

DESCRIPTION

TITLE OF INVENTION: CATALYST FOR PRODUCTION OF METHACRYLIC ACID, METHOD OF PRODUCING THE SAME, METHOD OF PRODUCING METHACRYLIC ACID, AND METHOD OF PRODUCING METHACRYLIC ACID
5 ESTER

TECHNICAL FIELD

[0001]

The present invention relates to a catalyst for production of methacrylic acid, a method of producing the same, a method of producing methacrylic acid, and a method
10 of producing a methacrylic acid ester.

BACKGROUND ART

[0002]

As a catalyst for production of methacrylic acid to be used in the production of methacrylic acid by vapor phase catalytic oxidation of methacrolein with molecular
15 oxygen, heteropoly acid-based catalysts containing a molybdenum element and a phosphorus element are known. Examples of such heteropoly acid-based catalysts may include proton heteropoly acids in which the counter cation is a proton and heteropoly acid salts in which a part of the protons is substituted with cations other than a proton. As the heteropoly acid salt, an alkali metal salt in which the cation is an
20 alkali metal ion and an ammonium salt in which the cation is an ammonium ion are known. Incidentally, the proton type heteropoly acid is soluble in water, but the alkali metal salt of heteropoly acid is generally insoluble because of a large ionic radius of the cation (Non-Patent Document 1).

[0003]

25 Patent Document 1 proposes a catalyst for production of methacrylic acid, which contains an acidic salt of a Keggin type heteropoly acid containing phosphorus and molybdenum and in which the ratio of the peak intensity at an interplanar spacing of from 3.24 to 3.26 Å to the peak intensity at an interplanar spacing of from 3.38 to 3.41

Å in the X-ray diffraction is from 0.001 to 0.01.

PRIOR ART LITERATURE

PATENT LITERATURE

[0004]

5 Patent Document 1: JP 2005-131577 A

NON-PATENT LITERATURE

[0005]

Non-Patent Document 1: Masayuki OTAKE, Takeshi ONODA, SHOKUBAI (CATALYST), vol. 18, No. 6 (1976)

10 SUMMARY OF THE INVENTION

PROBLEM TO BE SOLVED BY THE INVENTION

[0006]

15 However, the catalyst described in Patent Document 1 does not provide a sufficient methacrylic acid yield as an industrial catalyst in the case of being used in the production of methacrylic acid by vapor phase catalytic oxidation of methacrolein with molecular oxygen, and the catalyst is thus desired to be further improved. An object of the invention is to provide a catalyst for production of methacrylic acid providing a high methacrylic acid yield.

MEANS FOR SOLVING PROBLEM

20 [0007]

The invention is the following [1] to [11].

[0008]

25 [1] A catalyst for production of methacrylic acid, containing a heteropoly acid salt containing at least phosphorus, molybdenum, and vanadium, in which the catalyst is used in production of methacrylic acid by vapor phase catalytic oxidation of methacrolein with molecular oxygen, and a ratio (I_1/I_0) of an absolute value of a peak intensity I_1 of a (322) plane attributed to a cubic crystal structure of a proton type heteropoly acid to an absolute value of a peak intensity I_0 of a (222) plane attributed to a

cubic crystal structure of a heteropoly acid salt is 0.01 or more and 0.80 or less in an X-ray diffraction pattern of the catalyst for production of methacrylic acid left to stand for 12 hours in an environment kept at a temperature of 30°C and a humidity of 90% measured using Cu-K α radiation.

5 [0009]

[2] The catalyst for production of methacrylic acid according to [1], in which I_1/I_0 is 0.05 or more and 0.75 or less.

[0010]

10 [3] The catalyst for production of methacrylic acid according to [2], in which I_1/I_0 is 0.40 or more and 0.73 or less.

[0011]

15 [4] A method of producing the catalyst for production of methacrylic acid according to any one of [1] to [3], including a step of obtaining a catalyst precursor by drying, using a heteropoly acid salt-containing liquid i containing at least a phosphorus raw material and an alkali metal ion raw material, and a heteropoly acid salt-containing liquid ii containing at least a phosphorous raw material and an ammonium ion raw material.

[0012]

20 [5] The method of producing the catalyst for production of methacrylic acid according to [4], including a step of obtaining a catalyst precursor by mixing a dried product of the heteropoly acid salt-containing liquid i and a dried product of the heteropoly acid salt-containing liquid ii.

[0013]

25 [6] The method of producing the catalyst for production of methacrylic acid according to [4], including a step of obtaining a heteropoly acid salt-containing liquid iii by mixing the heteropoly acid salt-containing liquid i and the heteropoly acid salt-containing liquid ii, and obtaining a catalyst precursor by drying this heteropoly acid salt-containing liquid iii.

[0014]

[7] The method of producing the catalyst for production of methacrylic acid according to [4], including a step of obtaining a heteropoly acid salt-containing liquid iv by mixing a dried product of either the heteropoly acid salt-containing liquid i or the heteropoly acid salt-containing liquid ii with the other heteropoly acid salt-containing liquid, and obtaining a catalyst precursor by drying this heteropoly acid salt-containing liquid iv.

[0015]

[8] The method of producing the catalyst for production of methacrylic acid according to any one of [4] to [7], in which the heteropoly acid salt-containing liquids i and ii satisfy the following Formulas (1) to (3).

[0016]

$$1.5 \leq \text{AMi}/\text{Pi} \leq 3.0 \quad (1)$$

$$4.0 \leq \text{NH}_{4\text{ii}}/\text{Pii} \leq 5.0 \quad (2)$$

$$1.0 \leq \text{Pii}/\text{Pi} \leq 2.0 \quad (3)$$

(In Formulas (1) to (3), AMi denotes the number of moles of an alkali metal ion contained in the heteropoly acid-containing liquid i, Pi denotes the number of moles of phosphorus contained in the heteropoly acid-containing liquid i, NH_{4ii} denotes the number of moles of an ammonium ion contained in the heteropoly acid-containing liquid ii, and Pii denotes the number of moles of phosphorus contained in the heteropoly acid-containing liquid ii, respectively.).

[0017]

[9] A method of producing methacrylic acid, including producing methacrylic acid by vapor phase catalytic oxidation of methacrolein with molecular oxygen in presence of the catalyst for production of methacrylic acid according to any one of [1] to [3].

[0018]

[10] A method of producing a methacrylic acid ester, including esterifying methacrylic acid produced by the method of producing methacrylic acid according to [9].

[0019]

[11] A method of producing a methacrylic acid ester, including producing methacrylic acid by the method according to [9] and esterifying the methacrylic acid.

EFFECT OF THE INVENTION

5 [0020]

According to the invention, it is possible to provide a catalyst for production of methacrylic acid providing a high methacrylic acid yield.

MODE(S) FOR CARRYING OUT THE INVENTION

[0021]

10 [Catalyst for production of methacrylic acid]

The catalyst for production of methacrylic acid according to the invention is a catalyst which is used in the production of methacrylic acid by vapor phase catalytic oxidation of methacrolein with molecular oxygen and contains a heteropoly acid salt containing at least phosphorus, molybdenum, and vanadium. The ratio (I_1/I_0) (hereinafter also referred to as the peak intensity ratio (I_1/I_0)) of an absolute value of a peak intensity I_1 of a (322) plane attributed to a cubic crystal structure of a proton type heteropoly acid to an absolute value of a peak intensity I_0 of a (222) plane attributed to a cubic crystal structure of a heteropoly acid salt is 0.01 or more and 0.80 or less in an X-ray diffraction pattern of the catalyst (hereinafter also referred to as the catalyst after pretreatment) obtained by leaving the catalyst for production of methacrylic acid to stand (hereinafter also referred to as the pretreatment) for 12 hours in an environment kept at a temperature of 30°C and a humidity of 90% measured using Cu-K α radiation.

[0022]

The element composition of the catalyst for production of methacrylic acid according to the invention is not particularly limited as long as at least phosphorus, molybdenum and vanadium are contained, but other elements may be further contained in addition to phosphorus, molybdenum and vanadium. Examples of other elements may include copper and cesium. One kind of these may be further contained or two or more kinds of these may be further contained. It is preferable that the catalyst for production of methacrylic acid according to the invention has an element composition

represented by the following Formula (4) from the viewpoint of methacrylic acid yield.

[0023]



In Formula (4), Mo, P, V, Cu, and O are symbols for elements molybdenum, phosphorus, vanadium, copper, and oxygen, respectively. A denotes at least one kind of element selected from the group consisting of antimony, bismuth, arsenic, germanium, zirconium, tellurium, silver, selenium, silicon, tungsten, and boron. E denotes at least one kind of element selected from the group consisting of iron, zinc, chromium, magnesium, calcium, strontium, tantalum, cobalt, nickel, manganese, barium, titanium, tin, lead, niobium, indium, sulfur, palladium, gallium, cerium, and lanthanum. G denotes at least one kind of element selected from the group consisting of lithium, sodium, potassium, rubidium, cesium, and thallium. a, b, c, d, e, f, g, and h denote the atomic ratios of the respective elements. When $a = 12$, $b = 0.5$ to 3 , $c = 0.01$ to 3 , $d = 0.01$ to 2 , $e = 0.1$ to 3 , $f = 0$ to 3 , $g = 0.01$ to 3 , and h is the atomic ratio of oxygen required to satisfy the valences of the respective elements. Incidentally, the element composition is a value to be calculated by analyzing the components of the catalyst dissolved in ammonia water by ICP atomic emission spectroscopy.

[0024]

In the invention, the peak intensity ratio (I_1/I_0) satisfies the range of 0.01 or more and 0.80 or less when the X-ray diffraction pattern of the catalyst after pretreatment obtained by subjecting the catalyst according to the invention to the pretreatment is measured using Cu-K α radiation. The adsorption sites of methacrolein on the catalyst surface increase and the catalytic activity is improved as the peak intensity ratio (I_1/I_0) is 0.01 or more. In addition, the progress of sequential oxidation of methacrylic acid can be suppressed as the peak intensity ratio (I_1/I_0) is 0.80 or less. Hence, methacrylic acid can be obtained at a high yield when the catalyst according to the invention is used in the production of methacrylic acid. In addition, it can be expected that a high methacrylic acid yield is maintained even when the catalyst is used for a long period of time as a heteropoly acid salt and a proton type heteropoly acid are contained in a predetermined proportion as in the invention.

[0025]

In the measurement of X-ray diffraction pattern, the catalyst for production of methacrylic acid is first subjected to the pretreatment. The pretreatment is conducted by leaving the catalyst to stand for 12 hours in an environment kept at a temperature of 30°C and a humidity of 90%. As the pretreatment is conducted, the water molecules in the heteropoly acid contained in the catalyst for production of methacrylic acid are hydrated and the cubic crystal structure of the proton type heteropoly acid is formed. The diffraction pattern of the catalyst after pretreatment which has been subjected to the pretreatment is attained by X-ray diffraction (anticathode Cu-K α radiation), and the ratio (I_1/I_0) of the absolute value of the peak intensity I_1 of the (322) plane attributed to the cubic crystal structure of the proton type heteropoly acid to the absolute value of the peak intensity I_0 of the (222) plane attributed to the cubic crystal structure of the heteropoly acid salt is calculated.

[0026]

For example, in the case of $\text{Cs}_4\text{PVMo}_{11}\text{O}_{40}$ which is a heteropoly acid salt containing cesium as a cation, the peak of the (222) plane appears at a position of $2\theta = 26.241^\circ$ (Troemel, M., Inst. f. Anorganische Chem, Frankfurt, Germany., ICDD Grant-in-Aid, (1995)). In addition, in the case of $\text{H}_4\text{PVMo}_{11}\text{O}_{40}\cdot 32\text{H}_2\text{O}$ which is a proton type heteropoly acid, the peak of the (322) plane appears at a position of $2\theta = 26.801^\circ$ (Troemel, M., Inst. f. Anorganische Chem, Frankfurt, Germany., ICDD Grant-in-Aid (1994)). In addition, the peak positions do not necessarily match in a case in which poly atoms or hetero atoms of the heteropoly acid are substituted with other elements or since the number of equivalent of cation of the heteropoly acid salt is different, but the positions of the planes can be confirmed by observing the peak pattern. In addition, in a case in which a plurality of salts are present as the heteropoly acid salt and a plurality of peak patterns can be confirmed, the sum of the absolute values of the intensities of the respective peaks of the (222) planes attributed to the cubic crystal structures of the heteropoly acid salts is taken as I_0 . The same applies to I_1 . The X-ray diffraction pattern can be measured by using an apparatus for X-ray structure analysis (trade name: X'Pert PRO MPD, manufactured by PANalytical B.V.).

[0027]

The peak intensity ratio (I_1/I_0) is 0.01 or more and 0.80 or less, and the lower

limit thereof is preferably 0.05 or more, more preferably 0.40 or more, and still more preferably 0.50 or more from the viewpoint of achieving a higher methacrylic acid yield. The upper limit thereof is preferably 0.75 or less, more preferably 0.73 or less, and still more preferably 0.70 or less.

5 [0028]

[Method of producing catalyst for production of methacrylic acid]

The method of producing the catalyst for production of methacrylic acid according to the invention is not particularly limited, but for example, the catalyst for production of methacrylic acid can be produced by the following method. The method
10 includes a step (hereinafter also referred to as the catalyst raw material liquid preparing step) of preparing a catalyst raw material liquid by dissolving or suspending at least a phosphorous raw material, a molybdenum raw material, and a vanadium raw material in a solvent, a step (hereinafter also referred to as the cation adding step) of adding a cation raw material to the catalyst raw material liquid to obtain a heteropoly acid salt-
15 containing liquid, a step (hereinafter also referred to as the drying step) of drying the heteropoly acid salt-containing liquid to obtain a catalyst precursor, and a step (hereinafter also referred to as the heat treatment step) of subjecting the catalyst precursor to a heat treatment to produce a catalyst for production of methacrylic acid. Here, a step (hereinafter also referred to as the molding step) of molding the catalyst
20 precursor before the heat treatment step may be included. It is particularly preferable that the method of producing the catalyst for production of methacrylic acid according to the invention includes a step of obtaining a catalyst precursor by drying, using a heteropoly acid salt-containing liquid i containing at least a phosphorus raw material and an alkali metal ion raw material, and a heteropoly acid salt-containing liquid ii
25 containing at least a phosphorous raw material and an ammonium ion raw material.

[0029]

(Catalyst raw material liquid preparing step)

In the present step, a catalyst raw material liquid is prepared by dissolving or suspending at least a phosphorus raw material, a molybdenum raw material, and a
30 vanadium raw material in a solvent.

[0030]

The raw material compounds of the respective elements are not particularly limited, and nitrates, carbonates, acetates, ammonium salts, oxides, halides, oxo acids, oxo acid salts, and the like of the respective elements can be used singly or in
5 combination of two or more kinds thereof. For example, phosphoric acid, phosphorus pentaoxide, ammonium phosphate, and the like can be used as the phosphorous raw material. Molybdenum trioxide, ammonium paramolybdate, molybdic acid, molybdenum chloride, and the like can be used as the molybdenum raw material. Ammonium metavanadate, phosphovanadomolybdic acid, vanadium pentoxide, and the
10 like can be used as the vanadium raw material. These may be used singly or two or more kinds thereof may be used concurrently.

[0031]

Water, ethyl alcohol, acetone, and the like can be used as the solvent for dissolving or suspending the raw material compounds. These may be used singly or
15 two or more kinds thereof may be used concurrently. Among these, water is preferable as the solvent.

[0032]

Incidentally, in the present step, one kind of catalyst raw material liquid may be prepared or two or more kinds of catalyst raw material liquids may be prepared. It is
20 particularly preferable to prepare two or more kinds of catalyst raw material liquids and to mix these liquids before and after the drying step to be described later from the viewpoint of being easy to control the peak intensity ratio (I_1/I_0) to be in the range of the invention.

[0033]

25 (Cation adding step)

In the present step, a cation raw material is added to the catalyst raw material liquid obtained in the catalyst raw material liquid preparing step to obtain a heteropoly acid salt-containing liquid.

[0034]

Here, the cation is one capable of forming a heteropoly acid salt having a cubic crystal structure, and alkali metal ions such as potassium, rubidium, and cesium and an ammonium ion are particularly preferable. In a case in which the cation is an alkali metal ion, examples of the cation raw material may include carbonates, hydrogencarbonates, hydroxides, chloride salts, sulfates and nitrates of alkali metals. In a case in which the cation is an ammonium ion, examples of the cation raw material may include ammonium hydrogencarbonate, ammonium carbonate, ammonium nitrate, and ammonia water. These may be used singly or two or more kinds thereof may be used concurrently. Incidentally, in the catalyst raw material liquid preparing step, alkali metal salts or ammonium salts of the respective elements may be used as raw materials of the respective elements so that cations may be contained in the catalyst raw material liquid. It is preferable to use both an alkali metal ion raw material and an ammonium ion raw material as a cation raw material from the viewpoint of methacrylic acid yield.

[0035]

It is preferable to add the cation raw material to the catalyst raw material liquid while stirring the catalyst raw material liquid at the time of addition. The temperature at which the cation raw material is added is preferably from 1°C to 100°C. Moreover, it is preferable to heat and stir the mixture at from 90°C to 150°C for from 1 to 10 hours after the entire amount or a part of the cation raw material is added.

[0036]

By changing the amount of the cation raw material to be added in the present step, it is possible to adjust the peak intensity ratio (I_1/I_0) to 0.01 or more and 0.80 or less. In addition, in a case in which two or more kinds of the catalyst raw material liquids are prepared in the catalyst raw material liquid preparing step, it is possible to prepare a heteropoly acid salt-containing liquid by adding the cation raw material to at least one kind of catalyst raw material liquid in the present step. It is particularly preferable to prepare the heteropoly acid salt-containing liquid i containing at least a phosphorus raw material and an alkali metal ion raw material and the heteropoly acid salt-containing liquid ii containing at least a phosphorous raw material and an ammonium ion raw material from the viewpoint of being easy to control the peak intensity ratio (I_1/I_0). Furthermore, it is more preferable that the heteropoly acid salt-

containing liquids i and ii satisfy the following Formulas (1) to (3) from the viewpoint of being easy to control the peak intensity ratio (I_1/I_0).

[0037]

$$1.5 \leq \text{AMi}/\text{Pi} \leq 3.0 \quad (1)$$

5 $4.0 \leq \text{NH}_{4\text{ii}}/\text{Pii} \leq 5.0 \quad (2)$

$$1.0 \leq \text{Pii}/\text{Pi} \leq 2.0 \quad (3)$$

In Formulas (1) to (3), AMi denotes the number of moles of the alkali metal ion contained in the heteropoly acid-containing liquid i, Pi denotes the number of moles of phosphorus contained in the heteropoly acid-containing liquid i, $\text{NH}_{4\text{ii}}$ denotes the number of moles of the ammonium ion contained in the heteropoly acid-containing liquid ii, and Pii denotes the number of moles of phosphorus contained in the heteropoly acid-containing liquid ii, respectively. In Formula (1) above, AMi/Pi denotes the ratio of the number of moles of the alkali metal ion to the number of moles of the phosphorus element in the heteropoly acid-containing liquid i. It is preferable that the lower limit of AMi/Pi is 1.7 or more and the upper limit thereof is 2.8 or less, and it is more preferable that the lower limit thereof is 1.9 or more and the upper limit thereof is 2.6 or less. In Formula (2) above, $\text{NH}_{4\text{ii}}/\text{Pii}$ denotes the ratio of the number of moles of the ammonium ion to the number of moles of the phosphorus element in the heteropoly acid-containing solution ii. It is preferable that the lower limit of $\text{NH}_{4\text{ii}}/\text{Pii}$ is 4.1 or more and the upper limit thereof is 4.9 or less and it is more preferable that the lower limit thereof is 4.2 or more and the upper limit thereof is more 4.8 or less. In Formula (3) above, Pii/Pi denotes the mixing ratio of the heteropoly acid-containing liquid i to the heteropoly acid-containing liquid ii. It is preferable that the lower limit of Pii/Pi is 1.1 or more and the upper limit thereof is 1.9 or less and it is more preferable that the lower limit thereof is 1.2 or more and the upper limit thereof is 1.8 or less.

[0038]

Examples of a method of adjusting the peak intensity ratio (I_1/I_0) may include a method in which the value of Pii/Pi is increased or decreased in a range in which the heteropoly acid salt-containing liquids i and ii satisfy Formulas (1) to (3) above. The peak intensity ratio (I_1/I_0) tends to increase as Pii/Pi is increased and the peak intensity ratio (I_1/I_0) tends to decrease as Pii/Pi is decreased.

[0039]

(Drying step)

In the present step, the heteropoly acid salt-containing liquid obtained in the cation adding step is dried to obtain a catalyst precursor.

5 [0040]

The drying method and the conditions such as drying temperature are not particularly limited and can be appropriately selected depending on the shape and size of the desired dried product. Examples of the drying method may include a drying method using a tray dryer, a drum drying method, a flush drying method, an evaporation
10 to dryness method, and a spray drying method. The drying temperature can be set to, for example, from 120°C to 500°C, the lower limit thereof is preferably 140°C or more, and the upper limit thereof is preferably 400°C or less. Drying can be conducted until the heteropoly acid salt-containing liquid is dried up.

[0041]

15 The structure of the catalyst precursor obtained can be confirmed by being measured by infrared absorption analysis. It is preferable that the catalyst precursor has a Keggin type heteropoly acid structure. In a case in which the catalyst precursor has a Keggin type heteropoly acid structure, the infrared absorption spectrum obtained has characteristic peaks in the vicinity of 1060, 960, 870, and 780 cm⁻¹.

20 [0042]

Incidentally, in a case in which the heteropoly acid salt-containing liquids obtained in the cation adding step are two or more kinds, these can be mixed before and after the present step. In other words, the mixing may be conducted in the state of a heteropoly acid salt-containing liquid before being subjected to the drying or in the state
25 of a catalyst precursor after being subjected to the drying. In addition, one or more kinds of heteropoly acid salt-containing liquids may be dried and then mixed with other heteropoly acid salt-containing liquids and the mixture may be dried again to obtain a catalyst precursor. It is preferable to control the peak intensity ratio (I_1/I_0) of the catalyst to be obtained to be in the range of the invention by mixing two or more kinds
30 of heteropoly acid salt-containing liquids containing heteropoly acid salts having

different atomic ratios or two or more kinds of catalyst precursors containing heteropoly acid salts having different atomic ratios from the viewpoint of methacrylic acid yield. It is possible to obtain a catalyst having a higher methacrylic acid yield particularly by mixing two or more kinds of catalyst precursors containing heteropoly acid salts having different atomic ratios.

[0043]

It is possible to obtain a catalyst precursor through the drying described above in the case of using the heteropoly acid salt-containing liquids i and ii. For example, it is possible to obtain a catalyst precursor by mixing a dried product of the heteropoly acid salt-containing liquid i and a dried product of the heteropoly acid salt-containing liquid ii. In addition, it is possible to obtain a catalyst precursor by mixing the heteropoly acid salt-containing liquid i and the heteropoly acid salt-containing liquid ii to obtain a heteropoly acid salt-containing liquid iii and drying this liquid iii. In addition, it is possible to obtain a catalyst precursor by mixing a dried product of either the heteropoly acid salt-containing liquid i or the heteropoly acid salt-containing liquid ii with the other heteropoly acid salt-containing liquid to obtain a heteropoly acid salt-containing liquid iv and drying this liquid iv.

[0044]

(Molding step)

The catalyst precursor obtained in the drying step may be molded before the heat treatment step to be described later. The molding method is not particularly limited, and a known dry or wet molding method can be applied. Examples thereof may include tableting molding, press molding, extrusion molding, and granulation molding. The shape of the molded article is not particularly limited, and examples thereof may include a cylindrical shape, a ring shape, and a spherical shape. In addition, it is preferable to mold only the catalyst precursor without adding a carrier, a binder, and the like to the catalyst precursor at the time of molding, but for example, known additives such as graphite and talc and known binders derived from organic substances and inorganic substances may be added, if necessary.

[0045]

(Heat treatment step)

In the present step, the catalyst precursor obtained in the drying step or the molded article of the catalyst precursor obtained in the molding step (hereinafter collectively referred to as the catalyst precursor) is subjected to a heat treatment to produce a catalyst for production of methacrylic acid. For example, the catalyst precursor can be subjected to a heat treatment under the flow of at least either of air or an inert gas. Here, the inert gas refers to a gas which does not diminish the catalytic activity, and examples thereof may include nitrogen, carbon dioxide gas, helium, and argon. These may be used singly or two or more kinds thereof may be used in mixture. It is preferable that the heat treatment is conducted under the flow of an oxygen-containing gas such as air.

[0046]

The shape of the heat treatment vessel is not particularly limited, but it is preferable to use a tubular heat treatment vessel of which the cross sectional area is 2 square centimeters or more and 100 square centimeters or less. The heat treatment temperature is preferably 300°C or more and 700°C or less, and it is more preferable that the lower limit thereof is 320°C or more and the upper limit thereof is 450°C or less.

[0047]

The structure of the catalyst for production of methacrylic acid obtained can be confirmed by being measured by infrared absorption analysis. It is preferable that the catalyst for production of methacrylic acid has a Keggin type heteropoly acid structure. In a case in which the catalyst for production of methacrylic acid has a Keggin type heteropoly acid structure, the infrared absorption spectrum obtained has characteristic peaks in the vicinity of 1060, 960, 870, and 780 cm^{-1} .

25 [0048]

[Method of producing methacrylic acid]

In the method of producing methacrylic acid according to the invention, methacrylic acid is produced by vapor phase catalytic oxidation of methacrolein with molecular oxygen in the presence of the catalyst for production of methacrylic acid according to the invention. According to this method, it is possible to produce

methacrylic acid at a high yield and to maintain a high methacrylic acid yield for a long period of time.

[0049]

Specifically, it is possible to produce methacrylic acid by bringing a raw material gas containing methacrolein and molecular oxygen into contact with the catalyst for production of methacrylic acid according to the invention. This reaction can be conducted in a fixed bed. The catalyst layer may be one layer or two or more layers. The catalyst for production of methacrylic acid may contain other additives. The concentration of methacrolein in the raw material gas is not particularly limited, but it is preferably from 1% to 20% by volume, and it is more preferable that the lower limit thereof is 3% by volume or more and the upper limit thereof is 10% by volume or less. Methacrolein may contain impurities which do not substantially affect the present reaction such as a lower saturated aldehyde in a small amount. The concentration of molecular oxygen in the raw material gas is preferably from 0.4 to 4.0 moles with respect to 1.0 mole of methacrolein, and it is more preferable that the lower limit thereof is 0.5 mole or more and the upper limit thereof is 3.0 moles or less. Incidentally, air is preferable as the molecular oxygen source from the viewpoint of economic efficiency. If necessary, a gas in which molecular oxygen is enriched by adding pure oxygen to air, and the like may be used.

[0050]

The raw material gas may be one obtained by diluting methacrolein and molecular oxygen with an inert gas such as nitrogen or carbon dioxide gas. Furthermore, water vapor may be added to the raw material gas. It is possible to obtain methacrylic acid at a higher selectivity by conducting the reaction in the presence of water vapor. The concentration of water vapor in the raw material gas is preferably from 0.1% to 50.0% by volume, and it is more preferable that the lower limit thereof is 1.0% by volume or more and the upper limit thereof is 40.0% by volume or less. The contact time between the raw material gas and the catalyst for production of methacrylic acid is preferably from 1.5 to 15.0 seconds, and it is more preferable that the lower limit thereof is 2.0 seconds or more and the upper limit thereof is 5.0 seconds or less. The reaction pressure is preferably from 0.1 MPa (G) to 1.0 MPa (G). Incidentally, (G) means that the pressure is the gauge pressure. The reaction temperature is preferably

from 200°C to 450°C and it is more preferable that the lower limit thereof is 250°C or more and the upper limit thereof is 400°C or less.

[0051]

[Method of producing methacrylic acid ester]

5 In the method of producing a methacrylic acid ester according to the invention, methacrylic acid produced by the method according to the invention is esterified. According to this method, it is possible to obtain a methacrylic acid ester using methacrylic acid obtained by vapor phase catalytic oxidation of methacrolein. The alcohol to be reacted with methacrylic acid is not particularly limited, and examples
10 thereof may include methanol, ethanol, isopropanol, n-butanol, and isobutanol. Examples of a methacrylic acid ester to be obtained may include methyl methacrylate, ethyl methacrylate, propyl methacrylate, and butyl methacrylate. The reaction can be conducted in the presence of an acidic catalyst such as a sulfonic acid type cation exchange resin. The reaction temperature is preferably from 50°C to 200°C.

15 EXAMPLES

[0052]

Hereinafter, the invention will be described in detail with reference to Examples and Comparative Examples, but the invention is not limited to these Examples. The term "part(s)" in Examples and Comparative Examples means parts by mass. The X-
20 ray diffraction pattern was measured by using an apparatus for X-ray structure analysis (trade name: X'Pert PRO MPD, manufactured by PANalytical B.V.). the analysis of raw material gases and products was conducted by gas chromatography. From the results of gas chromatography, the conversion of methacrolein, the selectivity for methacrylic acid to be formed, and the yield of methacrylic acid were determined by the
25 following formulas.

[0053]

$$\text{Methacrolein conversion (\%)} = (\beta/\alpha) \times 100$$

$$\text{Methacrylic acid selectivity (\%)} = (\gamma/\beta) \times 100$$

$$\text{Methacrylic acid yield (\%)} = (\gamma/\alpha) \times 100$$

30 where α denotes the number of carbon atoms in methacrolein supplied, β

denotes the number of carbon atoms in methacrolein reacted, and γ denotes the number of carbon atoms in methacrylic acid produced.

[0054]

[Example 1]

5 In 132 parts of pure water, 33 parts of molybdenum trioxide, 2.5 parts of ammonium metavanadate, 2.2 parts of a 85% by mass aqueous solution of phosphoric acid, and 2.3 parts of copper(II) nitrate trihydrate were dissolved. The temperature was raised to 95°C while stirring this solution, and this solution was stirred for 2 hours while keeping the liquid temperature at 95°C. While maintaining the liquid
10 temperature at 95°C and stirring the solution by using a rotary blade stirrer, a solution in which 8.6 parts of cesium bicarbonate was dissolved in 20 parts of pure water was added to the solution and the mixture was stirred for 15 minutes to precipitate a cesium salt of heteropoly acid. The heteropoly acid salt-containing liquid i-1 thus obtained was evaporated to dryness, thereby obtaining a catalyst precursor A1. Meanwhile, 54
15 parts of molybdenum trioxide, 4.1 parts of ammonium metavanadate, 3.6 parts of a 85% by mass aqueous solution of phosphoric acid, and 3.8 parts of copper(II) nitrate trihydrate were dissolved in 216 parts of pure water. The temperature was raised to 95°C while stirring this solution, and this solution was stirred for 2 hours while keeping the liquid temperature at 95°C. While maintaining the liquid temperature at 95°C and
20 stirring the solution by using a rotary blade stirrer, a solution in which 4.8 parts of ammonium carbonate was dissolved in 20 parts of pure water was added to the solution and the mixture was stirred for 15 minutes to precipitate an ammonium salt of heteropoly acid. The heteropoly acid salt-containing liquid ii-1 thus obtained was evaporated to dryness, thereby obtaining a catalyst precursor B1. Next, the catalyst
25 precursors A1 and B1 were mixed together to obtain a catalyst precursor.

[0055]

 The catalyst precursor obtained was molded and the molded product was placed in a cylindrical quartz glass vessel for calcination having an inner diameter of 3 centimeters. Under the flow of air, the temperature was raised at 10°C/h and the
30 catalyst precursor was calcined at 380°C for 5 hours to prepare a catalyst for production of methacrylic acid. This catalyst for production of methacrylic acid had a Keggin type heteropoly acid structure. The composition of this catalyst was

Mo₁₂P_{1.0}V_{1.1}Cu_{0.5}CS_{0.9}. Incidentally, the element composition was calculated by analyzing the components of this catalyst dissolved in ammonia water by ICP atomic emission spectroscopy. In addition, the X-ray diffraction pattern of the catalyst after pretreatment obtained by leaving this catalyst to stand for 12 hours in an environment kept at a temperature of 30°C and a humidity of 90% was measured using Cu-K α radiation, and as a result, I₀ was confirmed at a position of 2 θ = 26.1°, I₁ was confirmed at a position of 2 θ = 26.3°, and the peak intensity ratio I₁/I₀ was 0.43.

[0056]

The catalyst for production of methacrylic acid obtained was filled in a reaction tube, a raw material gas composed of 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 pass through the reaction tube, and the reaction was thus conducted at a reaction temperature of 300°C. The product was collected and analyzed by gas chromatography to calculate the methacrylic acid yield and the like. The results are presented in Table 1.

[0057]

[Example 2]

The catalyst precursor A1 was obtained by the same method as in Example 1. Meanwhile, 60 parts of molybdenum trioxide, 4.6 parts of ammonium metavanadate, 4.0 parts of a 85% by mass aqueous solution of phosphoric acid, and 4.2 parts of copper(II) nitrate trihydrate were dissolved in 240 parts of pure water. The temperature was raised to 95°C while stirring this solution, and this solution was stirred for 2 hours while keeping the liquid temperature at 95°C. While maintaining the liquid temperature at 95°C and stirring the solution by using a rotary blade stirrer, a solution in which 5.3 parts of ammonium carbonate was dissolved in 22.2 parts of pure water was added to the solution and the mixture was stirred for 15 minutes to precipitate an ammonium salt of heteropoly acid. The heteropoly acid salt-containing liquid ii-2 obtained was evaporated to dryness, thereby obtaining a catalyst precursor B2. Next, the catalyst precursors A1 and B2 were mixed together to obtain a catalyst precursor.

[0058]

Thereafter, a catalyst for production of methacrylic acid was produced from the catalyst precursor by the same method as in Example 1, and methacrylic acid was produced using this catalyst. This catalyst for production of methacrylic acid had a Keggin type heteropoly acid structure. The composition of this catalyst was $\text{Mo}_{12}\text{P}_{1.0}\text{V}_{1.1}\text{Cu}_{0.5}\text{C}_{0.8}$. Incidentally, the element composition was calculated by analyzing the components of this catalyst dissolved in ammonia water by ICP atomic emission spectroscopy. In addition, a catalyst after pretreatment was prepared in the same manner as in Example 1, and the X-ray diffraction pattern of this catalyst after pretreatment was measured using Cu-K α radiation, and as a result, I_0 was confirmed at a position of $2\theta = 26.1^\circ$, I_1 was confirmed at a position of $2\theta = 26.5^\circ$, and the peak intensity ratio I_1/I_0 was 0.69. The results are presented in Table 1.

[0059]

[Example 3]

In 200 parts of pure water, 50 parts of molybdenum trioxide, 3.8 parts of ammonium metavanadate, 3.3 parts of a 85% by mass aqueous solution of phosphoric acid, and 3.5 parts of copper(II) nitrate trihydrate were dissolved. The temperature was raised to 95°C while stirring this solution, and this solution was stirred for 2 hours while keeping the liquid temperature at 95°C. While maintaining the liquid temperature at 95°C and stirring the solution by using a rotary blade stirrer, a solution in which 13.0 parts of cesium bicarbonate was dissolved in 20 parts of pure water was added to the solution and the mixture was stirred for 15 minutes to precipitate a cesium salt of heteropoly acid. A heteropoly acid salt-containing liquid i-2 was thus obtained. Meanwhile, 70 parts of molybdenum trioxide, 5.3 parts of ammonium metavanadate, 4.7 parts of a 85% by mass aqueous solution of phosphoric acid, and 4.9 parts of copper(II) nitrate trihydrate were dissolved in 280 parts of pure water. The temperature was raised to 95°C while stirring this solution, and this solution was stirred for 2 hours while keeping the liquid temperature at 95°C. While maintaining the liquid temperature at 95°C and stirring the solution by using a rotary blade stirrer, a solution in which 6.8 parts of ammonium carbonate was dissolved in 20 parts of pure water was added to the solution and the mixture was stirred for 15 minutes to precipitate an ammonium salt of heteropoly acid. A heteropoly acid salt-containing liquid ii-3 was thus obtained. The heteropoly acid salt-containing liquids i-2 and ii-3 were mixed together, and the heteropoly acid salt-containing liquid iii-1 thus obtained was stirred for

15 minutes while being kept at 95°C and then evaporated to dryness, thereby obtaining a catalyst precursor.

[0060]

5 Thereafter, a catalyst for production of methacrylic acid was produced from the catalyst precursor by the same method as in Example 1, and methacrylic acid was produced using this catalyst. This catalyst for production of methacrylic acid had a Keggin type heteropoly acid structure. The composition of this catalyst was $\text{Mo}_{12}\text{P}_{1.0}\text{V}_{1.1}\text{Cu}_{0.5}\text{Cs}_{1.0}$. Incidentally, the element composition was calculated by analyzing the components of this catalyst dissolved in ammonia water by ICP atomic
10 emission spectroscopy. In addition, a catalyst after pretreatment was prepared in the same manner as in Example 1, and the X-ray diffraction pattern of this catalyst after pretreatment was measured using Cu-K α radiation, and as a result, I_0 was confirmed at a position of $2\theta = 26.2^\circ$, I_1 was confirmed at a position of $2\theta = 26.5^\circ$, and the peak intensity ratio I_1/I_0 was 0.09. The results are presented in Table 1.

15 [0061]

[Example 4]

 In 100 parts of pure water, 25 parts of molybdenum trioxide, 1.9 parts of ammonium metavanadate, 1.7 parts of a 85% by mass aqueous solution of phosphoric acid, and 1.8 parts of copper(II) nitrate trihydrate were dissolved. The temperature
20 was raised to 95°C while stirring this solution, and this solution was stirred for 2 hours while keeping the liquid temperature at 95°C. While maintaining the liquid temperature at 95°C and stirring the solution by using a rotary blade stirrer, a solution in which 6.5 parts of cesium bicarbonate was dissolved in 10 parts of pure water was added to the solution and the mixture was stirred for 15 minutes to precipitate a cesium
25 salt of heteropoly acid. The heteropoly acid salt-containing liquid i-3 thus obtained was evaporated to dryness, thereby obtaining a catalyst precursor A2. Meanwhile, 75 parts of molybdenum trioxide, 5.6 parts of ammonium metavanadate, 5.0 parts of a 85% by mass aqueous solution of phosphoric acid, and 5.3 parts of copper(II) nitrate trihydrate were dissolved in 300 parts of pure water. The temperature was raised to
30 95°C while stirring this solution, and this solution was stirred for 2 hours while keeping the liquid temperature at 95°C. The heteropoly acid salt-containing liquid ii-4 thus obtained was evaporated to dryness, thereby obtaining a catalyst precursor B3. Next,

the catalyst precursors A2 and B3 were mixed together to obtain a catalyst precursor.

[0062]

Thereafter, a catalyst for production of methacrylic acid was produced from the catalyst precursor by the same method as in Example 1, and methacrylic acid was produced using this catalyst. This catalyst for production of methacrylic acid had a Keggin type heteropoly acid structure. The composition of this catalyst was $\text{Mo}_{12}\text{P}_{1.0}\text{V}_{1.1}\text{Cu}_{0.5}\text{Cs}_{0.6}$. Incidentally, the element composition was calculated by analyzing the components of this catalyst dissolved in ammonia water by ICP atomic emission spectroscopy. In addition, a catalyst after pretreatment was prepared in the same manner as in Example 1, and the X-ray diffraction pattern of this catalyst after pretreatment was measured using Cu-K α radiation, and as a result, I_0 was confirmed at a position of $2\theta = 26.1^\circ$, I_1 was confirmed at a position of $2\theta = 26.5^\circ$, and the peak intensity ratio I_1/I_0 was 0.75. The results are presented in Table 1.

[0063]

[Comparative Example 1]

In 400 parts of pure water, 100 parts of molybdenum trioxide, 7.5 parts of ammonium metavanadate, 6.7 parts of a 85% by mass aqueous solution of phosphoric acid, and 7.0 parts of copper(II) nitrate trihydrate were dissolved. The temperature was raised to 95°C while stirring this solution, and this solution was stirred for 2 hours while keeping the liquid temperature at 95°C. While maintaining the liquid temperature at 95°C and stirring the solution by using a rotary blade stirrer, a solution in which 26.0 parts of cesium bicarbonate was dissolved in 40 parts of pure water was added to the solution and the mixture was stirred for 15 minutes to precipitate a cesium salt of heteropoly acid. The heteropoly acid salt-containing liquid i-4 thus obtained was evaporated to dryness, thereby obtaining a catalyst precursor.

[0064]

Thereafter, a catalyst for production of methacrylic acid was produced from the catalyst precursor by the same method as in Example 1, and methacrylic acid was produced using this catalyst. The composition of this catalyst was $\text{Mo}_{12}\text{P}_{1.0}\text{V}_{1.1}\text{Cu}_{0.5}\text{Cs}_{2.3}$. Incidentally, the element composition was calculated by

analyzing the components of this catalyst dissolved in ammonia water by ICP atomic emission spectroscopy. In addition, a catalyst after pretreatment was prepared in the same manner as in Example 1, and the X-ray diffraction pattern of this catalyst after pretreatment was measured using Cu-K α radiation, and as a result, I₀ was confirmed at a position of $2\theta = 26.0^\circ$. Meanwhile, I₁ was not confirmed and thus set to 0. Hence, the peak intensity ratio I₁/I₀ was 0.00. The results are presented in Table 1.

[0065]

[Comparative Example 2]

The catalyst precursor A1 was obtained by the same method as in Example 1. Meanwhile, 70 parts of molybdenum trioxide, 5.3 parts of ammonium metavanadate, 4.7 parts of a 85% by mass aqueous solution of phosphoric acid, and 4.9 parts of copper(II) nitrate trihydrate were dissolved in 280 parts of pure water. The temperature was raised to 95°C while stirring this solution, and this solution was stirred for 2 hours while keeping the liquid temperature at 95°C. While maintaining the liquid temperature at 95°C and stirring the solution by using a rotary blade stirrer, a solution in which 6.2 parts of ammonium carbonate was dissolved in 25.9 parts of pure water was added to the solution and the mixture was stirred for 15 minutes to precipitate an ammonium salt of heteropoly acid. The heteropoly acid salt-containing liquid ii-5 thus obtained was evaporated to dryness, thereby obtaining a catalyst precursor B4. Next, the catalyst precursors A1 and B4 were mixed together to obtain a catalyst precursor.

[0066]

Thereafter, a catalyst for production of methacrylic acid was produced from the catalyst precursor by the same method as in Example 1, and methacrylic acid was produced using this catalyst. The composition of this catalyst was Mo₁₂P_{1.0}V_{1.1}Cu_{0.5}CS_{0.7}. Incidentally, the element composition was calculated by analyzing the components of this catalyst dissolved in ammonia water by ICP atomic emission spectroscopy. In addition, a catalyst after pretreatment was prepared in the same manner as in Example 1, and the X-ray diffraction pattern of this catalyst after pretreatment was measured using Cu-K α radiation, and as a result, I₀ was confirmed at a position of $2\theta = 26.1^\circ$, I₁ was confirmed at a position of $2\theta = 26.5^\circ$, and the peak intensity ratio I₁/I₀ was 0.81. The results are presented in Table 1.

[0067]

[Comparative Example 3]

The catalyst precursor A1 was obtained by the same method as in Example 1. Meanwhile, 114 parts of molybdenum trioxide, 8.6 parts of ammonium metavanadate, 5 7.6 parts of a 85% by mass aqueous solution of phosphoric acid, and 8.0 parts of copper(II) nitrate trihydrate were dissolved in 455.2 parts of pure water. The temperature was raised to 95°C while stirring this solution, and this solution was stirred for 2 hours while keeping the liquid temperature at 95°C. While maintaining the liquid temperature at 95°C and stirring the solution by using a rotary blade stirrer, a solution in 10 which 10.1 parts of ammonium carbonate was dissolved in 42.1 parts of pure water was added to the solution and the mixture was stirred for 15 minutes to precipitate an ammonium salt of heteropoly acid. The heteropoly acid salt-containing liquid ii-6 thus obtained was evaporated to dryness, thereby obtaining a catalyst precursor B5. Next, the catalyst precursors A1 and B5 were mixed together to obtain a catalyst precursor.

15 [0068]

Thereafter, a catalyst for production of methacrylic acid was produced from the catalyst precursor by the same method as in Example 1, and methacrylic acid was produced using this catalyst. The composition of this catalyst was $\text{Mo}_{12}\text{P}_{1.0}\text{V}_{1.1}\text{Cu}_{0.5}\text{Cs}_{0.5}$. Incidentally, the element composition was calculated by 20 analyzing the components of this catalyst dissolved in ammonia water by ICP atomic emission spectroscopy. In addition, a catalyst after pretreatment was prepared in the same manner as in Example 1, and the X-ray diffraction pattern of this catalyst after pretreatment was measured using Cu-K α radiation, and as a result, I_0 was confirmed at a position of $2\theta = 26.2^\circ$, I_1 was confirmed at a position of $2\theta = 26.4^\circ$, and the peak 25 intensity ratio I_1/I_0 was 2.25. The results are presented in Table 1.

[0069]

[Comparative Example 4]

In 400 parts of pure water, 100 parts of molybdenum trioxide, 7.5 parts of ammonium metavanadate, 6.7 parts of a 85% by mass aqueous solution of phosphoric acid, and 7.0 parts of copper(II) nitrate trihydrate were dissolved. The temperature 30 was raised to 95°C while stirring this solution, and this solution was stirred for 2 hours while keeping the liquid temperature at 95°C. The heteropoly acid salt-containing

liquid ii-7 thus obtained was evaporated to dryness, thereby obtaining a catalyst precursor.

[0070]

5 Thereafter, a catalyst for production of methacrylic acid was produced from the catalyst precursor by the same method as in Example 1, and methacrylic acid was produced using this catalyst. The composition of this catalyst was $\text{Mo}_{12}\text{P}_{1.0}\text{V}_{1.1}\text{Cu}_{0.5}$. Incidentally, the element composition was calculated by analyzing the components of this catalyst dissolved in ammonia water by ICP atomic emission spectroscopy. In addition, a catalyst after pretreatment was prepared in the same manner as in Example 1,
10 and the X-ray diffraction pattern of this catalyst after pretreatment was measured using $\text{Cu-K}\alpha$ radiation, and as a result, I_1 was confirmed at a position of $2\theta = 26.5^\circ$. Meanwhile, I_0 was not confirmed and thus set to 0. Hence, it was impossible to calculate the peak intensity ratio I_1/I_0 . The results are presented in Table 1.

[0071]

[Table 1]

	AMi/Pi	NH ₄ ii/Pii	Pii/Pi	I ₁ /I ₀	Methacrolein conversion (%)	Methacrylic acid selectivity (%)	Methacrylic acid yield (%)
Example 1	2.3	4.3	1.6	0.43	18.1	94.0	17.0
Example 2	2.3	4.3	1.8	0.69	19.5	92.4	18.0
Example 3	2.3	4.6	1.4	0.09	14.5	92.0	13.3
Example 4	2.3	1.1	3.0	0.75	15.3	90.3	13.9
Comparative Example 1	2.3	-	0.0	0.00	7.3	91.6	6.7
Comparative Example 2	2.3	4.3	2.1	0.81	11.8	93.4	11.0
Comparative Example 3	2.3	4.3	3.4	2.25	10.1	90.2	9.1
Comparative Example 4	-	1.1	-	-	7.5	91.2	6.8

[0072]

In Examples 1 to 4, it has been confirmed that the catalysts have a peak intensity ratio (I_1/I_0) in the range regulated in the invention and provide a high methacrylic acid yield. Among these, the highest methacrylic acid yield has been obtained in Example 2 in which the peak intensity ratio (I_1/I_0) is 0.69 and it has been thus found that there is an optimum range of the peak intensity ratio (I_1/I_0).

[0073]

On the other hand, in Comparative Examples 1 to 4, the peak intensity ratio (I_1/I_0) is out of the range regulated in the invention, and the methacrylic acid yield is lower than that in Examples 1 to 4. Incidentally, in Comparative Example 4, a peak pattern attributed to a heteropoly acid salt has not been confirmed and I_0 is thus 0 so that it has not been possible to calculate the peak intensity ratio (I_1/I_0). The methacrylic acid yield is low even in such a case, and it has been confirmed that the methacrylic acid yield is low in a case in which the peak intensity ratio (I_1/I_0) is out of the range regulated in the invention. Incidentally, it is possible to obtain a methacrylic acid ester by esterifying methacrylic acid obtained in the present Examples.

[0074]

This application is based upon and claims the benefit of priority of the prior Japanese Patent Application No. 2016-179403 filed on September 14, 2016, the entire contents of which are incorporated herein by reference.

[0075]

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

INDUSTRIAL APPLICABILITY

[0076]

The catalyst for production of methacrylic acid according to the invention is industrially useful since it provides a high methacrylic acid yield in the case of being

used in the production of methacrylic acid by vapor phase catalytic oxidation of methacrolein with molecular oxygen. In addition, by forming the catalyst to have crystal structures of a heteropoly acid salt and a proton type heteropoly acid as described above, the proton heteropoly acid effectively functions as an active site while
5 maintaining the stability of the heteropoly acid salt, and it can be thus expected that a high methacrylic acid yield is attained for a long period of time.

CLAIMS

1. A catalyst for production of methacrylic acid, comprising a heteropoly acid salt containing at least phosphorus, molybdenum, and vanadium, wherein
the catalyst is used in production of methacrylic acid by vapor phase catalytic oxidation of methacrolein with molecular oxygen, and
a ratio (I_1/I_0) of an absolute value of a peak intensity I_1 of a (322) plane attributed to a cubic crystal structure of a proton type heteropoly acid to an absolute value of a peak intensity I_0 of a (222) plane attributed to a cubic crystal structure of a heteropoly acid salt is 0.01 or more and 0.80 or less in an X-ray diffraction pattern of the catalyst for production of methacrylic acid left to stand for 12 hours in an environment kept at a temperature of 30°C and a humidity of 90% measured using Cu-K α radiation.
2. The catalyst for production of methacrylic acid according to claim 1, wherein I_1/I_0 is 0.05 or more and 0.75 or less.
3. The catalyst for production of methacrylic acid according to claim 2, wherein I_1/I_0 is 0.40 or more and 0.73 or less.
4. A method of producing the catalyst for production of methacrylic acid according to any one of claims 1 to 3, comprising a step of obtaining a catalyst precursor by drying, using a heteropoly acid salt-containing liquid i containing at least a phosphorus raw material and an alkali metal ion raw material, and a heteropoly acid salt-containing liquid ii containing at least a phosphorous raw material and an ammonium ion raw material.
5. The method of producing the catalyst for production of methacrylic acid according to claim 4, comprising a step of obtaining a catalyst precursor by mixing a dried product of the heteropoly acid salt-containing liquid i and a dried product of the heteropoly acid salt-containing liquid ii.
6. The method of producing the catalyst for production of methacrylic acid

according to claim 4, comprising a step of obtaining a heteropoly acid salt-containing liquid iii by mixing the heteropoly acid salt-containing liquid i and the heteropoly acid salt-containing liquid ii, and obtaining a catalyst precursor by drying this heteropoly acid salt-containing liquid iii.

7. The method of producing the catalyst for production of methacrylic acid according to claim 4, comprising a step of obtaining a heteropoly acid salt-containing liquid iv by mixing a dried product of either the heteropoly acid salt-containing liquid i or the heteropoly acid salt-containing liquid ii with the other heteropoly acid salt-containing liquid, and obtaining a catalyst precursor by drying this heteropoly acid salt-containing liquid iv.

8. The method of producing the catalyst for production of methacrylic acid according to any one of claims 4 to 7, wherein the heteropoly acid salt-containing liquids i and ii satisfy the following Formulas (1) to (3):

$$1.5 \leq \text{AMi}/\text{Pi} \leq 3.0 \quad (1)$$

$$4.0 \leq \text{NH}_{4\text{ii}}/\text{Pii} \leq 5.0 \quad (2)$$

$$1.0 \leq \text{Pii}/\text{Pi} \leq 2.0 \quad (3)$$

(in Formulas (1) to (3), AMi denotes the number of moles of an alkali metal ion contained in the heteropoly acid-containing liquid i, Pi denotes the number of moles of phosphorus contained in the heteropoly acid-containing liquid i, $\text{NH}_{4\text{ii}}$ denotes the number of moles of an ammonium ion contained in the heteropoly acid-containing liquid ii, and Pii denotes the number of moles of phosphorus contained in the heteropoly acid-containing liquid ii, respectively.).

9. A method of producing methacrylic acid, comprising producing methacrylic acid by vapor phase catalytic oxidation of methacrolein with molecular oxygen in presence of the catalyst for production of methacrylic acid according to any one of claims 1 to 3.

10. A method of producing a methacrylic acid ester, comprising esterifying methacrylic acid produced by the method of producing methacrylic acid according to claim 9.

11. A method of producing a methacrylic acid ester, comprising producing methacrylic acid by the method according to claim 9 and esterifying the methacrylic acid.