

DESCRIPTION

[Title of the Invention]

Catalyst precursors, methods for producing catalysts, methods for producing methacrylic acid and acrylic acid, and methods for producing methacrylic acid esters and acrylic acid esters

TECHNICAL FIELD

【0001】

The present invention relates to a catalyst precursor, a method for producing a catalyst using the precursor, a method for producing methacrylic acid and acrylic acid, and a method for producing methacrylic acid ester and acrylic acid ester.

The present invention also relates to a precursor of a catalyst used in producing methacrylic acid or acrylic acid by gas phase catalytic oxidation of methacrolein or acrolein using molecular oxygen, a process for producing a catalyst for producing methacrylic acid or acrylic acid using the precursor, a process for producing methacrylic acid or acrylic acid, and a process for producing a methacrylic acid ester or acrylic acid ester.

BACKGROUND ART

【0002】

A number of studies have been made on the structure of catalysts used in chemical reactions. For example, as a catalyst for a production of methacrylic acid, a catalyst having a heteropolyacid such as phosphomolybdic acid or phosphomolybdic acid salt as a main component is known.

In Patent Document 1, an X-ray diffraction pattern after calcinating is defined for a gas phase oxidation catalyst containing a heteropolyacid salt.

Patent Document 2 describes an X-ray diffraction peak of a raw material for producing a catalyst, and defines an XRD diffraction peak after a precipitate obtained from a mixed liquid containing molybdenum and an element A, where A represents at least one element selected from the group consisting of phosphorus and arsenic, is heat-treated at 250 to 350° C.

PRIOR-ART DOCUMENT

Patent Application

【0003】

[Patent Document 1] JP-A-57-177348

[Patent Document 2] JP-A-2009-22945

SUMMARY OF THE INVENTION

TECHNICAL PROBLEMS

【0004】

However, when methacrylic acid and acrylic acid are produced using the catalyst obtained by these methods, there is a problem that the yield is not sufficient.

Accordingly, it is an object of the present invention to provide catalyst precursors for producing catalysts having higher yields of methacrylic acid and acrylic acid than conventional catalysts, methods for producing catalysts from said precursors, methacrylic acid and acrylic acid, and esters thereof using said catalysts.

MEANS FOR SOLVING THE PROBLEMS

【0005】

In order to achieve the above object, the present inventors have made extensive studies on a technique for producing a catalyst having a high yield of methacrylic acid and acrylic acid.

As a result, the inventors have found that it is possible to produce a catalyst having a high yield of methacrylic acid and acrylic acid by producing a catalyst precursor having a specific structure and heat-treating the catalyst precursor to produce a catalyst, and thus the present invention has been achieved.

【0006】

The present invention is as shown in the following [1] to [8] and [1'] to [5'].

【0007】

[1] A catalyst precursor including a heteropolyacid salt, the catalyst precursor having a peak P1 in which 2θ is $26.16^\circ \pm 0.06^\circ$ and a peak P2 in which 2θ is further toward the high-angle side than the peak P1 and equal to or less 26.44° in an X-ray diffraction pattern using an anti-cathode Cu-K α line.

[2] The catalyst precursor according to [1], wherein the ratio (I1/I2) of the height I1 of the peak P1 to the height I2 of the peak P2 is 0.05 to 0.92.

[3] The catalyst precursor according to [1] or [2], wherein the catalyst is used in producing at least one selected from the group consisting of methacrylic acid and acrylic acid by gas phase catalytic oxidation of at least one selected from the group consisting of methacrolein and acrolein using molecular oxygen.

[4] The catalyst precursor according to any one of [1] to [3], which has a composition represented by the following formula (I).



(In formula (I), P, Mo, V, Cu, and O are elemental symbols representing phosphorus, molybdenum, vanadium, copper and oxygen, respectively; A represents at least one element selected from the group consisting of antimony, bismuth, arsenic, germanium, zirconium, tellurium, silver, selenium, silicon, tungsten and boron; and E represents at least one element selected from the group consisting of iron, zinc, chromium, magnesium, calcium, strontium, tantalum, cobalt, nickel, manganese, barium, titanium, tin, lead, niobium, indium, sulfur, palladium, gallium, cerium and lanthanum; and G represents at least one element selected from the group consisting of potassium, rubidium, cesium and thallium; and a, b, c, d, e, f, g and h represent the atomic ratios of each element, and when $b=12$, $a=0.5$ to 3, $c=0.01$ to 3, $d=0.01$ to 2, $e=0$ to 3, $f=0$ to 3, and $g=0.01$ to 3, h is the atomic ratio of oxygen required to satisfy the valence of each of the above components.)

[5] A method for producing a catalyst, comprising a step of heat treating the catalyst precursor according to any one of [1] to [4].

[6] The method for producing a catalyst according to [5], wherein the heat treatment temperature in the step of heat treating is from 300 to 450° C.

[7] A method for producing at least one selected from the group consisting of methacrylic acid and acrylic acid comprising steps of:

- (1) producing a catalyst by the method according to [5] or [6], and
- (2) producing at least one selected from the group consisting of methacrylic acid and acrylic acid by gas phase catalytic oxidation of at least one selected from the group consisting of

methacrolein and acrolein using molecular oxygen in the presence of said catalyst.

[8] A method for producing at least one selected from the group consisting of methacrylic acid esters and acrylic acid esters comprising steps of:

- (1) producing a catalyst by the method according to [5] or [6];
- (2) producing at least one selected from the group consisting of methacrylic acid and acrylic acid by gas phase catalytic oxidation of at least one selected from the group consisting of methacrolein and acrolein using molecular oxygen in the presence of the catalyst; and
- (3) esterifying at least one selected from the group consisting of methacrylic acid and acrylic acid.

【0008】

[1'] A catalyst precursor for producing methacrylic acid, which is used in producing a catalyst for producing methacrylic acid by gas phase catalytic oxidation of methacrolein with molecular oxygen, and the catalyst precursor includes a heteropolyacid salt and have a peak P1 in which 2θ is $26.16^\circ \pm 0.06^\circ$ and a peak P2 in which 2θ is further toward the high-angle side than the peak P1 and equal to or less than 26.44° in an X-ray diffraction pattern using an anti-cathode Cu-K α line.

[2'] The catalyst precursor for producing methacrylic acid according to [1'], wherein the catalyst precursor has a composition represented by the following formula (I).



(In formula (I), P, Mo, V, Cu, and O are elemental symbols representing phosphorus, molybdenum, vanadium, copper and oxygen, respectively; A represents at least one element selected from the group consisting of antimony, bismuth, arsenic, germanium, zirconium, tellurium, silver, selenium, silicon, tungsten and boron; and E represents at least one element selected from the group consisting of iron, zinc, chromium, magnesium, calcium, strontium, tantalum, cobalt, nickel, manganese, barium, titanium, tin, lead, niobium, indium, sulfur, palladium, gallium, cerium and lanthanum and G represents at least one element selected from the group consisting of potassium, rubidium, cesium and thallium; and a, b, c, d, e, f, g and h represent the atomic ratios of each element, and when $b=12$, $a=0.5$ to 3, $c=0.01$ to 3, $d=0.01$ to 2, $e=0$ to 3, $f=0$ to 3 and $g=0.01$ to 3, h is the atomic ratio of oxygen required to satisfy the valence of each of the above components.

[3'] A method for producing a catalyst for producing methacrylic acid comprising the step of heat treating the catalyst precursor for producing methacrylic acid according to [1'] or [2'].

[4'] The method for producing a catalyst for producing methacrylic acid according to [3'], wherein the heat treatment temperature in the heat treatment step is 300 to 450° C.

[5'] A method for producing methacrylic acid, wherein a catalyst for producing methacrylic acid is produced by the method for producing a catalyst for producing methacrylic acid described in [3'], or [4'], and methacrylic acid is produced by gas phase catalytic oxidation of methacrolein with molecular oxygen in the presence of the catalyst.

[6'] A process for producing methacrylic acid ester for esterifying methacrylic acid produced by the method for producing methacrylic acid according to [5'].

EFFECT OF INVENTION

【0009】

According to the present invention, when methacrylic acid and acrylic acid are produced by gas phase catalytic oxidation of methacrolein and acrolein using molecular oxygen, it is possible to produce catalyst precursors capable of producing catalysts having high yields of

methacrylic acid and acrylic acid.

DETAILED DESCRIPTION OF THE PRESENT INVENTION

【0010】

[Catalyst Precursor]

In the present invention, a catalyst precursor is composed of a raw material of a catalyst constituent element, and is the catalyst precursor which becomes a catalyst by heat treatment.

【0011】

The catalyst produced from the catalyst precursor of the present invention can be used in various oxidation reactions, for example, in reactions producing methacrylic acid from methacrolein or acrylic acid from acrolein, and particularly preferably in reactions producing methacrylic acid from methacrolein.

【0012】

Hereinafter, the case where methacrylic acid is produced from methacrolein will be described as an example, but these are also applicable to the case where acrylic acid is produced from acrolein.

【0013】

The catalyst precursor of the present invention contains a heteropolyacid salt, and has a peak P1 in which 2θ is $26.16^\circ \pm 0.06^\circ$ and a peak P2 in which 2θ is further toward the high-angle side than the peak P1 and equal to or less than 26.44° in the X-ray diffraction pattern (X-ray diffraction line) using the anti-cathode Cu-K α line.

【0014】

In the X-ray diffraction pattern, the peak at which 2θ appears in the vicinity of 26° is derived from the (222) plane of the cubic crystal structure of the heteropolyacid salt. Catalyst precursors having two or more peaks in this region are meant to contain at least two heteropolyacid salts or heteropolyacid complex salts (hereinafter, collectively referred as "heteropolyacid (complex) salts") having different structures. Here, the heteropolyacid complex salt indicates a salt in which a heteropolyacid salt having a different structure is complex at a specific ratio. Methacrylic acid can be produced in high yield by performing oxidation of methacrolein using a catalyst produced by heat treating the catalyst precursor of the present invention. The peaks P1 and P2 have a height of 5/100 or more with respect to the diffraction pattern at around 25.5° derived from α -alumina shown below.

The ratio (I1/I2) of the height I1 of the peak P1 to the height I2 of the peak P2 is preferably 0.05 to 0.92 from the viewpoint of the yield of methacrylic acid. More preferably, the lower limit of the I1/I2 is 0.1 or more and the upper limit is 0.9 or less.

【0015】

Although the reason for this is not clear, it is considered that heteropolyacid (complex) salts having different structures also have different characteristics, and by containing heteropolyacid (complex) salts having different characteristics derived from the peaks P1 and P2 in the X-ray diffraction pattern, an active point structure advantageous in the gas phase catalytic oxidation reaction of methacrolein is formed.

【0016】

The X-ray diffraction pattern is measured for a mixed powder obtained by forming a catalyst precursor in powder and mixing α -alumina at the mass of the catalyst precursor: mass of α -alumina=1:4. Measurements are carried out using "trade name: X'Pert Pro MPD"

manufactured by PANalytical under the following conditions; radiation source: Cu-K α ray ($\lambda=0.15406\text{nm}$), tube voltage: 45 kV, tube current: 40 mA, scattering slit: 1°, anti-diffusion slit: 2°, scanning step: 0.008°. The obtained data are subjected to K α 2 ray removing operations using data collection software for X-ray diffractometers "trade name: X'Pert" manufactured by PANalytical Device. At this time, a diffraction pattern caused by the (012) plane of α -alumina appears near 25.5°. Assuming that the angle of the diffraction pattern is 25.583°, the diffraction pattern appearing from the vicinity of 26° to the vicinity of 26.5° is calculated as the angle of the diffraction pattern derived from the (222) plane of the heteropolyacid (complex) salt in the catalyst precursor. In addition, the heteropolyacid (complex) salt also has a diffraction pattern in the vicinity of $2\theta=10.6$ to 10.7° , 13.0 to 13.2° , 15.1 to 15.3° , 18.4 to 18.6° , 21.3 to 21.5° , 23.8 to 24.2° and 30.2 to 30.7° .

【0017】

The catalyst precursor of the present invention preferably has a composition represented by the following formula (I) from the viewpoint of methacrylic acid yield. The molar ratio of the element composition is a value calculated by analyzing a component in which the catalyst precursor is dissolved in ammonia water by an ICP luminescence analysis method.



In formula (I), P, Mo, V, Cu and O are elemental symbols representing phosphorus, molybdenum, vanadium, copper and oxygen, respectively. A represents at least one element selected from the group consisting of antimony, bismuth, arsenic, germanium, zirconium, tellurium, silver, selenium, silicon, tungsten and boron, E represents at least one element selected from the group consisting of iron, zinc, chromium, magnesium, calcium, strontium, tantalum, cobalt, nickel, manganese, barium, titanium, tin, lead, niobium, indium, sulfur, palladium, gallium, cerium and lanthanum, and G represents at least one element selected from the group consisting of potassium, rubidium, cesium and thallium. a, b, c, d, e, f, g and h represent atomic ratios of the respective elements, when $b=12$, $a=0.5$ to 3, $c=0.01$ to 3, $d=0.01$ to 2, $e=0$ to 3, $f=0$ to 3, $g=0.01$ to 3 and h is the atomic ratio of oxygen required to satisfy the valence of the respective components.

【0018】

[Method for Producing Catalyst Precursors]

The method for producing the catalyst precursor according to the present invention is not particularly limited, for example, the method including a step of preparing a dry powder K1 having the peak P1 (hereinafter, also referred to as "dry powder K1 preparation step"), a step of preparing a dry powder K2 having the peak P2 (hereinafter, also referred to as "dry powder K2 preparation step"), and a step of producing the catalyst precursor by mixing the dry powder K1 and the dry powder K2 (hereinafter, also referred to as "dry powder mixing step").

【0019】

(Dry powder K1 preparation step)

In the present step, a dry powder K1 having the peak P1 is prepared.

As a method for preparing the dry powder K1, for example, a heteropolyacid-containing liquid is prepared by mixing a catalyst raw material and heating and stirring at first. The catalyst raw material preferably contains at least phosphorus and molybdenum, and more preferably contains vanadium, copper, the above-mentioned element A and the above-mentioned element E.

【0020】

The raw material compound of each element is not particularly limited, and nitrates, carbonates, acetates, ammonium salts, oxides, halides, oxoacids, oxoacid salts and the like of each element can be used alone or in combination of two or more kinds. For example, ammonium paramolybdate, molybdenum trioxide, molybdic acid, molybdenum chloride and the like can be used as the molybdenum raw material. As phosphorus raw materials, for example, orthophosphoric acid, phosphorus pentoxide, or phosphates such as ammonium phosphate and cesium phosphate can be used. As the vanadium raw material, for example, ammonium vanadate, ammonium metavanadate, vanadium pentoxide, vanadium chloride and the like can be used. As the copper raw material, for example, copper sulfate, copper nitrate, copper acetate, cuprous chloride, cupric chloride and the like can be used. Only one of these may be used, or two or more of these may be used in combination.

【0021】

As a raw material of molybdenum, phosphorus and vanadium, heteropolyacid containing at least one element selected from molybdenum, phosphorus and vanadium may be used as a raw material. Examples of the heteropolyacid includes phosphomolybdic acid, phosphovanadomolybdic acid, silicomolybdic acid and the like. Only one of these may be used, or two or more of these may be used in combination.

【0022】

As a solvent for dissolving or suspending the raw material compound, water, ethyl alcohol, acetone or the like can be used. One of these may be used, or two or more of these may be used in combination. Among these, water is preferable as a solvent.

【0023】

The temperature at the time of heating and stirring is desirably 50 to 120° C.

【0024】

Subsequently, the raw material of the G element and the ammonium raw material are added to the prepared heteropolyacid-containing liquid to prepare a heteropolyacid (complex) salt-containing liquid. The temperature of the heteropolyacid-containing liquid at the time of adding the raw material of the element G and the raw material of ammonium is preferably 70 to 120° C.

【0025】

The G element is at least one element selected from the group consisting of potassium, rubidium, cesium and thallium, and it is preferable to use cesium from the viewpoint of methacrylic acid yield.

【0026】

The term "ammonium" as used herein is a generic term for ammonium contained in ammonium-containing compounds such as ammonia (NH_3) and ammonium salts, which can be ammonium ions (NH_4^+). Examples of the ammonium raw material includes ammonia, ammonium nitrate, ammonium bicarbonate, ammonium carbonate, ammonium acetate, ammonium vanadate and the like; it is preferable to use ammonium bicarbonate, ammonium carbonate and the like, and it is more preferable to use ammonium carbonate. Only one of these may be used, or two or more of these may be used in combination.

【0027】

In the prepared heteropolyacid (complex) salt-containing liquid, when the smaller one of the number of moles of phosphorus and 1/12 of the number of moles of molybdenum is defined as Mp1, the number of moles Mg1 of the added G element and the number of moles Mn1 of

ammonium contained in the added ammonium raw material satisfy the following formulae (II) and (III), whereby a dry powder K1 having peak P1 can be obtained.

$$1.85 \leq \text{Mg1}/\text{Mp1} \leq 2.75 \quad (\text{II})$$

$$2.7 \leq (\text{Mg1}+\text{Mn1})/\text{Mp1} \leq 6.0 \quad (\text{III})$$

【0028】

The lower limit of the $(\text{Mg1}+\text{Mn1})/\text{Mp1}$ value is preferably 2.8 or more, and more preferably 2.9 or more. The upper limit is preferably 4.0 or less, and more preferably 3.5 or less.

【0029】

The pH of the heteropolyacid (complex) salt-containing liquid is preferably 0.1 to 4, more preferably 0.1 to 2, from the viewpoint of methacrylic acid yield.

【0030】

The obtained heteropolyacid (complex) salt-containing liquid is dried to prepare dry powder K1. Drying methods are not particularly limited. For example, it is possible to use an evaporation-dry method, a spray-dry method, a drum-dry method, an airflow-dry method, etc., but the spray-dry method is most suitable. It is preferable to perform drying until the water content of the obtained dry powder K1 is 2wt% or less.

【0031】

(Dry powder K2 preparation step)

In the present step, a dry powder K2 having the peak P2 is prepared.

As a method of preparing the dry powder K2, for example, a heteropolyacid-containing liquid is prepared by a method similar to the dry powder K1 preparation step at first.

【0032】

Subsequently, the raw material of the G element and the ammonium raw material are added to the prepared heteropolyacid-containing liquid to prepare a heteropolyacid (complex) salt-containing liquid. The temperature of the heteropolyacid-containing liquid at the time of adding the raw material of the element G and the raw material of ammonium is preferably 70 to 120° C.

【0033】

The G element is at least one element selected from the group consisting of potassium, rubidium, cesium and thallium, and the use of cesium is preferable from the viewpoint of methacrylic acid yield.

【0034】

In the prepared heteropolyacid (complex) salt-containing liquid, when the smaller one of the number of moles of phosphorus and 1/12 of the number of moles of molybdenum is defined as Mp2, the number of moles Mg2 of the added G element and the number of moles Mn2 of ammonium contained in the added ammonium raw material satisfy the following formulae (IV) and (V), whereby a dry powder K2 having peak P2 can be obtained.

$$0.15 \leq \text{Mg2}/\text{Mp2} < \text{Mg1}/\text{Mp1} \quad (\text{IV})$$

$$2.7 \leq (\text{Mg2}+\text{Mn2})/\text{Mp2} \leq 6.0 \quad (\text{V})$$

The lower limit of the $(\text{Mg2}+\text{Mn2})/\text{Mp2}$ value is preferably 2.8 or more, and more preferably 2.9 or more. The upper limit is preferably 4.0 or less, and more preferably 3.5 or less.

【0035】

The pH of the heteropolyacid (complex) salt-containing liquid is preferably 0.1 to 4, more preferably 0.1 to 2 from the viewpoint of methacrylic acid yield.

【0036】

The obtained heteropolyacid (complex) salt-containing liquid is dried to prepare dry powder K2. Drying methods are not particularly limited. For example, it is possible to use an evaporation-dry method, a spray-dry method, a drum-dry method, an airflow-dry method, etc., but the spray-dry method is most suitable. It is preferable to perform drying until the water content of the obtained dry powder K2 is 2wt% or less.

【0037】

(Dry powder mixing step)

In the present step, the dry powder K1 and the dry powder K2 are mixed to prepare a catalyst precursor. The mixing method is not particularly limited, but when the dry powder K1 and the dry powder K2 are dried using the spray-dry method, the dry powder K1 and the dry powder K2 are simply dry-mixed. In the case where the dry powder K1 and the dry powder K2 are dried by an evaporation-dry method or a drum-dry method, it is preferable to perform mixing by crushing using a crusher.

The mixing ratio of the dry powders K1 and K2 makes it possible to adjust the I1/I2 values. It is preferable to mix so that the K1 mixing ratio calculated by the following formula becomes 5 to 95%. More preferably, the lower limit of the K 1 mixture ratio is 10% or more and the upper limit is 94% or less.

$$\text{K1 mixing ratio} = \text{mass of dry powder K1} / (\text{mass of dry powder K1} + \text{mass of dry powder K2}) \times 100$$

In addition to the method of preparing and mixing the two kinds of dry powders as described above, a catalyst precursor having both the peak P1 and the peak P2 may be prepared in one step by adjusting the stirring speed, the temperature of the heteropolyacid-containing liquid and the addition speed of the raw material of the G element and the ammonium raw material, when adding the raw material of the G element and the ammonium raw material to the heteropolyacid-containing liquid.

【0038】

(Molding step)

Before the heat treatment step described later, the catalyst precursor obtained by the dry powder mixing step may be molded. The molding method is not particularly limited, and known dry or wet molding methods can be applied. For example, compression molding, press molding, extrusion molding, granulation molding and the like can be exemplified. The shape of the molded article is not particularly limited, for example, a cylindrical shape, a ring shape, a spherical shape or the like can be exemplified. In addition, it is preferable to form only the catalyst precursor without adding a carrier, a binder or the like to the catalyst precursor at the time of molding, but a known additive such as graphite or talc, a known binder derived from an organic substance or an inorganic substance may be added as necessary.

【0039】

[Catalyst or Methacrylic Acid Production Catalyst Production Method]

In order to produce the catalyst, it is preferable to include a step of heat-treating the catalyst precursor (hereinafter also referred to as "heat-treating step") obtained by the dry powder mixing step or a molded article of the catalyst precursor obtained by the molding step (hereinafter collectively also referred to as "catalyst precursor").

【0040】

(Heat-treating step)

In this step, the catalyst precursor is heat-treated to produce a catalyst. The heat-treating step makes it possible to obtain a catalyst having a low local exotherm and a high activity per reactor under industrial use conditions. The heat-treating method and conditions are not particularly limited, and known methods and conditions can be applied. It is preferable that the heat-treating temperature is 300 to 450° C. By setting the heat-treating temperature to 300° C or more, ammonium in the catalyst can be removed and the catalyst activity can be improved, and by setting the temperature to 450° C or less, thermal decomposition of the heteropolyacid can be suppressed and rapid decrease in the catalyst activity can be suppressed. The lower limit of the heat-treating time is preferably 0.5 hours or more, more preferably 1 hour or more. The upper limit of the heat treatment time is preferably 40 hours or less.

【0041】

The heat-treating can be performed, for example, under the flow of at least one of air and an inert gas. Here, the inert gas refers to a gas which does not reduce the catalyst activity, and includes, for example, nitrogen, carbon dioxide, helium, argon and the like. One of these may be used, or two or more of those may be mixed and used. The heat-treating is preferably performed under the flow of an oxygen-containing gas such as air.

【0042】

[Methods for Producing Methacrylic Acid]

The method for producing methacrylic acid according to the present invention comprises gas phase catalytic oxidation of methacrolein with molecular oxygen in the presence of a catalyst obtained from a catalyst precursor according to the present invention to produce methacrylic acid. According to the method, methacrylic acid can be produced in high yield.

Methacrylic acid may be produced after a certain period of time has elapsed after the catalyst is obtained. The catalyst and methacrylic acid may be produced at different locations.

【0043】

Specifically, methacrylic acid can be produced by contacting a raw material gas containing methacrolein and molecular oxygen with a catalyst according to the present invention. Preferably, the reaction is carried out in a fixed bed.

【0044】

The catalyst may be used undiluted or diluted with an inert carrier, or may be used by laminating undiluted and diluted layers to form a plurality of layers.

【0045】

The concentration of the methacrolein in the raw material gas is not particularly limited, but is preferably 1 to 20% by volume, and the lower limit is more preferably 3% or more by volume and the upper limit is more preferably 10% or less by volume. Methacrolein may also contain small amounts of impurities such as lower saturated aldehydes which do not substantially affect the reaction. The molar ratio of methacrolein and molecular oxygen in the raw material gas is preferably 0.5 to 4.0 mol per 1.0 mol of methacrolein, the lower limit is more preferably 1.0 mol or more, and the upper limit is more preferably 3.0 mol or less. Although it is economical to use air as the molecular oxygen source, air enriched in pure oxygen can also be used if necessary.

【0046】

As the raw material gas, methacrolein and molecular oxygen may be diluted with an inert gas such as nitrogen or carbon dioxide. The raw material gas may contain water vapor.

By carrying out the reaction in the presence of water vapor, methacrylic acid can be obtained with a higher selectivity. The concentration of water vapor in the raw material gas is preferably 0.1 to 50.0 % by volume, more preferably 1.0 to 40.0 % by volume. The contact time between the raw material gas and the catalyst is preferably 1.5 to 15.0 seconds, the lower limit is more preferably 2.0 seconds or more, and the upper limit is more preferably 5.0 seconds or less. The reaction pressure can be set within the range of atmospheric pressure to several hundred kPa(G). Here, (G) means gauge pressure. The reaction temperature is preferably 200° C to 450° C, the lower limit is more preferably 250° C or more, and the upper limit is more preferably 400° C or less.

【0047】

[Methods for Producing Methacrylic Acid Esters]

The process for producing methacrylic acid esters according to the present invention can be carried out by esterification of methacrylic acid obtained by the process according to the invention. According to the method, methacrylic acid esters can be obtained using methacrylic acid obtained by gas phase catalytic oxidation of methacrolein. Alcohols reacted with methacrylic acid include methanol, ethanol, isopropanol, n-butanol, isobutanol and the like. Examples of the obtained methacrylate ester include methyl methacrylate, ethyl methacrylate, propyl methacrylate, butyl methacrylate and the like. The reaction can be carried out in the presence of an acidic catalyst, such as a sulfonic acid type cation exchange resin. The reaction temperature is preferably 50 to 200° C.

EXAMPLES:

【0048】

Hereinafter, the present invention will be explained in detail by examples and comparative examples, but the present invention is not limited to these examples. In the examples and comparative examples, "parts" means parts by weight. The X-ray diffractions were measured by an X-ray structural analyzer (trade name: X'Pert PRO MPD, manufactured by PANalytical Corporation). The analysis of the raw material gas and the product was carried out using gas chromatography. From the results of gas chromatography, the conversion rate of methacrolein, the selectivity of methacrylic acid produced and the yield of methacrylic acid were determined by the following formula.

Methacrolein conversion rate (%) = $(B/A) \times 100$

Methacrylic acid selectivity (%) = $(C/B) \times 100$

Methacrylic acid yield (%) = $(C/A) \times 100$

Where A represents the number of moles of methacrolein supplied, B represents the number of moles of methacrolein reacted and C represents the number of moles of methacrylic acid produced.

【0049】

[EXAMPLE 1]

100 parts of molybdenum trioxide, 6.67 parts of 85% by weight phosphoric acid, 3.36 parts of ammonium metavanadate and 2.10 parts of cupric nitrate were dissolved in 600 parts of pure water. The temperature was raised while stirring, and the mixture was stirred under reflux at 100° C for 5 hours. While the temperature was lowered and the liquid temperature was maintained at 80° C, 24.14 parts of cesium bicarbonate dissolved in 200 parts of pure water was added and stirred for 15 minutes, and then 3.84 parts of ammonium bicarbonate dissolved in 200 parts of pure water was added. The obtained heteropolyacid (complex) salt-containing liquid was spray-dried at an outlet temperature of 250° C, and further dried at

130° C for 16 hours to obtain a dry powder K1a. On the other hand, 100 parts of molybdenum trioxide, 6.67 parts of 85 mass % phosphoric acid, 3.36 parts of ammonium metavanadate and 2.10 parts of cupric nitrate were dissolved in 600 parts of pure water. The temperature was raised while stirring, and the mixture was stirred under reflux at 100° C for 5 hours. While the temperature was lowered and the liquid temperature was maintained at 80° C, 4.04 parts of cesium bicarbonate dissolved in 200 parts of pure water was added and stirred for 15 minutes, and then 11.93 parts of ammonium bicarbonate dissolved in 200 parts of pure water was added. The obtained heteropolyacid (complex) salt-containing liquid was spray-dried at an outlet temperature of 250° C, and further dried at 130° C for 16 hours to obtain a dry powder K2a. Next, dry powder K1a at a ratio of 90 parts was mixed with dry powder K2a at a ratio of 10 parts to obtain a catalyst precursor. As a result of X-ray diffraction pattern measurement using an anti-cathode Cu-K α line with respect to the catalyst precursor, peaks shown in Table 1 were confirmed.

【0050】

The catalyst precursor was molded by a tablet molding machine and placed in a calcinating container made of cylindrical quartz glass having an inner diameter of 3 cm. The temperature was raised at 10° C/h under air flow, and heat treating was performed at 380° C for 2 hours to prepare a catalyst. The compositions of the catalysts excluding hydrogen, nitrogen and oxygen were P₁Mo₁₂V_{0.5}Cu_{0.15}Cs_{1.97}. The molar ratio of the element composition was calculated by analyzing a component in which the catalyst precursor was dissolved in ammonia water by ICP luminescence analysis.

【0051】

The catalyst was charged into a reaction tube, and the reaction was carried out at a reaction temperature of 290° C, a reaction pressure of 256 kPa and a contact time of 3.6 seconds through a raw material gas consisting of 5% by volume of methacrolein, 10% by volume of oxygen, 30% by volume of water vapor and 55% by volume of nitrogen. The results are shown in Table 1.

【0052】

[EXAMPLE 2]

100 parts of molybdenum trioxide, 6.67 parts of 85% by weight phosphoric acid, 3.36 parts of ammonium metavanadate and 2.10 parts of cupric nitrate were dissolved in 600 parts of pure water. The temperature was raised while stirring, and the mixture was stirred under reflux at 100° C for 5 hours. While the temperature was lowered and the liquid temperature was maintained at 80° C, 30.10 parts of cesium bicarbonate dissolved in 200 parts of pure water was added and stirred for 15 minutes, and then 1.45 parts of ammonium bicarbonate dissolved in 200 parts of pure water was added. The obtained heteropolyacid (complex) salt-containing liquid was spray-dried at an outlet temperature of 250° C, and further dried at 130° C for 16 hours to obtain a dry powder K1b. On the other hand, 100 parts of molybdenum trioxide, 6.67 parts of 85 mass % phosphoric acid, 3.36 parts of ammonium metavanadate and 2.10 parts of cupric nitrate were dissolved in 600 parts of pure water. The temperature was raised while stirring, and the mixture was stirred under reflux at 100° C for 5 hours. While the temperature was lowered and the liquid temperature was maintained at 80° C, 3.14 parts of cesium bicarbonate dissolved in 200 parts of pure water was added and stirred for 15 minutes, and then 12.29 parts of ammonium bicarbonate dissolved in 200 parts of pure water was added. The obtained heteropolyacid (complex) salt-containing liquid was spray-dried at an outlet temperature of 250° C, and further dried at 130° C for 16 hours to obtain a dry

powder K2b.

【0053】

Next, dry powder K1b at a ratio of 70 parts was mixed with dry powder K2b at a ratio of 30 parts to obtain a catalyst precursor. The compositions of the obtained catalyst precursors excluding hydrogen, nitrogen and oxygen were $P_1Mo_{12}V_{0.5}Cu_{0.15}Cs_{1.96}$. As a result of X-ray diffraction pattern measurement using an anti-cathode Cu-K α line with respect to the catalyst precursor, peaks shown in Table 1 were confirmed.

【0054】

The catalyst precursor was formed and heat treated in the same manner as in Example 1 to prepare a catalyst.

Using this catalyst, methacrylic acid was produced in the same manner as in Example 1. The results are shown in Table 1.

【0055】

[EXAMPLE 3]

100 parts of molybdenum trioxide, 6.67 parts of 85% by weight phosphoric acid, 3.36 parts of ammonium metavanadate and 2.10 parts of cupric nitrate were dissolved in 600 parts of pure water. The temperature was raised while stirring, and the mixture was stirred under reflux at 100° C for 5 hours. While the temperature was lowered and the liquid temperature was maintained at 80° C, 21.56 parts of cesium bicarbonate dissolved in 200 parts of pure water was added and stirred for 15 minutes, and then 4.88 parts of ammonium bicarbonate dissolved in 200 parts of pure water was added. The obtained heteropolyacid (complex) salt-containing liquid was spray-dried at an outlet temperature of 250° C, and further dried at 130° C for 16 hours to obtain a dry powder K1c. On the other hand, 100 parts of molybdenum trioxide, 6.67 parts of 85 mass % phosphoric acid, 3.36 parts of ammonium metavanadate and 2.10 parts of cupric nitrate were dissolved in 600 parts of pure water. The temperature was raised while stirring, and the mixture was stirred under reflux at 100° C for 5 hours. While the temperature was lowered and the liquid temperature was maintained at 80° C, 5.62 parts of cesium bicarbonate dissolved in 200 parts of pure water was added and stirred for 15 minutes, and then 11.30 parts of ammonium bicarbonate dissolved in 200 parts of pure water was added. The obtained heteropolyacid (complex) salt-containing liquid was spray-dried at an outlet temperature of 250° C, and further dried at 130° C for 16 hours to obtain a dry powder K2c.

【0056】

Next, dry powder K1c at a ratio of 80 parts was mixed with dry powder K2c at a ratio of 20 parts to obtain a catalyst precursor. The compositions of the obtained catalyst precursors excluding hydrogen, nitrogen and oxygen were $P_1Mo_{12}V_{0.5}Cu_{0.15}Cs_{1.64}$. As a result of X-ray diffraction pattern measurement using an anti-cathode Cu-K α line with respect to the catalyst precursor, peaks shown in Table 1 were confirmed.

【0057】

The catalyst precursor was formed and heat treated in the same manner as in Example 1 to prepare a catalyst.

Using this catalyst, methacrylic acid was produced in the same manner as in Example 1. The results are shown in Table 1.

【0058】

[EXAMPLE 4]

A dry powder K1a and a dry powder K2a were obtained by the same method as in

Example 1. Next, dry powder K1a at a ratio of 94 parts was mixed with dry powder K2a at a ratio of 6 parts to obtain a catalyst precursor. The compositions of the obtained catalyst precursors excluding hydrogen, nitrogen and oxygen were $P_1Mo_{12}V_{0.5}Cu_{0.15}Cs_{2.04}$. As a result of X-ray diffraction pattern measurement using an anti-cathode Cu-K α line with respect to the catalyst precursor, peaks shown in Table 1 were confirmed.

【0059】

The catalyst precursor was formed and heat treated in the same manner as in Example 1 to prepare a catalyst.

Using this catalyst, methacrylic acid was produced in the same manner as in Example 1. The results are shown in Table 1.

【0060】

[EXAMPLE 5]

A dry powder K1a and a dry powder K2a were obtained by the same method as in Example 1. Next, the dry powder K1a at a ratio of 97 parts was mixed with the dry powder K2a at a ratio of 3 parts, thereby obtaining a catalyst precursor. The compositions of the obtained catalyst precursors excluding hydrogen, nitrogen and oxygen were $P_1Mo_{12}V_{0.5}Cu_{0.15}Cs_{2.10}$. As a result of X-ray diffraction pattern measurement using an anti-cathode Cu-K α line with respect to the catalyst precursor, peaks shown in Table 1 were confirmed.

【0061】

The catalyst precursor was formed and heat treated in the same manner as in Example 1 to prepare a catalyst.

Using this catalyst, methacrylic acid was produced in the same manner as in Example 1. The result is shown in Table 1.

【0062】

[EXAMPLE 6]

A dry powder K1a and a dry powder K2a were obtained by the same method as in Example 1. Next, dry powder K1a at a rate of 10 parts was mixed with dry powder K2a at a rate of 90 parts to obtain a catalyst precursor. The compositions of the obtained catalyst precursors excluding hydrogen, nitrogen and oxygen were $P_1Mo_{12}V_{0.5}Cu_{0.15}Cs_{0.54}$. As a result of X-ray diffraction pattern measurement using an anti-cathode Cu-K α line with respect to the catalyst precursor, peaks shown in Table 1 were confirmed.

【0063】

The catalyst precursor was formed and heat treated in the same manner as in Example 1 to prepare a catalyst.

Using this catalyst, methacrylic acid was produced in the same manner as in Example 1. The results are shown in Table 1.

【0064】

[Comparative Example 1]

A dry powder K1a was obtained by the same method as in Example 1, and was used as a catalyst precursor. The compositions of the catalyst precursors excluding hydrogen, nitrogen and oxygen were $P_1Mo_{12}V_{0.5}Cu_{0.15}Cs_{2.15}$. As a result of X-ray diffraction pattern measurement using an anti-cathode Cu-K α line with respect to the catalyst precursor, peaks shown in Table 1 were confirmed.

【0065】

The catalyst precursor was formed and heat treated in the same manner as in Example

1 to prepare a catalyst.

Using this catalyst, methacrylic acid was produced in the same manner as in Example 1. The results are shown in Table 1.

【0066】

[Comparative Example 2]

A dry powder K2a was obtained by the same method as in Example 1, and was used as a catalyst precursor. The compositions of the catalyst precursors excluding hydrogen, nitrogen and oxygen were $P_1Mo_{12}V_{0.5}Cu_{0.15}Cs_{0.36}$. As a result of X-ray diffraction pattern measurement using an anti-cathode Cu-K α line with respect to the catalyst precursor, peaks shown in Table 1 were confirmed.

【0067】

The catalyst precursor was formed and heat treated in the same manner as in Example 1 to prepare a catalyst.

Using this catalyst, methacrylic acid was produced in the same manner as in Example 1. The results are shown in Table 1.

【0068】

[Comparative Example 3]

A dry powder K1a was obtained in the same manner as in Example 1. On the other hand, 100 parts of molybdenum trioxide, 6.67 parts of 85 mass % phosphoric acid, 3.36 parts of ammonium metavanadate and 2.10 parts of cupric nitrate were dissolved in 600 parts of pure water. The temperature was raised while stirring, and the mixture was stirred under reflux at 100° C for 5 hours. While the temperature was lowered and the liquid temperature was maintained at 80° C, 1.46 parts of cesium bicarbonate dissolved in 200 parts of pure water was added and stirred for 15 minutes, and then 12.97 parts of ammonium bicarbonate dissolved in 200 parts of pure water was added. The obtained heteropolyacid salt-containing liquid was spray-dried at an outlet temperature of 250° C, and further dried at 130° C for 16 hours to obtain a dry powder K2e.

【0069】

Next, dry powder K1a was mixed at a rate of 90 parts with dry powder K2e at a rate of 10 parts to obtain a catalyst precursor. The compositions of the obtained catalyst precursors excluding hydrogen, nitrogen and oxygen were $P_1Mo_{12}V_{0.5}Cu_{0.15}Cs_{1.95}$. As a result of X-ray diffraction pattern measurement using an anti-cathode Cu-K α line with respect to the catalyst precursor, peaks shown in Table 1 were confirmed.

【0070】

The catalyst precursor was formed and heat treated in the same manner as in Example 1 to prepare a catalyst.

Using this catalyst, methacrylic acid was produced in the same manner as in Example 1. The results are shown in Table 1.

【0071】

Table 1

	P1 [°]	P2[°]	I1/I2	K1 mixture rate[%]	Methacrolein conversion rate [%]	Methacrylic acid selectivity[%]	Methacrylic acid yield[%]	Cs composition rate[/Mo12]
Example 1	26.18	26.42	0.87	90	81.2	84.0	68.2	1.97
Example 2	26.11	26.43	0.67	70	86.1	78.7	67.8	1.96
Example 3	26.21	26.40	0.77	80	74.6	88.9	66.3	1.64
Example 4	26.18	26.42	0.90	94	83.1	74.8	62.2	2.04
Example 5	26.18	26.42	0.93	97	84.8	61.1	51.8	2.10
Example 6	26.18	26.42	0.10	10	66.0	89.3	58.9	0.54
Comparative Example 1	26.18	-	0.96	100	90.3	53.9	48.7	2.15
Comparative Example 2	-	26.42	0.00	0	41.2	89.5	36.9	0.36
Comparative Example 3	26.18	26.45	0.87	90	79.0	57.0	45.0	1.95

【0072】

As shown in Table 1, the catalyst precursors obtained in Examples 1 to 6, in which the peaks P1 and P2 were within the specified range of the present invention, were heat-treated to obtain catalysts. As a result, the methacrylic acid yields were high by using the catalysts. Among them, in Examples 1 to 4 and 6, in which the value of I1/I2 was in the range of 0.05 to 0.92, the methacrylic acid yields were particularly high, and it was found that there was an optimum range for the value of I1/I2.

On the other hand, the peak P2 does not appear in the X-ray diffraction pattern of the catalyst precursor obtained in Comparative Example 1, the peak P1 does not appear in the X-ray diffraction pattern of the catalyst precursor obtained in Comparative Example 2, and the 2θ of the peak P2 of the catalyst precursor obtained in Comparative Example 3 is outside the prescribed range. As a result of using a catalyst obtained by heat-treating such catalyst precursors as catalysts, the methacrylic acid yields were low as compared with the examples.

Claims

[Claim 1]

A catalyst precursor including a heteropolyacid salt, the catalyst precursor having a peak P1 in which 2θ is $26.16^\circ \pm 0.06^\circ$ and a peak P2 in which 2θ is further toward the high-angle side than the peak P1 and equal to or less than 26.44° in an X-ray diffraction pattern using an anti-cathode Cu-K α line.

[Claim 2]

The catalyst precursor according to claim 1, wherein the ratio (I1/I2) of the height I1 of the peak P1 to the height I2 of the peak P2 is 0.05 to 0.92.

[Claim 3]

The catalyst precursor according to claim 1 or 2, wherein the catalyst is used in producing at least one selected from the group consisting of methacrylic acid and acrylic acid by gas phase catalytic oxidation of at least one selected from the group consisting of methacrolein and acrolein using molecular oxygen.

[Claim 4]

The catalyst precursor according to any one of claims 1 to 3, which has a composition represented by the following formula (I).



(In formula (I), P, Mo, V, Cu, and O are elemental symbols representing phosphorus, molybdenum, vanadium, copper and oxygen, respectively; A represents at least one element selected from the group consisting of antimony, bismuth, arsenic, germanium, zirconium, tellurium, silver, selenium, silicon, tungsten and boron; and E represents at least one element selected from the group consisting of iron, zinc, chromium, magnesium, calcium, strontium, tantalum, cobalt, nickel, manganese, barium, titanium, tin, lead, niobium, indium, sulfur, palladium, gallium, cerium and lanthanum; and G represents at least one element selected from the group consisting of potassium, rubidium, cesium and thallium; and a, b, c, d, e, f, g and h represent the atomic ratios of each element, and when $b=12$, $a=0.5$ to 3, $c=0.01$ to 3, $d=0.01$ to 2, $e=0$ to 3, $f=0$ to 3, and $g=0.01$ to 3, h is the atomic ratio of oxygen required to satisfy the valence of each of the above components.)

[Claim 5]

A method for producing a catalyst, comprising a step of heat treating the catalyst precursor according to any one of claims 1 to 4.

[Claim 6]

The method for producing a catalyst according to claim 5, wherein the heat treatment temperature in the step of heat treating is from 300 to 450° C.

[Claim 7]

A method for producing at least one selected from the group consisting of methacrylic acid and acrylic acid comprising steps of:

- (1) producing a catalyst by the method according to claim 5 or 6; and
- (2) producing at least one selected from the group consisting of methacrylic acid and acrylic acid by gas phase catalytic oxidation of at least one selected from the group consisting of methacrolein and acrolein using molecular oxygen in the presence of said catalyst.

[Claim 8]

A method for producing at least one selected from the group consisting of methacrylic acid esters and acrylic acid esters comprising steps of:

- (1) producing a catalyst by the method according to claim 5 or 6;
- (2) producing at least one selected from the group consisting of methacrylic acid and acrylic acid by gas phase catalytic oxidation of at least one selected from the group consisting of methacrolein and acrolein using molecular oxygen in the presence of the catalyst; and
- (3) esterifying at least one selected from the group consisting of methacrylic acid and acrylic acid.