as “structure B”). C corresponds to the area of a signal mainly derived from a structure having phosphorus as heteroatoms, and atoms such as tungsten and vanadium as 6 to 12 polyatoms and molybdenum as the balance (hereinafter, also designated as “structure C”).

The catalyst includes the structure A and the structure B, and thus exhibits a favorable yield in methacrylic acid production. In this regard, in a case where the structure A is excessively present, sequential oxidation reaction of methacrylic acid is promoted and thus the yield tends to be decreased. The structure B and the structure C are high in pyrolysis temperature and excellent in heat resistance as compared with the structure A. The structure C, in which most of polyatoms are atoms such as W and V, is particularly excellent in heat resistance.

[0014]

In a ^{31}P-NMR spectrum of the catalyst for methacrylic acid production according to the present embodiment, the C/(A + B + C) is 0.015 to 0.085. Here, the structure A and the structure B providing a favorable yield in methacrylic acid production, and the structure C particularly excellent heat resistance are present at a suitable abundance ratio in the catalyst. Therefore, it is considered that a catalyst high in heat resistance and excellent in yield of methacrylic acid is obtained. The lower limit of the C/(A + B + C) is preferably 0.02 or more, more preferably 0.025 or more. The upper limit of the C/(A + B + C) is preferably 0.08 or less, more preferably 0.75 or less.

The B/(A + B + C) is preferably 0.1 or more. The structure B excellent in both the yield in methacrylic acid production and heat resistance is properly present in the catalyst, and therefore a catalyst more excellent in heat resistance and yield of methacrylic acid is obtained. The B/(A + B + C) is more preferably 0.2 or more. The upper limit of the B/(A + B + C) is preferably 0.985 or less, more preferably 0.98 or less, further preferably 0.485 or less, particularly preferably 0.45 or less.

The lower limit of the A/(A + B + C) is preferably 0.5 or more, more preferably 0.53 or more, further preferably 0.56 or more from the viewpoint of the yield of methacrylic acid. The upper limit of the A/(A + B + C) is preferably 0.885 or less, more preferably 0.78 or less, particularly preferably 0.75 or less from the viewpoint of sequential oxidation suppression of methacrylic acid.

Preferred upper limits and preferred lower limits of the C/(A + B + C), the B/(A + B + C) and the A/(A + B + C) can be each set by selecting any combination, and, for example, C/(A + B + C) satisfying 0.015 to 0.085, B/(A + B + C)

satisfying 0.1 to 0.985, and A/(A + B + C) satisfying 0 to 0.885 may be set, C/(A + B + C) satisfying 0.015 to 0.085, B/(A + B + C) satisfying 0.1 to 0.485, and A/(A + B + C) satisfying 0.5 to 0.885 may be set, C/(A + B + C) satisfying 0.02 to 0.08, B/(A + B + C) satisfying 0 to 0.98, and A/(A + B + C) satisfying 0 to 0.98 may be set, C/(A + B + C) satisfying 0.02 to 0.08, B/(A + B + C) satisfying 0.2 to 0.98, and A/(A + B + C) satisfying 0 to 0.78 may be set, and C/(A + B + C) satisfying 0.02 to 0.08, B/(A + B + C) satisfying 0.2 to 0.45, and A/(A + B + C) satisfying 0.53 to 0.75 may be set.

[0015]

Examples of the method for obtaining a catalyst having C/(A + B + C) and A/(A + B + C) respectively falling within prescribed ranges in the ^{31}P-NMR spectrum include a method including producing such a catalyst by a method including steps (i) to (iii) described below, in which the amount of a tungsten raw material used and the pH of the resulting liquid A are adjusted in step (i), or the firing temperature and time are adjusted in step (iii).

[0016]

The ^{31}P-NMR spectrum is obtained by filling a sample tube with 300 mg of a powdery catalyst and performing measurement at room temperature with an apparatus such as AVANCE 300 (manufactured by Bruker). A 7-mm MAS probe is used in the measurement, and there are adopted measurement conditions of a resonant frequency of 121.4 MHz, a pulse width of 5.5 μs, a signal capture time of 0.066 seconds, a cumulative number of 64, a repetition waiting time of 150 seconds, and a MAS rotation frequency of 5000 Hz. The respective absolute values of the areas calculated by sectional measurement with respect to signals observed in ranges of -5.2 ppm or more and less than 0 ppm, -10 ppm or more and less than -5.2 ppm and -20 ppm or more and less than -10 ppm in the ^{31}P-NMR spectrum

in which the horizontal axis represents the chemical shift (ppm) and the vertical axis represents the signal detected are defined as A, B and C. The horizontal axis is drawn under the assumption that the chemical shift of an aqueous 85% phosphoric acid solution is 0 ppm.

[0017]

<Composition of catalyst>

The catalyst for methacrylic acid production according to the present embodiment preferably has a composition represented by the following formula (I) from the viewpoint of the yield of methacrylic acid. The catalyst may include a small amount of any element not described in the following formula (I).

$P_aMo_bW_cV_dCu_eA_fE_gG_hO_i$ (I)

In the formula (I), P, Mo, W, V, Cu and O respectively represent phosphorus, molybdenum, tungsten, vanadium, copper, and oxygen. A represents at least one element selected from the group consisting of antimony, bismuth, arsenicum, germanium, tellurium, selenium, and silicon. E represents at least one element selected from the group consisting of iron, zinc, chromium, tantalum, cobalt, nickel, manganese, titanium, and niobium. G represents at least one element selected from the group consisting of potassium, rubidium and cesium. a to i each represent the molar ratio of each component, b + c = 12, a = 0.5 to 3, c = 0.22 to 5, d = 0.01 to 3, e = 0.01 to 2, f = 0 to 3, g = 0 to 3, and h = 0.01 to 3 are satisfied, and i is the molar ratio of oxygen necessary for satisfying the valence of such each component.

[0018]

In the formula (I), c as the molar ratio of W (tungsten) satisfies c = 0.22 to 5. Thus, the structure C, which is particularly excellent in heat resistance, is favorably formed. The lower limit of c is preferably 0.23 or more, more

preferably 0.3 or more. The upper limit of c is preferably 3 or less, more preferably 2 or less, further preferably 1 or less, particularly preferably 0.8 or less.

[0019]

In the formula (I), from the viewpoint of an enhancement in yield of methacrylic acid, the lower limit of a is preferably 0.6 or more, more preferably 0.7 or more. The upper limit of a is preferably 2.5 or less, more preferably 2 or less. The lower limit of d is preferably 0.1 or more, more preferably 0.15 or more, further preferably 0.2 or more. The upper limit of d is preferably 2.5 or less, more preferably 2 or less, further preferably 1.5 or less. The lower limit of e is preferably 0.03 or more, more preferably 0.05 or more. The upper limit of e is preferably 2.5 or less, more preferably 2 or less. The lower limit of f is preferably 0.01 or more, more preferably 0.1 or more. The upper limit of f is preferably 2.5 or less, more preferably 2 or less. The upper limit of g is preferably 2 or less, more preferably 1.5 or less, further preferably 1 or less. The lower limit of h is preferably 0.1 or more, more preferably 0.3 or more. The upper limit of h is preferably 2.8 or less, more preferably 2.5 or less.

[0020]

The molar ratio of each component is a value determined by analyzing such each component of the catalyst dissolved in ammonia water, with ICP emission spectroscopy.

[0021]

[Method for producing catalyst for methacrylic acid production]

The catalyst for methacrylic acid production according to the present embodiment can be produced according to a known catalyst production method as long as the C/(A + B + C) in the ^{31}P-NMR spectrum is 0.015 to 0.085, and the catalyst is

preferably produced by a method including the following steps (i) to (iii).

(i) A step of mixing a phosphorus raw material, a molybdenum raw material and a tungsten raw material with a solvent, to prepare a solution or slurry (liquid A) having a pH of 0.1 to 4.

(ii) A step of drying the liquid A, to obtain a dried product.

(iii) A step of firing the dried product, to obtain a calcination product.

The method for producing the catalyst for methacrylic acid production according to the present embodiment may further include a molding step described below.

[0022]

Hereinafter, each step is described in detail.

<Step (i)>

In step (i), a phosphorus raw material, a molybdenum raw material and a tungsten raw material are mixed with a solvent, to prepare a solution or slurry (liquid A) having a pH of 0.1 to 4. The liquid A may be mixed with a raw material of any element other than phosphorus, molybdenum and tungsten in the formula (I), and is preferably mixed with a raw material of the element G.

The liquid A can be prepared by dissolving or suspending raw materials of catalyst components including the phosphorus raw material, the molybdenum raw material and the tungsten raw material, in a solvent.

[0023]

(Raw materials of catalyst components)

The raw materials of the catalyst component are not particularly limited, and nitrate, carbonate, acetate, an ammonium salt, oxide, halide, oxyacid, an oxyacid salt, and/or the like of each constituent element of the catalyst can be

used singly or in combination of two or more kinds thereof.

[0024]

Examples of the phosphorus raw material include phosphoric acid, phosphorus pentoxide, and ammonium phosphate. Examples of the molybdenum raw material include molybdenum oxides such as molybdenum trioxide, ammonium molybdates such as ammonium paramolybdate and ammonium dimolybdate, and molybdenum chloride.

[0025]

Examples of the tungsten raw material include tungsten oxide, sodium tungstate, phosphotungstic acid, and ammonium metatungstate, and a tungsten raw material having a solubility at 20°C of 4.1 g/100 mL or more preferably occupies 50% by mass or more of the entire tungsten raw material. Thus, heteropoly acid with tungsten as polyatoms is efficiently formed, and a catalyst in which the C/(A + B + C) is within a prescribed range can be easily obtained. Examples of such a tungsten raw material having a solubility at 20°C of 4.1 g/100 mL or more include phosphotungstic acid and ammonium metatungstate. Such a tungsten raw material having a solubility at 20°C of 4.1 g/100 mL or more occupies more preferably 70% by mass or more, further preferably 90% by mass or more of the tungsten raw material.

[0026]

In a case where a catalyst further including vanadium and copper is produced, examples of a vanadium raw material include ammonium metavanadate, vanadium pentoxide, vanadium chloride, and vanadyl oxalate. Examples of a copper raw material include copper sulfate, copper nitrate, copper oxide, copper carbonate, copper acetate, and copper chloride.

[0027]

The concentration of the raw materials of the catalyst components in the liquid A is not particularly limited, and

is preferably within a range of 5 to 90% by mass.

[0028]

(Solvent)

Examples of the solvent include water, ethyl alcohol, and acetone. These may be used singly or in combination of two or more kinds thereof. In particular, water is preferably used from an industrial viewpoint.

[0029]

(Preparation of liquid A)

The liquid A is preferably prepared with a preparation container by adding the raw materials of the catalyst components to the solvent and stirring them with heating. Thus, heteropoly acid suitable for production of methacrylic acid is sufficiently produced.

[0030]

The preparation can be usually performed at a heating temperature in the range of 30 to 150°C, and is preferably performed at a heating temperature in the range of 60 to 150°C. When the heating temperature is 60°C or more, the rate of generation of the heteropoly acid can be sufficiently increased, and when the heating temperature is 150°C or less, evaporation of the solvent can be suppressed. The lower limit of the heating temperature is more preferably 80°C or more, further preferably 90°C or more. The upper limit of the heating temperature is more preferably 130°C or less, further preferably 110°C or less. In addition, concentration and/or reflux may be made during heating, depending on the vapor pressure of the solvent used, or heating treatment may be made under a pressurized condition by operation in a closed container.

[0031]

The rate of temperature rise is not particularly limited, and is preferably 0.8 to 15°C/min. When the rate of

temperature rise is 0.8°C/min or more, the time necessary for step (i) can be shortened. When the rate of temperature rise is 15°C/min or less, temperature rise can be made with usual temperature rise equipment.

[0032]

The stirring is preferably performed at a stirring power of 0.01 kW/m^3 or more, more preferably 0.05 kW/m^3 or more. When the stirring power is 0.01 kW/m^3 or more, local irregularities of the temperature of the liquid A, the component, and the temperature are decreased and a structure suitable in a catalyst for methacrylic acid production is stably formed. The stirring is usually preferably performed at a stirring power of 3.5 kW/m^3 or less from the viewpoint of production cost of the catalyst.

[0033]

(Physical properties of liquid A)

Preferably, the pH of the liquid A is 0.1 to 4, and the lower limit thereof is 0.5 or more and the upper limit thereof is 3 or less. Thus, production reaction of heteropoly acid suitable for methacrylic acid production is stabilized. Examples of the method for allowing the pH of the liquid A to be 0.1 to 4 include a method in which molybdenum trioxide is used as the molybdenum raw material or a method in which a raw material compound is appropriately selected to adjust the content of nitric acid ions or oxalic acid ions.

[0034]

<Step (ii)>

In step (ii), the liquid A obtained in step (i) is spray-dried, to obtain a dried product.

Examples of the drying method include known methods such as a drum drying method, a flash drying method, an evaporation drying method, and a spray drying method. In particular, a spray drying method is preferably used because

a particulate dried product is obtained and the shape of the dried product is a neat spherical shape.

[0035]

The drying temperature differs depending on the drying method, and can be usually 100 to 500°C, and the lower limit is preferably 140°C or more and the upper limit is preferably 400°C or less. The drying is preferably performed so that the content rate of moisture in the resulting dried product is 4.5% by mass or less, more preferably 0.1 to 4.5% by mass. These conditions are not particularly limited, and can be appropriately selected depending on the desired shape and size of the dried product.

The dried product obtained in step (ii) may be, if necessary, subjected to molding described below.

[0036]

<Molding step>

In the molding step, the dried product obtained in step (ii) is, if necessary, molded. Here, the molding may be performed after step (iii) described below.

[0037]

The molding method is not particularly limited, any known dry or wet molding method can be applied, and examples include tablet molding, press molding, extrusion molding, and granulation molding. The shape of a molded product is not particularly limited, and examples include a columnar shape, a ring shape, and a spherical shape. When the molding is made, only the dried product is preferably molded without addition of any carrier or the like to the dried product, and, for example, a known additive such as graphite or talc may be, if necessary, added. In a case where a carrier is used, the carrier is not particularly limited, and examples preferably include silica.

[0038]

<Step (iii)>

In the firing step, the dried product obtained in step (ii), and the dried product after molding, obtained in the molding step, are calcined, to obtain a clacination product.

[0039]

The firing can be performed under flow of at least one of an oxygen-containing gas such as air, and an inert gas, and the firing is preferably performed under flow of an oxygen-containing gas such as air. The inert gas here refers to a gas causing no reduction in catalyst activity, and examples include nitrogen, carbon dioxide gas, helium, and argon. These may be used singly, or as a mixture of two or more kinds thereof.

[0040]

The shape of a firing container is not particularly limited, and, for example, a box-type or tubular container can be used. The firing can also be performed with division into a plurality of containers and filling. In particular, a tubular container having a cross-sectional area of 1 to 100 cm^2 is preferably used.

[0041]

The firing temperature (the highest temperature during the firing) is preferably 200 to 700°C, and the lower limit is more preferably 320°C or more and the upper limit is more preferably 450°C or less.

[0042]

The calcination product obtained as above can be used as the catalyst for methacrylic acid production. The calcination product may be molded as described with respect to the molding step. In the present embodiment, the calcination product, and the calcination product after the molding are collectively referred to as “catalyst”.

[0043]

[Method for producing methacrylic acid]

A method for producing methacrylic acid according to the present embodiment includes oxidizing methacrolein with the catalyst for methacrylic acid production according to the present embodiment. The method for producing methacrylic acid according to the present embodiment includes oxidizing methacrolein with a catalyst for methacrylic acid production, produced by the production method according to the present embodiment. According to such a method, methacrylic acid can be produced at a high yield.

[0044]

The method for producing methacrylic acid according to the present embodiment can be carried out by contacting the catalyst for methacrylic acid production according to the present embodiment and a raw material gas containing methacrolein. A fixed bed-type reactor can be used in this reaction. This reaction can be performed by filling the reactor with the catalyst, and feeding the raw material gas to the reactor. A catalyst layer may be a single layer, or a plurality of such catalysts different in activity may be divided respectively to a plurality of layers and subjected to filling. The catalyst may be diluted with an inert carrier and subjected to filling in order to control activity.

[0045]

The concentration of methacrolein in the raw material gas is preferably 1 to 20% by volume, and the lower limit thereof is more preferably 3% by volume or more and the upper limit thereof is more preferably 10% by volume or less. Methacrolein as a raw material may include a small amount of impurities having no substantial influence on the present reaction of lower saturated aldehyde or the like.

[0046]

The oxygen source of the raw material gas is not

particularly limited, and air is preferably used from an industrial viewpoint. A gas in which pure oxygen is mixed with air or the like can also be, if necessary, used. The proportion of oxygen in the raw material gas is not particularly limited, the proportion based on 1 mol of methacrolein is preferably 0.4 to 4 mol, the lower limit thereof is more preferably 0.5 mol or more, and the upper limit thereof is more preferably 3 mol or less.

[0047]

The raw material gas may be one diluted with an inert gas such as nitrogen or carbon dioxide from the viewpoint of economic performance. Water vapor may also be further added to the raw material gas. Methacrylic acid can be obtained at a high yield by reaction performed in the presence of water vapor. The concentration of water vapor in the raw material gas is preferably 0.1 to 50% by volume, the lower limit is more preferably 1% by volume or more, and the upper limit is more preferably 40% by volume.

[0048]

The contact time between the raw material gas and the catalyst for methacrylic acid production is preferably 1.5 to 15 seconds, the lower limit is more preferably 2 seconds or more, and the upper limit is more preferably 10 seconds or less. The reaction pressure is preferably 0.1 to 1 MPa (G). Herein, (G) means the gauge pressure. The reaction temperature is preferably 200 to 450°C, and the lower limit is more preferably 250°C or more and the upper limit is more preferably 400°C or less.

[0049]

In the production of methacrylic acid, the location of the catalyst in the reactor, the proportion of the catalyst in the reactor, and the like are not particularly limited, and any form commonly used can be applied.

[0050]

[Method for producing methacrylic acid ester]

A method for producing methacrylic acid ester according to the present embodiment includes esterifying methacrylic acid produced by the production method according to the present embodiment. In other words, the method for producing methacrylic acid ester according to the present embodiment includes a step of producing methacrylic acid by the production method according to the present embodiment and a step of esterifying the methacrylic acid.

[0051]

The alcohol to be allowed to react with the methacrylic acid is not particularly limited, and examples include methanol, ethanol, n-propanol, isopropanol, n-butanol, and isobutanol. Examples of the methacrylic acid ester obtained include methyl methacrylate, ethyl methacrylate, propyl methacrylate, isopropyl methacrylate, butyl methacrylate, and isobutyl methacrylate. Such esterification reaction can be performed in the presence of an acidic catalyst such as a sulfonic acid-type cation-exchange resin. The temperature in the esterification reaction is preferably 50 to 200°C.

[0052]

The pressure in the esterification reaction, the location of the catalyst in the reactor, the proportion of the catalyst in the reactor, and the like are not particularly limited, and any form commonly used can be applied.

EXAMPLES

[0053]

Hereinafter, Production Examples of the catalyst according to the present embodiment, and Reaction Examples with the catalyst are described together with Comparative Examples. In the following Examples and Comparative Examples, “part(s)” means part(s) by mass.

[0054]

(Composition ratio of catalyst)

The molar ratio of each component was determined by analyzing such each component of the catalyst dissolved in ammonia water, with ICP emission spectroscopy.

[0055]

(^{31}P-NMR measurement)

The ^{31}P-NMR spectrum was obtained by filling a sample tube with 300 mg of a powdery catalyst and performing measurement at room temperature with AVANCE 300 (manufactured by Bruker). A 7-mm MAS probe was used in the measurement, and there were adopted measurement conditions of a resonant frequency of 121.4 MHz, a pulse width of 5.5 μs, a signal capture time of 0.066 seconds, a cumulative number of 64, a repetition waiting time of 150 seconds, and a MAS rotation frequency of 5000 Hz. The respective absolute values of the areas calculated by sectional measurement with respect to signals observed in ranges of -5.2 ppm or more and less than 0 ppm, -10 ppm or more and less than -5.2 ppm, and -20 ppm or more and less than -10 ppm in the ^{31}P-NMR spectrum in which the horizontal axis represented the chemical shift (ppm) and the vertical axis represented the signal detected were defined as A, B, and C. The horizontal axis was drawn under the assumption that the chemical shift of an aqueous 85% phosphoric acid solution was 0 ppm.

[0056]

(Pyrolysis temperature of catalyst)

The pyrolysis temperature as an index of heat resistance of the catalyst was measured with a TG/DTA measurement apparatus, as follows. Fifty mg of alumina was used as reference, and 50 mg of a powdery catalyst was heated from room temperature to 550°C at 10°C/min in an air atmosphere. The exothermic onset temperature at which exotherm

corresponding to 1.8 μV or more at a temperature rise of 15°C or more was observed in a temperature region of 380°C or more in the resulting DTA curve was defined as the pyrolysis temperature. It is meant that, as the pyrolysis temperature of the catalyst is higher, heat resistance is higher.

[0057]

(Analysis of raw material gas and product)

The raw material gas and the product were analyzed with the following gas chromatography.

GC-2014 manufactured by Shimadzu Corporation (column: DB-FFAP manufactured by J&W, 30 m × 0.32 mm, film thickness 1.0 μm)

GC-8A manufactured by Shimadzu Corporation (column: Molecular Sieve, 2.0 M × 3.0 mm ID)

GC-8A manufactured by Shimadzu Corporation (column: Porapak Q, 2.0 M × 3.0 mm ID)

The yield of methacrylic acid was calculated by the following expression.

Yield of methacrylic acid (%) = (N2/N1) × 100

Here, N1 represents the number of moles of methacrolein fed and N2 represents the number of moles of methacrylic acid produced.

[0058]

(Tungsten raw material)

Tungsten raw materials used in Examples and Comparative Examples are as follows.

Ammonium metatungstate (manufactured by NIPPON INORGANIC COLOUR & CHEMICAL CO., LTD.) Solubility in water at 20°C: 10 g/100 mL

Phosphotungstic acid (manufactured by NIPPON INORGANIC COLOUR & CHEMICAL CO., LTD.) Solubility in water at 20°C: 40 g/100 mL or more

[0059]

<Example 1>

A diluted product obtained by diluting 294.0 parts of molybdenum trioxide, 10.2 parts of ammonium metavanadate, 10.6 parts of ammonium metatungstate, and 30.0 parts of an aqueous 85% by mass phosphoric acid solution with 36 parts of pure water, and a dissolved product obtained by dissolving 6.3 parts of copper (II) nitrate trihydrate in 9.0 parts of pure water were mixed with 1200 parts of pure water at room temperature. The resulting slurry was heated to 95°C at 2°C/min, and stirred for 2 hours. Next, a dissolved product obtained by dissolving 40.4 parts of cesium bicarbonate in 60 parts of pure water at room temperature was mixed, and stirred at 95°C for 15 minutes. Next, a dissolved product obtained by dissolving 27.5 parts of ammonium carbonate in 78 parts of pure water was mixed, and stirred at 95°C for 15 minutes, and thus a liquid A was obtained. The pH of the liquid A is shown in Table 1.

The liquid A obtained was heated, and evaporated to dryness, and thus a dried product was obtained.

The dried product obtained was pressure molded, ground, and classified with a sieve so that the particle size was within a range of 710 μm to 2.36 mm. The resulting ground object was calcined at 380°C for 5 hours under flow of air, and the resulting calcination product was adopted as a catalyst. The composition excluding oxygen, of the catalyst, satisfied $P_{1.5}Mo_{11.8}W_{0.2}V_{0.5}Cu_{0.15}Cs_{1.2}$. The catalyst was subjected to ^{31}P-NMR measurement and pyrolysis temperature measurement. The results are shown in Table 1.

A fixed bed flow type reactor was filled with 8 g of the resulting catalyst diluted with 10 g of silicon carbide. Next, a raw material gas including 5% by volume of methacrolein, 10% by volume of oxygen, 30% by volume of water vapor and 55% by volume of nitrogen was allowed to flow for a contact time

of 178 hr·g/mol, to perform oxidation reaction of methacrolein at a reaction temperature of 300°C. The reaction performance is shown in Table 1.

<Example 2>

A liquid A was obtained by the same method as in Example 1 except that 292.1 parts of molybdenum trioxide and 13.6 parts of ammonium metatungstate were used. The pH of the liquid A is shown in Table 1.

The liquid A obtained was heated, and evaporated to dryness, and thus a dried product was obtained.

The dried product obtained was used, and a catalyst was obtained by the same method as in Example 1. The composition excluding oxygen, of the catalyst, satisfied $P_{1.5}Mo_{11.7}W_{0.3}V_{0.5}Cu_{0.15}Cs_{1.2}$. The catalyst was subjected to ^{31}P-NMR measurement and pyrolysis temperature measurement. The results are shown in Table 1.

The catalyst obtained was used, and oxidation reaction of methacrolein was performed by the same method as in Example 1. The reaction performance is shown in Table 1.

<Example 3>

A liquid A was obtained by the same method as in Example 1 except that 287.1 parts of molybdenum trioxide and 22.6 parts of ammonium metatungstate were used. The pH of the liquid A is shown in Table 1.

The liquid A obtained was heated, and evaporated to dryness, and thus a dried product was obtained.

The dried product obtained was used, and a catalyst was obtained by the same method as in Example 1. The composition excluding oxygen, of the catalyst, satisfied $P_{1.5}Mo_{11.5}W_{0.5}V_{0.5}Cu_{0.15}Cs_{1.2}$. The catalyst was subjected to ^{31}P-NMR measurement and pyrolysis temperature measurement. The results are shown in Table 1.

The catalyst obtained was used, and oxidation reaction

of methacrolein was performed by the same method as in Example 1. The reaction performance is shown in Table 1.

[0060]

<Example 4>

A liquid A was obtained by the same method as in Example 1 except that 285.0 parts of molybdenum trioxide and 29.0 parts of an aqueous 85% by mass phosphoric acid solution were used, and 29.7 parts of phosphotungstic acid was used instead of 10.6 parts of ammonium metatungstate. The pH of the liquid A is shown in Table 1.

The liquid A obtained was heated, and evaporated to dryness, and thus a dried product was obtained.

The dried product obtained was used, and a catalyst was obtained by the same method as in Example 1. The composition excluding oxygen, of the catalyst, satisfied $P_{1.5}Mo_{11.4}W_{0.6}V_{0.5}Cu_{0.15}Cs_{1.2}$. The catalyst was subjected to ^{31}P-NMR measurement and pyrolysis temperature measurement. The results are shown in Table 1.

The catalyst obtained was used, and oxidation reaction of methacrolein was performed by the same method as in Example 1. The reaction performance is shown in Table 1.

<Example 5>

A liquid A was obtained by the same method as in Example 1 except that 277.2 parts of molybdenum trioxide and 40.8 parts of ammonium metatungstate were used. The pH of the liquid A is shown in Table 1.

The liquid A obtained was heated, and evaporated to dryness, and thus a dried product was obtained.

The dried product obtained was used, and a catalyst was obtained by the same method as in Example 1. The composition excluding oxygen, of the catalyst, satisfied $P_{1.5}Mo_{11.1}W_{0.9}V_{0.5}Cu_{0.15}Cs_{1.2}$. The catalyst was subjected to ^{31}P-NMR measurement and pyrolysis temperature measurement. The

results are shown in Table 1.

The catalyst obtained was used, and oxidation reaction of methacrolein was performed by the same method as in Example 1. The reaction performance is shown in Table 1.

[0061]

<Comparative Example 1>

A liquid A was obtained by the same method as in Example 1 except that 270.0 parts of molybdenum trioxide and 53.2 parts of ammonium metatungstate were used. The pH of the liquid A is shown in Table 1.

The liquid A obtained was heated, and evaporated to dryness, and thus a dried product was obtained.

The dried product obtained was used, and a catalyst was obtained by the same method as in Example 1. The composition excluding oxygen, of the catalyst, satisfied $P_{1.5}Mo_{10.8}W_{1.2}V_{0.5}Cu_{0.15}Cs_{1.2}$. The catalyst was subjected to ^{31}P-NMR measurement and pyrolysis temperature measurement. The results are shown in Table 1.

The catalyst obtained was used, and oxidation reaction of methacrolein was performed by the same method as in Example 1. The reaction performance is shown in Table 1.

[0062]

<Comparative Example 2>

A liquid A was obtained by the same method as in Example 1 except that 255.0 parts of molybdenum trioxide and 79.8 parts of ammonium metatungstate were used. The pH of the liquid A is shown in Table 1.

The liquid A obtained was heated, and evaporated to dryness, and thus a dried product was obtained.

The dried product obtained was used, and a catalyst was obtained by the same method as in Example 1. The composition excluding oxygen, of the catalyst, satisfied $P_{1.5}Mo_{10.2}W_{1.8}V_{0.5}Cu_{0.15}Cs_{1.2}$. The catalyst was subjected to ^{31}P-NMR

measurement and pyrolysis temperature measurement. The results are shown in Table 1.

The catalyst obtained was used, and oxidation reaction of methacrolein was performed by the same method as in Example 1. The reaction performance is shown in Table 1.

[0063]

<Comparative Example 3>

A liquid A was obtained by the same method as in Example 1 except that 270.0 parts of molybdenum trioxide and 27.4 parts of an aqueous 85% by mass phosphoric acid solution were used, and 59.4 parts of phosphotungstic acid was used instead of 10.6 parts of ammonium metatungstate. The pH of the liquid A is shown in Table 1.

The liquid A obtained was heated, and evaporated to dryness, and thus a dried product was obtained.

The dried product obtained was used, and a catalyst was obtained by the same method as in Example 1. The composition excluding oxygen, of the catalyst, satisfied $P_{1.47}Mo_{10.8}W_{1.2}V_{0.5}Cu_{0.15}Cs_{1.2}$. The catalyst was subjected to ^{31}P-NMR measurement and pyrolysis temperature measurement. The results are shown in Table 1.

The catalyst obtained was used, and oxidation reaction of methacrolein was performed by the same method as in Example 1. The reaction performance is shown in Table 1.

[0064]

<Comparative Example 4>

300.0 parts of phosphotungstic acid was pressure molded, ground, and classified with a sieve so that the particle size was within a range of 710 μm to 2.36 mm. The resulting ground object was calcined at 380°C for 5 hours under flow of air, and the resulting cacination product was adopted as a catalyst. The composition excluding oxygen, of the catalyst, satisfied P_1W_{12}. The catalyst was subjected to ^{31}P-NMR measurement and

pyrolysis temperature measurement. The results are shown in Table 1.

The catalyst obtained was used, and oxidation reaction of methacrolein was performed by the same method as in Example 1. The reaction performance is shown in Table 1.

[0065]

<Comparative Example 5>

A powder obtained by firing 300.0 parts of phosphomolybdic acid (manufactured by NIPPON INORGANIC COLOUR & CHEMICAL CO., LTD.) at 380°C for 5 hours was ground, and classified with a sieve so that the particle size was within a range of 710 μm to 2.36 mm. The resulting ground object was calcined at 380°C for 5 hours under flow of air, and thus a catalyst was produced. The composition excluding oxygen, of the catalyst, satisfied P_1Mo_{12}. The catalyst was subjected to ^{31}P-NMR measurement and pyrolysis temperature measurement. The results are shown in Table 1.

The catalyst obtained was used, and oxidation reaction of methacrolein was performed by the same method as in Example 1. The reaction performance is shown in Table 1.

[0066]

[Table 1]

Table 1

	Tungsten raw material	Compositional ratio of catalyst						pH of liquid A	P-NMR area ratio			Pyrolysis temperature	Yield of methacrylic acid [%]
		a	b	c	d	e	h		A/(A+B+C)	B/(A+B+C)	C/(A+B+C)		
Example 1	Ammonium metatungstate	1.5	11.8	0.2	0.5	0.15	1.2	1.9	0.65	0.31	0.04	442	49.6
Example 2	Ammonium metatungstate	1.5	11.7	0.3	0.5	0.15	1.2	2.7	0.69	0.28	0.03	447	50.6
Example 3	Ammonium metatungstate	1.5	11.5	0.5	0.5	0.15	1.2	2.8	0.64	0.32	0.04	446	45.3
Example 4	Phosphotungstic acid	1.5	11.4	0.6	0.5	0.15	1.2	2.3	0.58	0.36	0.06	439	50.5
Example 5	Ammonium metatungstate	1.5	11.1	0.9	0.5	0.15	1.2	3.0	0.57	0.38	0.05	451	34.8
Comparative Example 1	Ammonium metatungstate	1.5	10.8	1.2	0.5	0.15	1.2	3.2	0.40	0.37	0.23	453	7.6
Comparative Example 2	Ammonium metatungstate	1.5	10.2	1.8	0.5	0.15	1.2	3.4	0.29	0.41	0.30	453	4.8
Comparative Example 3	Phosphotungstic acid	1.47	10.8	1.2	0.5	0.15	1.2	1.8	0.48	0.42	0.10	439	33.2
Comparative Example 4	Phosphotungstic acid	1	0	12	0	0	0	–	0.01	0.05	0.94	600	1.3
Comparative Example 5	–	1	12	0	0	0	0	–	1.00	0.00	0.00	416	13.9

[0067]

As shown in Table 1, each of Examples 1 to 5, in which the catalyst having C/(A + B + C) within a prescribed range in the ^{31}P-NMR spectrum was used, allowed the catalyst to be high in pyrolysis temperature and could provide methacrylic acid at a high yield.

Here, methacrylic acid obtained in the present Examples can be esterified, thereby obtaining methacrylic acid ester.

INDUSTRIAL APPLICABILITY

[0068]

According to the present invention, there can be provided a catalyst which has high heat resistance and which can allow for production of methacrylic acid at a high yield.