

Description

Title of Invention: METHOD FOR PRODUCING CATALYST FOR
PRODUCING METHACRYLIC ACID

5

Technical Field

[0001]

The present invention relates to a method for producing a catalyst used
in producing methacrylic acid through a catalytic gas-phase oxidation reaction
10 of methacrolein with molecular oxygen (hereinafter, referred to as a catalyst for
producing methacrylic acid), and a catalyst produced by the method, and a
method for producing methacrylic acid using the catalyst.

Background Art

15 [0002]

A heteropoly acid compound represented by phosphomolybdic acid has
been known as a catalyst component for a catalyst for producing methacrylic
acid. Further, a large number of methods for forming an effective pore
structure in a catalyst in order to allow the catalyst component to work
20 effectively in a catalytic gas-phase oxidation reaction have been proposed.

[0003]

In Patent Literature 1, there is proposed a method of molding a catalyst
by adding a polymer organic compound that decomposes to a monomer and
vaporizes at a relatively low temperature such as polymethyl methacrylate or
25 polystyrene. In Patent Literature 2, there is proposed a method for producing
a catalyst in which a dried material of a mixed solution or an aqueous slurry

containing a catalyst component, the particle diameter of which is adjusted to a range of 1 to 250 μm is molded. In Patent Literature 3, there is proposed a method for producing a catalyst including: a step of making a primary molded article by mixing a particle including a catalyst component and a liquid; and
5 further, a secondary molding step of molding the primary molded article with a piston molding machine to a final form.

Citation List

Patent Literature

10 [0004]

Patent Literature 1: JP04-367737A

Patent Literature 2: JP08-10621A

Patent Literature 3: JP2003-93882A

15 Summary of Invention

Technical Problem

[0005]

However, the development of a catalyst that is capable of further improving a yield of methacrylic acid in the catalytic gas-phase oxidation
20 reaction of methacrolein has been desired.

[0006]

An object of the present invention is to provide a catalyst for producing methacrylic acid that is capable of producing methacrylic acid in high yield through a catalytic gas-phase oxidation reaction of methacrolein with molecular
25 oxygen.

Solution to Problem

[0007]

A method for producing a catalyst for producing methacrylic acid according to the present invention is a method for producing a catalyst for producing methacrylic acid used in producing methacrylic acid through a catalytic gas-phase oxidation reaction of methacrolein with molecular oxygen, the catalyst containing at least molybdenum and phosphorus as catalyst components, the method including: producing a dried material having an apparent density (X) of 1.00 to 1.80 kg/L by drying an aqueous liquid mixture containing raw material compounds for catalyst components; and producing a catalyst molded body having a molded article density (Y) of 1.60 to 2.40 kg/L and a ratio of the apparent density (X) to the molded article density (Y), (X/Y), of 0.50 to 0.80 by molding the dried material or a mixture containing the dried material.

15

Advantageous Effect of Invention

[0008]

According to the present invention, a catalyst for producing methacrylic acid that is capable of producing methacrylic acid in high yield through a catalytic gas-phase oxidation reaction of methacrolein with molecular oxygen can be provided.

20

Description of Embodiments

[0009]

25

[Catalyst for producing methacrylic acid]

A catalyst for producing methacrylic acid according to the present invention is a catalyst for producing methacrylic acid used in producing methacrylic acid through a catalytic gas-phase oxidation reaction of methacrolein with molecular oxygen, the catalyst containing at least molybdenum and phosphorus as catalyst components, and the catalyst is produced by a method to be described later.

[0010]

The composition of the catalyst components that constitutes the catalyst according to the present invention is not specifically limited as long as the composition contains at least molybdenum and phosphorus, and can be selected appropriately depending on the intended performance of the catalyst for producing methacrylic acid. The catalyst for producing methacrylic acid according to the present invention preferably has a composition represented by the following formula (A), for example.

[0011]



In the above formula (A), P, Mo, V, Cu, and O represent phosphorus, molybdenum, vanadium, copper, and oxygen, respectively. X represents at least one element selected from the group consisting of arsenic, antimony, and tellurium. Y represents at least one element selected from the group consisting of bismuth, germanium, zirconium, silver, selenium, silicon, tungsten, boron, iron, zinc, chromium, magnesium, tantalum, cobalt, manganese, barium, gallium, cerium, and lanthanum. Z represents at least one element selected from the group consisting of potassium, rubidium, and cesium. a, b, c, d, e, f, g, and h represent the atomic ratio of each element. When b is 12, a is 0.1 to 3, c is 0.01 to 3, d is 0.01 to 2, e is 0 to 3, f is 0 to 3, g is 0.01 to 3, and h

represents the atomic ratio of oxygen necessary for satisfying the valence of each element mentioned above. The above composition is calculated from the amount of the raw material of each element to be added.

[0012]

5 [Method for producing a catalyst for producing methacrylic acid]

A method for producing a catalyst for producing methacrylic acid according to the present invention is a method for producing a catalyst for producing methacrylic acid used in producing methacrylic acid through a catalytic gas-phase oxidation reaction of methacrolein with molecular oxygen,
10 the catalyst containing at least molybdenum and phosphorus as catalyst components, the method including: producing a dried material having an apparent density (X) of 1.00 to 1.80 kg/L by drying an aqueous liquid mixture containing raw material compounds for catalyst components; and producing a catalyst molded body having a molded article density (Y) of 1.60 to 2.40 kg/L
15 and a ratio of the apparent density (X) to the molded article density (Y), (X/Y), of 0.50 to 0.80 by molding the dried material or a mixture containing the dried material.

[0013]

Catalyst activity, selectivity to methacrylic acid, and methacrylic acid
20 yield in the methacrylic acid production have been found to be improved by making X, Y, and X/Y satisfy the ranges as specified in the present invention. Embodiments of the present invention are shown hereinafter.

[0014]

(Preparation of aqueous liquid mixture containing raw material
25 compounds for catalyst components)

First of all, a raw material compound for a catalyst component for a catalyst for producing methacrylic acid containing at least molybdenum and phosphorus is dissolved or suspended in water to prepare an aqueous liquid mixture. A method for preparing the aqueous liquid mixture is not specifically limited, and examples thereof include known methods such as a precipitation method and an oxide mixing method.

[0015]

A raw material compound for a catalyst component used for preparing an aqueous liquid mixture is not specifically limited. Examples thereof that can be used include nitrates; carbonates; acetates; ammonium salts; oxides; halides; oxo acids; and salts of oxo acids of each constituent element of the catalyst. These may be used singly or in combinations of two or more. Examples of a raw material compound of molybdenum include molybdenum oxides such as molybdenum trioxide, and ammonium molybdates such as ammonium paramolybdate and ammonium dimolybdate. Examples of a raw material compound of phosphorus include phosphoric acid, phosphorus pentaoxide, and ammonium phosphate. Examples of a raw material compound of vanadium include ammonium metavanadate, vanadium pentoxide, and vanadyl oxalate. Examples of a raw material compound of copper include copper nitrate, copper oxide, copper carbonate, and copper acetate. These raw material compounds for catalyst components may be used singly or in combinations of two or more for each element that constitutes a catalyst component.

[0016]

The aqueous liquid mixture may include ethyl alcohol, acetone, or the like, in addition to water, as a solvent.

[0017]

(Drying)

Next, the obtained aqueous liquid mixture including the raw material compounds for the catalyst components is dried. A drying method is not specifically limited, and, for example, an evaporation to dryness method, a spray drying method (spray drying), a drum drying method, or a flash drying method may be used. Among these, a spray drying is preferable.

[0018]

The apparent density (X) of the dried material in the present invention is in the range of 1.00 to 1.80 kg/L, preferably in the range of 1.00 to 1.60 kg/L, more preferably in the range of 1.00 to 1.50 kg/L, and even more preferably in the range of 1.05 to 1.40 kg/L. With the apparent density (X) in the range of 1.00 to 1.80 kg/L, catalyst activity and selectivity to methacrylic acid in the methacrylic acid production are improved because it becomes possible to allow pores effective in selective oxidation of methacrolein to be formed while obtaining a sufficient molded body density. In the case where the apparent density (X) is less than 1.00 kg/L, it is possible to form pores effective in the reaction, but the molded article density becomes smaller in molding, and the amount of the catalyst to be packed into a reaction tube is decreased resulting in decreased reaction rate. On the other hand, in the case where the apparent density (X) is more than 1.80 kg/L, catalyst activity and selectivity to methacrylic acid are lowered. Here, the apparent density (X) is a value measured by the method as described in JIS K 7365. Namely, the obtained dried material is measured off into a 100 mL measuring cylinder, and the apparent density is a value calculated from the mass of 100 mL volume by the following formula.

[0019]

Apparent density (X) (kg/L (g/mL)) = Mass of the dried material packed into a 100 mL measuring cylinder (g) / 100

[0020]

5 A spray drying can be carried out by supplying the aqueous liquid mixture obtained by the above method and hot air to a spray drier and spraying the aqueous liquid mixture into the hot air. Examples of a spraying system for the aqueous liquid mixture include a rotating disk system and a pressure nozzle system. Furthermore, as hot air, an oxidizing gas such as air may be used,
10 and non-oxidizing gas such as nitrogen may also be used. The apparent density (X) of the obtained dried material tends to become larger as an inlet temperature of the hot air is lower; a liquid temperature of the aqueous liquid mixture to be supplied is lower; a stirring of the aqueous liquid mixture to be supplied is more vigorous; and the solid content rate of the aqueous liquid
15 mixture is higher. Thus, these may be adjusted so that the apparent density (X) falls within the range from 1.00 to 1.80 kg/L.

[0021]

The hot air inlet temperature of a spray drier is preferably 200 to 400°C, more preferably 210 to 370°C, even more preferably 220 to 300°C, and
20 particularly preferably 230 to 280°C.

[0022]

A stirring of the aqueous liquid mixture before feeding it into a spray drier is preferably carried out at the highest possible speed. Examples of a stirrer include known stirrers such as: a rotary stirrer such as a rotary blade stirrer or a
25 high-speed rotation shear stirrer (homogenizer and the like); a pendulum linear motion type stirrer; a shaker that shakes a container itself; and a vibration type

stirrer using ultrasonics or the like. As a stirrer, a rotary stirrer such as a rotary blade stirrer or a high-speed rotation shear stirrer (homogenizer and the like) is preferable because it is easy to adjust the intensity of stirring and it is a simple method from an industrial standpoint. A rotation speed of a stirring vane or a rotating blade in the rotary stirrer may be adjusted appropriately taking the shape of a container, a stirring vane, a baffle plate, and so on; and the liquid volume into consideration so as not for the liquid to scatter. A temperature of the aqueous liquid mixture at the time of stirring is preferably 25°C or lower, more preferably 20°C or lower, even more preferably 18°C or lower, and particularly preferably 15°C or lower. A stirring time is preferably 30 minutes or longer, more preferably 40 minutes or longer, even more preferably 50 minutes or longer, and particularly preferably one hour or longer.

[0023]

A solid content rate of the aqueous liquid mixture in the present invention is calculated, after drying a part of the aqueous liquid mixture with a hot air drier and so on, from the mass of solid content after drying by the following formula.

[0024]

Solid content rate (%) = (Mass of the solid content of the aqueous liquid mixture after drying / Mass of the aqueous liquid mixture before drying) × 100

[0025]

The solid content rate of the aqueous liquid mixture is preferably 18% or more, more preferably 20% or more, even more preferably 22% or more, and particularly preferably 25% or more. Furthermore, the solid content rate of the aqueous liquid mixture is preferably 50% or less, and more preferably 40% or less.

[0026]

An average particle diameter of the dried material is preferably 1 to 250 μm . In the case where the average particle diameter is 1 μm or more, a pore diameter necessary for the oxidation reaction of methacrolein can be assured, thus methacrylic acid can be obtained in a higher yield. Further, in the case
5 where the average particle diameter is 250 μm or less, the number of contact points between dried material particles per unit volume does not decrease, thus a catalyst having a sufficient mechanical strength can be obtained. The average particle diameter of the dried material is more preferably 5 to 150 μm . The average particle diameter means a volume average particle diameter, and
10 the value is measured by a laser particle diameter distribution measuring apparatus.

[0027]

Furthermore, a contact mode of sprayed liquid drops with the hot air may be any one of co-current, counter current, and co-counter current (mixed
15 current), and the drying can preferably be carried out in any one of these modes.

[0028]

The dried material thus obtained may be subjected to, if necessary, a heat treatment (calcination) at 200 to 500°C to make a calcined product. The
20 calcination condition is not specifically limited, but the calcination is usually carried out under the flow of oxygen, air, or nitrogen. Further, the calcination time is set appropriately according to the intended catalyst. Hereinafter, a dried material which has not been calcined and the calcined product described above are collectively referred to as a dried material. When the heat
25 treatment is carried out, the apparent density (X) is measured for the calcined

product after the heat treatment, and the measured value may be included within the range of the apparent density (X) according to the present invention.

[0029]

(Preparation of mixture containing dried material)

5 When extrusion is carried out in the molding to be described below, it is also possible to prepare a mixture containing the obtained dried material to carry out extrusion of the mixture. The mixture is not specifically limited as long as it contains the dried material; however the mixture is preferably a kneaded material that is produced by kneading a liquid and an organic binder
10 with the obtained dried material.

[0030]

 An apparatus to be used for kneading is not specifically limited, and for example, a batch type kneader with a double arm type stirring impeller; or a continuous kneader such as one having a rotating reciprocating screw, or one
15 having a self-cleaning function can be used. However, a batch type kneader is preferable from a viewpoint that it is possible to carry out kneading while checking the state of the kneaded material. The end point of kneading is defined as a point of time when the kneaded material is mixed until it is possible for the kneaded material to be extruded, and the end point is
20 determined by a visual observation or a touch.

[0031]

 The liquid is not specifically limited as long as the liquid has a function of wetting the dried material, and examples thereof include water; and an alcohol having 1 to 4 carbon atoms such as methyl alcohol, ethyl alcohol, propyl
25 alcohol, and butyl alcohol. Among these, ethyl alcohol and propyl alcohol are preferable from the standpoint that the particles in the dried material do not

collapse, and that pores effective in the oxidation reaction are easy to be formed. These may be used singly or in combinations of two or more.

[0032]

The amount of the liquid to be used is selected appropriately depending
5 on the type and size of the dried material, and the type of the liquid; however, it is preferably 10 to 60 parts by mass relative to 100 parts by mass of the dried material to be subjected to a kneading. When the amount of the liquid to be used is 10 parts by mass or more, it becomes possible to smoothly carry out extrusion, therefore particles in the dried material become difficult to be
10 crushed. Thereby, large voids, namely large pores are formed in the dried or calcined molded article, and the selectivity to methacrylic acid tends to be improved. On the other hand, when the amount of the liquid to be used is 60 parts by mass or less, adhesiveness at the time of molding is lowered resulting in improved handling characteristics. Furthermore, the strength of the molded
15 article tends to be improved because the molded article becomes denser. The amount of liquid to be used is more preferably 15 to 50 parts by mass relative to 100 parts by mass of the dried material to be subjected to a kneading, even more preferably 16 to 45 parts by mass, and particularly preferably 20 to 35 parts by mass.

20 [0033]

The organic binder is not specifically limited, and examples thereof include a polymer compound such as polyvinyl alcohol, α -glucan derivatives, and β -glucan derivatives. These may be used singly or in combinations of two or more.

25 [0034]

The α -glucan derivative is a polysaccharide in which glucose is bound in the form of α -configuration among polysaccharides that are constituted from glucose. Examples thereof include derivatives such as α -1,4 glucan, α -1,6 glucan, and α -1,4/1,6 glucan. Examples of such an α -glucan derivative include amylose, glycogen, amylopectin, pullulan, dextrin, and cyclodextrin. These may be used singly or in combinations of two or more.

[0035]

The β -glucan derivative is a polysaccharide in which glucose is bound in the form of β -configuration among polysaccharides that are constituted from glucose. Examples thereof include derivatives such as β -1,4 glucan, β -1,3 glucan, β -1,6 glucan, and β -1,3/1,6 glucan. Examples of such a β -glucan derivative include: a cellulose derivatives such as methyl cellulose, ethyl cellulose, carboxymethyl cellulose, sodium carboxymethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, hydroxypropyl methyl cellulose (HPMC), hydroxyethyl methyl cellulose, hydroxybutyl methyl cellulose, and ethyl hydroxyethyl cellulose; β -1,3 glucans such as curdlan, laminaran, paramylon, callose, pachyman, and scleroglucan. These may be used singly or in combinations of two or more.

[0036]

The organic binder may be used without being refined, or may be used as refined. However, in the case where metals or ignition residues as impurities are contained, the catalyst performance sometimes is reduced, therefore the content of metals or ignition residues is preferably smaller.

[0037]

The amount of the organic binder to be used is selected appropriately depending on the type and size of the dried material, and the type of liquid,

however it is preferably 0.05 to 15 parts by mass relative to 100 parts by mass of the dried material to be subjected to a kneading, and more preferably 0.1 to 10 parts by mass. With an amount of the organic binder to be used of 0.05 parts by mass or more, the moldability tends to be improved. On the other
5 hand, the amount of the organic binder to be used of 15 parts by mass or less makes it easy to carry out a process of removing the organic binder by, for example, a heat treatment after molding.

[0038]

In addition, in the kneading, an inert carrier such as an inorganic
10 compound such as silica, alumina, silica-alumina, silicon carbide, titania, magnesia, graphite, and diatomaceous earth; inorganic fiber such as glass fiber, ceramic fiber and carbon fiber; or ceramic ball or stainless steel can further be added to carry out kneading. These may be used singly or in combinations of two or more.

15 [0039]

(Molding)

Next, the dried material or the mixture containing the dried material is molded to produce a catalyst molded body. Examples of a molding method of the dried material include known methods for molding powders such as
20 tableting, extrusion, and a tumbling granulation. Among these, extrusion is preferable. In addition, as described above, in the case of extrusion, the mixture containing the dried material can be extruded. For example, an auger extrusion machine or a piston type extrusion machine can be used for the extrusion. A shape of the catalyst molded body is not specifically limited, and
25 it can be, for example, any shape such as ring shape, cylindrical shape, or star shape.

[0040]

In the case of extrusion, an extruded form obtained by extrusion may be dried to make a catalyst molded body. A method for drying is not specifically limited, and for example, commonly known methods such as a hot air drying, a far infrared drying, or a microwave drying can arbitrarily be used. The drying condition can appropriately be selected as long as the intended water content is obtained. In the case where the drying is applied to the extruded form, the molded article density (Y) to be described later is measured for the catalyst molded body after drying, and the measured value may be included within the range of the molded article density (Y) according to the present invention and the value of (X/Y) may be included within the range according to the present invention.

[0041]

The molded article density (Y) of the catalyst molded body of the present invention is in the range of 1.60 to 2.40 kg/L, preferably in the range of 1.65 to 2.30 kg/L, more preferably in the range of 1.70 to 2.20 kg/L, and even more preferably in the range of 1.75 to 2.10 kg/L. Furthermore, the ratio of the apparent density (X) to the molded article density (Y), (X/Y) in the present invention is in the range of 0.50 to 0.80, preferably in the range of 0.53 to 0.75 kg/L, more preferably in the range of 0.55 to 0.73 kg/L, and even more preferably 0.57 to 0.70 kg/L. Here, the molded article density (Y) is the value calculated from the average value of the mass (kg) per a catalyst molded article divided by the volume (L) for 100 catalyst molded articles.

[0042]

When the molded article density (Y) is in the range of 1.60 to 2.40 kg/L, catalyst activity is improved in the methacrylic acid production because the

amount of the catalyst to be packed effective in the oxidation of methacrolein can be assured. Furthermore, when the ratio (X/Y) is in the range of 0.50 to 0.80, the amount of pore effective in the selective oxidation of methacrolein and the amount of the catalyst to be packed effective in the oxidation of methacrolein are simultaneously assured, therefore the yield of methacrylic acid is improved.

[0043]

The molded article density (Y) of the catalyst molded body tends to become larger as the amount of liquid is smaller in the case where the liquid is added in preparing the mixture; and the molding pressure is higher. Therefore, these may be adjusted so that the molded article density (Y) is 1.60 to 2.40 kg/L, and, at the same time, the ratio of the apparent density (X) to the molded article density (Y), (X/Y) is 0.50 to 0.80.

[0044]

(Calcination)

The obtained catalyst molded body as such may be used as the catalyst for producing methacrylic acid, however it may also be used as the catalyst for producing methacrylic acid after calcination.

[0045]

The calcination condition is not specifically limited, and known calcination conditions can be applied. The calcination temperature may be 200 to 600°C, preferably 200 to 500°C, and more preferably 300 to 450°C. The calcination time may be 1 to 24 hours.

[0046]

[Method for producing methacrylic acid]

A method for producing methacrylic acid according to the present invention is a method for producing methacrylic acid through a catalytic gas-phase oxidation reaction of methacrolein with molecular oxygen in the presence of the catalyst for producing methacrylic acid produced by the method according to the present invention.

[0047]

The catalytic gas-phase oxidation reaction can be carried out in a fixed-bed. A catalyst layer is not specifically limited. The catalyst layer may be a non-diluted layer composed of only the catalyst or a diluted layer containing an inert carrier, and may be a monolayer or a mixed layer composed of a plurality of layers.

[0048]

It is preferable to use a raw material gas that contains methacrolein and molecular oxygen for the catalytic gas-phase oxidation reaction. The concentration of methacrolein in the raw material gas can be changed in a wide range, however the concentration of methacrolein in the raw material gas is preferably 1% by volume or more, and more preferably 3% by volume or more. Furthermore, the concentration of methacrolein in the raw material gas is preferably 20% by volume or less, and more preferably 10% by volume or less.

The concentration of molecular oxygen in the raw material gas is preferably 0.4 mol or more per 1 mol of methacrolein, and more preferably 0.5 mol or more. In addition, the concentration of molecular oxygen in the raw material gas is preferably 4 mol or less per 1 mol of methacrolein, and more preferably 3 mol or less. As a molecular oxygen source, it is economical to use air, however a pure oxygen-enriched air can be used, if necessary.

[0049]

The raw material gas preferably contains water (water vapor) besides methacrolein and molecular oxygen. When the reaction is carried out in the presence of water, methacrylic acid can be obtained in a higher yield. The concentration of water vapor in the raw material gas is preferably 0.1% by volume or more, and more preferably 1% by volume or more. Furthermore, the concentration of water vapor in the raw material gas is preferably 50% by volume or less, and more preferably 40% by volume or less. The raw material gas may contain a small quantity of impurities such as lower saturated aldehyde, however it is preferable to keep the quantity as small as possible. Moreover, the raw material gas may also contain an inert gas such as nitrogen or carbon dioxide gas.

[0050]

The reaction pressure of the catalytic gas-phase oxidation reaction is preferably from ordinary pressure (atmospheric pressure) to 5 atm. The reaction temperature is preferably 230°C or higher, and more preferably 250°C or higher. Furthermore, the reaction temperature is preferably 450°C or lower, and more preferably 400°C or lower. The flow rate of the raw material gas is not specifically limited and can be set appropriately so that a suitable contact time is realized. The space velocity of the raw material gas is preferably 300 to 3000 hr⁻¹, and more preferably 500 to 2000 hr⁻¹.

Examples

[0051]

Hereinafter, the present invention will be explained specifically with reference to Examples and Comparative Examples, however the present

invention is not limited to these Examples. The term "parts" in the following Examples and Comparative Examples means parts by mass.

[0052]

An analysis of the raw material gas and the products were carried out by
 5 gas chromatography. The reaction rate of methacrolein, the selectivity to methacrylic acid, and the yield of methacrylic acid are defined as follows.

[0053]

Reaction rate of methacrolein (%) = $(B/A) \times 100$

Selectivity to methacrylic acid (%) = $(C/B) \times 100$

10 Yield of methacrylic acid (%) = $(C/A) \times 100$

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

[0054]

15 Furthermore, the apparent density (X) of the dried material, the molded article density (Y) of the catalyst molded body, and the solid content rate of the slurry (the aqueous liquid mixture) were measured as follows.

[0055]

(Apparent density (X) of dried material)

20 The dried material was measured off into a 100 mL measuring cylinder according to the method as described in JIS K 7365. The apparent density (X) of the dried material was calculated from the mass of a volume of 100 mL by the following formula.

[0056]

25 Apparent density (X) (kg/L (g/mL)) = Mass of the dried material packed into a 100 mL measuring cylinder (g) / 100

[0057]

(Molded article density (Y) of catalyst molded body)

The mass (kg) per a catalyst molded article was divided by the volume (L). This calculation was carried out for 100 catalyst molded articles, and the
 5 molded article density (Y) of the catalyst molded body was determined by calculating the average value.

[0058]

(Solid content rate of slurry (aqueous liquid mixture))

300 g of the slurry was dried with a hot air drier. The solid content rate
 10 of the slurry (the aqueous liquid mixture) was calculated from the mass of the solid content after drying by the following formula.

[0059]

Solid content rate (%) = (Mass of the solid content after drying slurry /
 Mass of the slurry before drying slurry) × 100

15 [0060]

(Example 1)

100 parts of molybdenum trioxide, 3.4 parts of ammonium metavanadate,
 8.0 parts of 85% by mass aqueous phosphoric acid solution, and 1.4 parts of
 copper nitrate were dissolved in 400 parts of pure water. The resultant
 20 solution was heated to 95°C while being stirred, and the stirring was continued for 3 hours keeping the solution temperature at 95°C. After cooling the solution to 85°C, a solution obtained by dissolving 14.0 parts of cesium bicarbonate in 20 parts of pure water was added thereto while stirring with a rotary blade stirrer, and the resultant mixture was stirred for 15 minutes. Next,
 25 a solution obtained by dissolving 10.7 parts of ammonium nitrate in 20 parts of pure water was added thereto, and the resultant mixture was further stirred for

20 minutes. After that, the slurry was heated to 100°C while being stirred, and then condensed until the solid content rate of the slurry reached the value as shown in Table 1.

[0061]

5 The slurry (aqueous liquid mixture) containing the raw material compounds for the catalyst components thus obtained was subdivided into small batches of slurry each having a volume of 20 L, which were then stirred. After that, the subdivided slurry was spray dried using a co-current spray dryer under the condition of a rotation speed of a rotary disk for spraying slurry of
10 18,000 rpm. The method of stirring the slurry, the stirring rotation speed, the stirring time, and the liquid temperature of the slurry are shown in Table 1 as the condition of stirring the subdivided slurry each having a volume of 20 L before spray drying. Furthermore, the hot air inlet temperature in the spray drying and the apparent density (X) of the obtained dried material are shown in
15 Table 1. The solid content rate of the slurry shown in Table 1 was measured before stirring the subdivided slurry; however, the value does not change after stirring.

[0062]

 The dried material thus obtained, HPMC, ethyl alcohol, and pure water
20 were mixed, and kneaded until the dried material became clay-like by a batch-type kneader equipped with a double-arm type sigma-blade.

[0063]

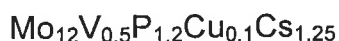
 Next, the kneaded mixture was extruded by a piston type extrusion machine. In the extrusion, the mixture was molded into a cylindrical shape
25 with an outer diameter of 4.8 mm and a length of 5 mm. This molded body was dried at 90°C for 12 hours to obtain a catalyst molded body. The amount

of each additive and the molded article density (Y) of the obtained catalyst molded body are shown in Table 2.

[0064]

Next, the catalyst molded body was calcined at 380°C under airflow for
5 18 hours to obtain a catalyst. The elemental composition of the obtained catalyst other than oxygen (the same applies hereinafter) was as follows.

[0065]



The above elemental composition is calculated from the amount of the
10 raw material of each element to be added.

[0066]

This catalyst was packed into a reaction tube made of stainless steel with an outer diameter of 27.5 mm and a height of 6 m which has a thermo-bath outside in such a way that the packing length of the catalyst was 5 m.
15 Then, the temperature of the thermo-bath was set to 285°C, and then the catalytic gas-phase oxidation reaction of methacrolein was carried out under the condition that allowed a reaction gas consisting of 6% by volume of methacrolein, 12% by volume of oxygen, 10% by volume of water vapor, and 72% by volume of nitrogen to pass through the catalyst layer at a space
20 velocity of 1100 hr⁻¹. The product obtained after 24 hours from the start of the reaction was collected and analyzed by gas chromatography to determine the reaction rate of methacrolein, the selectivity to methacrylic acid, and the yield of methacrylic acid. The results are shown in Table 3.

[0067]

25 (Example 2, Comparative Examples 1 to 4)

The catalysts were prepared and the catalytic gas-phase oxidation reaction of methacrolein was carried out in the same manner as in Example 1 except for adopting the conditions shown in Tables 1 and 2. The results are shown in Table 3.

5 [0068]

(Example 3)

100 parts of molybdenum trioxide, 2.7 parts of ammonium metavanadate, 7.3 parts of 85% by mass aqueous phosphoric acid solution, 7.5 parts of 60% by mass arsenic acid, and 2.8 parts of copper nitrate were dissolved in 400 parts of pure water. The resultant solution was heated to 95°C while being stirred, and the stirring was continued for 3 hours keeping the solution temperature at 95°C. After cooling the solution to 85°C, a solution obtained by dissolving: 12.4 parts of cesium bicarbonate dissolved in 20 parts of pure water; and 9.2 parts of ammonium carbonate dissolved in 20 parts of pure water in 26 parts of pure water was added thereto while stirring with a rotary blade stirrer, and the resultant mixture was further stirred for 20 minutes. After that, the slurry was heated to 100°C while being stirred, and then condensed until the solid content rate of the slurry reached the value as shown in Table 1.

15 [0069]

20 The slurry aqueous liquid mixture containing the raw material compounds for the catalyst components thus obtained was subdivided into small batches of slurry each having a volume of 20 L, which were then stirred. After that, the subdivided slurry was spray dried by a co-current spray dryer under the condition of a rotation speed of a rotary disk for spraying slurry of 18,000 rpm. The conditions of stirring and drying, and the apparent density (X) of the obtained dried material are shown in Table 1.

25

[0070]

The dried material thus obtained, HPMC, ethyl alcohol, and pure water were mixed, and kneaded until the dried material became clay-like by a batch-type kneader equipped with a double-arm type sigma-blade.

5 [0071]

Next, the kneaded mixture was extruded by a piston type extrusion machine. In the extrusion, the mixture was molded into a pellet shape with an outer diameter of 4.8 mm and a length of 5 mm. This molded body was dried at 90°C for 12 hours to obtain a catalyst molded body. The amount of each additive and the molded article density (Y) of the obtained catalyst molded body are shown in Table 2.

[0072]

Next, the catalyst molded body was calcined at 380°C under airflow for 15 hours to obtain a catalyst. The elemental composition of the obtained catalyst other than oxygen was as follows.

[0073]



This catalyst was packed into a reaction tube made of stainless steel with an outer diameter of 27.5 mm and a height of 6 m which has a thermo-bath outside in such a way that the packing length of the catalyst was 5 m. Then, the temperature of the thermo-bath was set to 285°C, and then the catalytic gas-phase oxidation reaction of methacrolein was carried out under the condition that allowed a reaction gas consisting of 6% by volume of methacrolein, 12% by volume of oxygen, 10% by volume of water vapor, and 72% by volume of nitrogen to pass through the catalyst layer at a space velocity of 1100 hr⁻¹. The product obtained after 24 hours from the start of the

reaction was collected and analyzed by gas chromatography to determine the reaction rate of methacrolein, the selectivity to methacrylic acid, and the yield of methacrylic acid. The results are shown in Table 3.

[0074]

5 (Examples 4 to 6, Comparative Examples 5 to 7)

The catalysts were prepared and the catalytic gas-phase oxidation reaction of methacrolein was carried out in the same manner as in Example 3 except for adopting the conditions shown in Tables 1 and 2. The results are shown in Table 3.

10 [0075]

The reaction each described in Example 3, Comparative Example 5, and Comparative Example 6 was carried out for 2400 consecutive hours. The results are shown in Table 4.

[0076]

[Table 1]

[Table 1]

Example and Comparative Example	Hot air inlet temperature [°C]	Method of stirring slurry	Stirring rotation speed [rpm]	Stirring time [min]	Liquid temperature of slurry [°C]	Solid content rate of slurry [%]	Apparent density (X) of dried material [kg/L]
Example 1	250	Rotary stirrer having 4 paddle impellers	150	45	20	22	1.05
Example 2	250	Rotary stirrer having 4 paddle impellers	150	45	20	22	1.05
Comparative Example 1	250	Rotary stirrer having 4 paddle impellers	150	45	20	22	1.05
Comparative Example 2	250	Rotary stirrer having 4 paddle impellers	150	45	20	22	1.05
Comparative Example 3	300	Rotary stirrer having 4 paddle impellers	100	30	25	18	0.90
Comparative Example 4	300	Rotary stirrer having 4 paddle impellers	100	30	25	18	0.90
Example 3	250	Rotary stirrer having 4 paddle impellers	150	60	15	27	1.17
Example 4	250	Rotary stirrer having 4 paddle impellers	150	60	15	27	1.17
Comparative Example 5	250	Rotary stirrer having 4 paddle impellers	150	60	15	27	1.17
Comparative Example 6	250	Rotary stirrer having 4 paddle impellers	150	60	15	27	1.17
Example 5	230	Homogenizer	8000	60	10	34	1.31
Comparative Example 7	230	Homogenizer	8000	60	10	34	1.31
Example 6	210	Homogenizer	8000	60	10	38	1.38

[0077]

[Table 2]

[Table 2]

Example and Comparative Example	Amount of dried material [parts]	Amount of HPMC [parts]	Amount of ethyl alcohol [parts]	Amount of pure water [parts]	Molded article density (Y) of catalyst molded body [kg/L]
Example 1	100	5	20	7	1.86
Example 2	100	5	26	5	1.65
Comparative Example 1	100	5	31	3	1.50
Comparative Example 2	100	5	17	6	2.19
Comparative Example 3	100	5	21	7	1.79
Comparative Example 4	100	5	32	4	1.45
Example 3	100	5	20	7	1.83
Example 4	100	5	19	6	1.99
Comparative Example 5	100	5	31	3	1.51
Comparative Example 6	100	5	15	5	2.41
Example 5	100	5	18	6	2.06
Comparative Example 7	100	5	31	3	1.52
Example 6	100	5	18	5	2.06

[0078]

[Table 3]

[Table 3]

Example and Comparative Example	Apparent density (X) of dried material [kg/L]	Molded article density (Y) of catalyst molded body [kg/L]	Ratio of apparent density to molded article density (X/Y)	Reaction rate of methacrolein [%]	Selectivity to methacrylic acid [%]	Yield of methacrylic acid [%]
Example 1	1.05	1.86	0.57	85.0	77.0	65.5
Example 2	1.05	1.65	0.64	84.2	77.3	65.1
Comparative Example 1	1.05	1.50	0.70	78.3	77.1	60.4
Comparative Example 2	1.05	2.19	0.48	85.3	73.1	62.4
Comparative Example 3	0.90	1.79	0.50	85.1	73.3	62.4
Comparative Example 4	0.90	1.45	0.62	78.1	77.3	60.4
Example 3	1.17	1.83	0.64	84.9	79.4	67.4
Example 4	1.17	1.99	0.59	85.3	79.3	67.6
Comparative Example 5	1.17	1.51	0.77	78.6	79.5	62.5
Comparative Example 6	1.17	2.41	0.49	85.9	76.2	65.5
Example 5	1.31	2.06	0.64	85.5	79.3	67.8
Comparative Example 7	1.31	1.52	0.86	78.1	79.4	62.0
Example 6	1.38	2.06	0.67	85.2	79.4	67.6

[0079]

[Table 4]

[Table 4]

Example and Comparative Example	Reaction rate of methacrolein [%]	Selectivity to methacrylic acid [%]	Yield of methacrylic acid [%]
Example 3	84.7	79.8	67.6
Comparative Example 5	73.5	79.9	58.7
Comparative Example 6	85.8	76.2	65.4

[0080]

- 5 As described above, when the Example and Comparative Example that have the same catalyst composition are compared, all the Examples, in which the apparent density (X) is in the range of 1.00 to 1.80 kg/L; the molded article density (Y) is in the range of 1.60 to 2.40 kg/L; and (X/Y) is in the range of 0.50 to 0.80, showed better yield of methacrylic acid than the Comparative
- 10 Examples.

Claims

[Claim 1]

A method for producing a catalyst for producing methacrylic acid used in
5 producing methacrylic acid through a catalytic gas-phase oxidation reaction of
methacrolein with molecular oxygen, the catalyst comprising at least
molybdenum and phosphorus as catalyst components, the method comprising:
producing a dried material having an apparent density (X) of 1.00 to 1.80
kg/L by drying an aqueous liquid mixture comprising raw material compounds
10 for catalyst components; and
producing a catalyst molded body having a molded article density (Y) of
1.60 to 2.40 kg/L and a ratio of the apparent density (X) to the molded article
density (Y), (X/Y), of 0.50 to 0.80 by molding the dried material or a mixture
comprising the dried material.

15 [Claim 2]

A catalyst for producing methacrylic acid produced by the method
according to claim 1.

[Claim 3]

A method for producing methacrylic acid through a catalytic gas-phase
20 oxidation reaction of methacrolein with molecular oxygen in the presence of the
catalyst for producing methacrylic acid according to claim 2.