DESCRIPTION

METHOD FOR PRODUCING METHACRYLIC ACID PRODUCTION CATALYST, METHOD FOR PRODUCING METHACRYLIC ACID, AND METHOD FOR PRODUCING METHACRYLIC ACID ESTER

TECHNICAL FIELD

[0001] The present invention relates to a method for producing a methacrylic acid production catalyst, a method for producing methacrylic acid, and a method for producing a methacrylic acid ester.

BACKGROUND ART

[0002] As a catalyst for producing methacrylic acid by the gas phase catalytic oxidation of methacrolein, a catalyst containing heteropoly acid such as molybdophosphoric acid or a molybdophosphoric acid salt as a main component is exemplified. In general, the catalyst is produced by preparing a raw material liquid such as an aqueous solution or aqueous slurry containing each element constituting the catalyst, drying the raw material liquid to produce dried catalyst powder, and then molding and firing the dried catalyst powder.

[0003] For example, Patent Literature 1 has proposed a method for producing a catalyst, the method including: kneading a dried product of an aqueous solution or aqueous slurry containing each element constituting the catalyst with a small amount of kneaded product in which a dried product, a liquid, and a binder are kneaded in advance.

[0004] Patent Literature 2 has proposed a method for producing a catalyst, the method including: mixing powder, which is obtained by firing a catalyst component containing

heteropoly acid and sieving the fired product, with a catalyst material before molding and then molding the resultant mixture.

[0005] Patent Literature 3 has proposed a method for producing a catalyst, the method including: firing and pulverizing a catalyst component containing molybdenum and bismuth, primarily molding the resultant product, pulverizing the primarily molded article again, and then secondarily molding the pulverized primarily-molded article.

PRIOR ART LITERATUREPATENT LITERATURE

[0006] Patent Literature 1: JP 2012-206107 A

Patent Literature 2: JP 2009-279555 A

Patent Literature 3: JP 2001-205090 A

SUMMARY OF THE INVENTION

PROBLEM TO BE SOLVED BY THE INVENTION

[0007] However, the catalysts produced by the methods described in Patent Literatures 1 to 3 all do not have a sufficient methacrylic acid yield, and thus there is a demand for further improvement. In addition, there is a demand for decreasing the cost of the catalysts. An object of the present invention is to provide a catalyst that is inexpensive and enables the production of methacrylic acid with a high yield, a method for producing methacrylic acid using the catalyst, and a method for producing a methacrylic acid ester.

MEANS FOR SOLVING PROBLEM

[0008] The above-described problems are solved by the following present inventions [1] to [11].

[0009] [1] A method for producing a methacrylic acid production catalyst that contains at least phosphorus and molybdenum and is used in the production of methacrylic acid by the gas phase catalytic oxidation of methacrolein with molecular oxygen, the method including the steps of:

(a) mixing and kneading a dried catalyst containing a catalyst component with a solvent to produce a kneaded product;

(b) molding the kneaded product to produce a molded article;

(c) drying the molded article to produce a dried molded article; and

(d) firing the dried molded article to produce the catalyst,

in which at least a portion of the dried molded article produced in the step (c) is used as at least a portion of the dried catalyst in the step (a).

[0010] [2] The method for producing a methacrylic acid production catalyst described in [1], in which the methacrylic acid production catalyst contains a heteropoly acid compound containing phosphorus and molybdenum.

[0011] [3] The method for producing a methacrylic acid production catalyst described in [2], in which the heteropoly acid compound has a composition represented by the following Formula (I).

[0012] $P_aMo_bV_cX_dY_eO_f$ (I)

(in Formula (I), P, Mo, V, and O each represent phosphorus, molybdenum, vanadium, and oxygen; X represents at least one element selected from the group consisting of antimony, bismuth, arsenic, germanium, zirconium, tellurium, copper, silver, selenium, silicon, tungsten, iron, zinc, chromium, magnesium, tantalum, cobalt, barium, gallium, lanthanum, and boron; Y represents at least one element selected from the group consisting of potassium, rubidium, and cesium; and a, b, c, d, e, and f represent an atomic ratio of each element, when b = 12, a = 0.1 to 3, c = 0.01 to 3, d = 0

to 3, e = 0.01 to 3, and f is an oxygen atomic ratio necessary for satisfying an atomic valence of the element.).

[0013] [4] The method for producing a methacrylic acid production catalyst described in any one of [1] to [3], in which a drying temperature in the step (c) is 20°C or higher and lower than 200°C.

[0014] [5] The method for producing a methacrylic acid production catalyst described in any one of [1] to [4], in which a firing temperature in the step (d) is 200°C or higher and 500°C or lower.

[0015] [6] The method for producing a methacrylic acid production catalyst described in any one of [1] to [5], in which, when at least a portion of the dried molded article produced in the step (c) is used as at least a portion of the dried catalyst in the step (a), a dried molded article use rate defined by the following equation is 0.3% by mass or more and 22.0% by mass or less.

[0016] Dried molded article use rate (% by mass) = $(\alpha/\beta) \times 100$

(in the equation, α represents a solid content mass of the dried molded article produced in the step (c), and β represents a total solid content mass of the dried catalyst.).

[0017] [7] The method for producing a methacrylic acid production catalyst described in any one of [1] to [6], in which, when at least a portion of the dried molded article produced in the step (c) is used as at least a portion of the dried catalyst in the step (a), the dried molded article is pulverized for use.

[0018] [8] The method for producing a methacrylic acid production catalyst described in [7], in which a median diameter of a pulverized product produced by pulverizing the dried molded article is 50% or less of a median diameter of the dried molded article before pulverization.

[0019] [9] The method for producing a methacrylic acid production catalyst described in any one of [1] to [8], in which molding in the step (b) is extrusion molding.

[0020] [10] A method for producing methacrylic acid, the method including producing a methacrylic acid production catalyst by the method described in any one of [1] to [9] and producing methacrylic acid by the gas phase catalytic oxidation of methacrolein with molecular oxygen in the presence of the methacrylic acid production catalyst.

[0021] [11] A method for producing a methacrylic acid ester, the method including esterificating methacrylic acid produced by the method for producing methacrylic acid described in [10].

EFFECT OF THE INVENTION

[0022] According to the invention, by effectively using the dried molded article as a catalyst raw material, a catalyst can be produced at low cost, and further, the catalyst thus produced exhibits a high methacrylic acid yield. In addition, it is possible to provide a method for producing methacrylic acid using the catalyst and a method for producing a methacrylic acid ester.

MODE(S) FOR CARRYING OUT THE INVENTION

[0023] [Method for Producing Methacrylic Acid Production Catalyst]

A method for producing a methacrylic acid production catalyst (hereinafter, also referred to as a catalyst) according to the present invention is a method for producing a methacrylic acid production catalyst that contains at least phosphorus and molybdenum and is used in the production of methacrylic acid by the gas phase catalytic oxidation of methacrolein with molecular oxygen, the method including the following steps of:

(a) mixing and kneading a dried catalyst containing a catalyst component with a

solvent to produce a kneaded product;

(b) molding the kneaded product to produce a molded article;

(c) drying the molded article to produce a dried molded article; and

(d) firing the dried molded article to produce the catalyst.

[0024] In the method according to the present invention, it is characterized in that at least a portion of the dried molded article produced in the step (c) is used as at least a portion of the dried catalyst in the step (a). According to this, it is speculated that, by kneading the dried molded article, which has been dried once, with the solvent and applying a shear force thereto, micropores existing in the dried molded article change, and micropore distribution particularly preferable in the methacrylic acid production is formed in the catalyst.

[0025] The catalyst produced by the method according to the present invention preferably contains a heteropoly acid compound containing phosphorus and molybdenum from the viewpoint of obtaining a high methacrylic acid yield. The composition of the heteropoly acid compound is not particularly limited as long as it contains at least phosphorus and molybdenum, but the heteropoly acid compound preferably has a composition represented by the following Formula (I) from the viewpoint of obtaining a higher methacrylic acid yield.

[0026] $P_aMo_bV_cX_dY_eO_f$ (I)

In Formula (I), P, Mo, V, and O each represent phosphorus, molybdenum, vanadium, and oxygen. X represents at least one element selected from the group consisting of antimony, bismuth, arsenic, germanium, zirconium, tellurium, copper, silver, selenium, silicon, tungsten, iron, zinc, chromium, magnesium, tantalum, cobalt, barium, gallium, lanthanum, and boron. Y represents at least one element selected from the group consisting of potassium, rubidium, and cesium. a, b, c, d, e, and f

represent an atomic ratio of each element, when b = 12, a = 0.1 to 3, c = 0.01 to 3, d = 0 to 3, e = 0.01 to 3, and f is an oxygen atomic ratio necessary for satisfying an atomic valence of the element. Incidentally, the composition of the catalyst is a value calculated on the basis of an amount of each raw material charged in the catalyst preparation.

[0027] (Step (a))

In the step (a), a dried catalyst containing a catalyst component is mixed and kneaded with a solvent to produce a kneaded product. In this step, as described later, at least a portion of the dried molded article produced in the step (c) is used as at least a portion of the dried catalyst in the step (a).

[0028] The dried catalyst containing a catalyst component can be produced, for example, by drying a solution or slurry containing a catalyst component (hereinafter, also referred to as a catalyst raw material solution or slurry). For example, the dried catalyst can be produced by dissolving or suspending a raw material compound of the catalyst component of the methacrylic acid production catalyst containing at least phosphorus and molybdenum in an appropriately selected solvent to prepare a catalyst raw material solution or slurry, and drying the produced catalyst raw material solution or slurry. A method for preparing the catalyst raw material solution or slurry is not particularly limited, and the catalyst raw material solution or slurry can be prepared, for example, by a precipitation method, an oxide mixing method, or the like.

[0029] The raw material compound of the catalyst component used in preparation of the catalyst raw material solution or slurry is not particularly limited, and nitrates, carbonates, acetates, ammonium salts, oxides, halides, oxo acids, oxo acid salts, or the like of each constituent element of the catalyst can be used alone or in combination of two or more kinds thereof. Examples of the raw material compound of molybdenum

include molybdenum oxide such as molybdenum trioxide and ammonium molybdate such as ammonium paramolybdate or ammonium dimolybdate. Examples of the raw material compound of phosphorus include phosphoric acid, phosphorus pentoxide, and ammonium phosphate. Examples of the raw material compound of vanadium include ammonium metavanadate, vanadium pentoxide, and vanadyl oxalate. The raw material compound of the catalyst component may be used alone or in combination of two or more kinds thereof with respect to each element constituting the catalyst component. The mixing ratio of the raw material compound of each constituent element of the catalyst is preferably a mixing ratio satisfying the composition represented by the above-described Formula (I).

[0030] Examples of the solvent used in preparation of the catalyst raw material solution or slurry include water, ethyl alcohol, and acetone. These may be used alone or in combination of two or more kinds thereof. Of these, water is preferably used.

[0031] The liquid content of the catalyst raw material solution or slurry is preferably set to 5.0% by mass or less by drying. Various methods can be used as a drying method. Examples thereof include an evaporation to dryness method, a spray drying method, a drum drying method, and a flash drying method. Of these, a spray drying method by which the particle shape of the dried catalyst becomes uniform is preferable. The type of a dryer and a temperature, an atmosphere, or the like used in drying are not particularly limited, and a drying temperature is preferably in a range of 90 to 500°C.

[0032] Incidentally, as the dried catalyst containing the catalyst component, only a dried molded article produced in the step (c) described later may be used.

[0033] The solvent to be mixed and kneaded with the dried catalyst is not particularly limited, but water or an organic solvent is preferable. Examples of the organic solvent include lower alcohols such as methyl alcohol, ethanol, propyl alcohol, butyl alcohol,

and isopropanol, acetone, dimethyl ether, diethyl ether, methyl ethyl ketone, and ethyl acetate. These solvents may be used alone or in combination of two or more kinds of solvents. The solvent preferably contains at least an organic solvent. The amount of the solvent used is appropriately selected depending on the type of the dried catalyst, the shape of the particle, and the type of the solvent, and the amount of the solvent used is preferably 5.0 to 40.0% by mass with respect to 100.0% by mass of the total amount of the dried catalyst and the solvent. When the amount of the solvent used is 5.0% by mass or more, extrusion molding can be performed more smoothly. Thus, the particles of the dried catalyst are less likely to be crushed, and micropores effective for reaction in the molded article thus produced tend to increase. On the other hand, when the amount of the solvent used is 40.0% by mass or less, the adhesiveness during the molding is decreased so that handleability is improved. In addition, the molded article is further densified so that the strength of the molded article tends to be improved.

[0034] In the step (a), other than the dried catalyst containing the catalyst component and the solvent, it is preferable that a molding aid is further mixed and kneaded. The molding aid is not particularly limited, and examples thereof include graphite, diatom earth, glass fiber, ceramic fiber, and an organic binder. Of these, an organic binder is preferable as the molding aid. Cellulose is preferable as the organic binder, and examples thereof include methyl cellulose, ethyl cellulose, carboxymethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, hydroxypropylmethyl cellulose, hydroxyethylmethyl cellulose, and hydroxybutylmethyl cellulose. These may be used alone or as a mixture of two or more kinds thereof. The amount of the molding aid used is appropriately selected depending on the type of the dried catalyst, the shape of the particle, and the type of the solvent, and from the viewpoint of moldability of the kneaded product and the strength of the molded article, the amount of the molding aid

used is preferably 0.05 to 15% by mass with respect to 100.0% by mass of the total amount of the dried catalyst.

[0035] In the step (a), the dried catalyst and the solvent are mixed and then kneaded. According to this, a kneaded product is produced. By performing kneading before the step (b) described later, the micropore diameter can be controlled to a micropore diameter effective for reaction.

[0036] The kneading can be performed using a kneading machine. The kneading machine is not particularly limited, and a batch-type kneading machine with double-arm sigma blades, continuous type kneading machine with reciprocating rotary shafts, continuous type kneading machine with self-cleaning functions, or the like can be used. From the viewpoint that the condition of the kneaded product can be checked, a batch-type kneading machine is preferable. In addition, when to finish kneading is a time point when mixing is performed until a moldable state is obtained, and is typically determined by time, visual inspection, or touching.

[0037] (Step (b))

In the step (b), the kneaded product is molded to produce a molded article. A molding method is not particularly limited, and examples thereof include tumbling granulation, tablet molding, and extrusion molding. Of these, from the viewpoint that the diameters of micropores, which are formed in kneading of the step (a), effective for reaction can be maintained, extrusion molding is preferable. When extrusion molding is performed, an auger type extruder, a piston type extruder, or the like can be used. The shape of the molded article is not particularly limited, and examples thereof include annular, columnar, honeycomb, and star-shaped.

[0038] (Step (c))

In the step (c), the molded article is dried to produce a dried molded article.

The drying in the step (c) indicates that the molded article is held at a temperature of 20°C or higher and lower than 200°C to remove a solvent component contained in the molded article. A drying method is not particularly limited, and a generally known drying method is arbitrarily used. Drying conditions are not particularly limited, and may be a drying condition under an air atmosphere or a nitrogen atmosphere. A drying temperature is preferably in a range of 50°C or higher and 180°C or lower and more preferably in a range of 80°C or higher and 150°C or lower.

[0039] (Use of Dried Molded Article as Dried Catalyst in Step (a))

In the present invention, in the step (a), at least a portion of the dried molded article produced in the step (c) is used as at least a portion of the dried catalyst in the step (a). At this time, it is considered that, by kneading the dried molded article, which has been dried once, with the solvent and applying a shear force thereto, micropores existing in the dried molded article change, and micropore distribution particularly preferable in the methacrylic acid production is formed in the catalyst.

[0040] When at least a portion of the dried molded article produced in the step (c) is used as at least a portion of the dried catalyst in the step (a), a dried molded article use rate defined by the following equation is preferably 0.3% by mass or more and 22.0% by mass or less.

[0041] Dried molded article use rate (% by mass) = $(\alpha/\beta) \times 100$

Herein, α represents a solid content mass of the dried molded article produced in the step (c), and β represents a total solid content mass of the dried catalyst. The solid content mass indicates a mass in which the liquid content is 5.0% by mass or less.

[0042] When the dried molded article use rate is 0.3% by mass or more, it is considered that micropore distribution particularly preferable in the methacrylic acid production is formed. Further, when the dried molded article use rate is 22.0% by mass or less,

moldability in the step (b) is improved, and the mechanical strength of the molded article thus obtained is improved. The dried molded article use rate is more preferably 0.7% by mass or more and 20.0% by mass or less and further preferably 5.0% by mass or more and 18.0% by mass or less. Incidentally, in the present invention, the dried molded article use rate may be 100.0% by mass.

[0043] When at least a portion of the dried molded article produced in the step (c) is used as at least a portion of the dried catalyst in the step (a), it is preferable that the dried molded article is pulverized for use. By pulverizing the dried molded article in advance and mixing the dried molded article in a state of having a small particle diameter, moldability in the step (b) can be improved. A method for pulverizing the dried molded article is not particularly limited, and a coarse crusher, a medium crusher, a fine pulverizer, and the like can be used. It is preferable to use a medium crusher or a fine pulverizer by which the particle diameter of a pulverized product thus pulverized can be further reduced.

[0044] A median diameter of a pulverized product produced by pulverizing the dried molded article (hereinafter, also referred to as a dried molded article pulverized product) is preferably 50% or less of a median diameter of the dried molded article before pulverization, more preferably 40% or less, and further preferably 20% or less. When the median diameter of the dried molded article pulverized product is 50% or less of the median diameter of the dried molded article before pulverization, moldability in the step (b) is improved. The lower limit of the proportion range of the median diameter is not particularly limited, and for example, can be set to 5% or more.

[0045] Herein, the median diameter is a value obtained by a sieving method. Specifically, 50 g of a sample is sieved using sieves having mesh sizes of 4750 μm, 4000 μm, 3350 μm, 2800 μm, 2000 μm, 1180 μm, 600 μm, 212 μm, and 106 μm and

saucers, and then the mass of particles remaining on each sieve and remaining in a saucer shape is measured. In a case where a mesh size of the sieve of which integrated mass ratio from the fine particle side is 50% or more is designated as x_1 μm, a mesh size of the sieve having a mesh size one level larger than x_1 μm is designated as x_2 μm, the integrated mass ratio from the saucer to the x_1-μm sieve is designated as Q_1%, and the mass ratio from the saucer to the X_2-μm sieve is designated as Q_2%, the median diameter is calculated by the following Equations (II) and (III).

[0046] Median diameter = 10^Z (II)

$$Z = \log(x_2) + (\log(x_1) - \log(x_2)) \times (50 - Q_2)/(Q_1 - Q_2) \quad \text{(III)}$$

[0047] (Step (d))

In the step (d), the dried molded article is fired to produce the catalyst. The firing in the present invention indicates a process of expressing a catalyst active site by performing heating treatment at 200°C or higher and 500°C or lower. Firing conditions are not particularly limited, and it is preferable that firing is performed in oxygen-containing gas circulation such as air or inert gas circulation. Herein, the inert gas indicates a gas that does not degrade the catalyst activity, and examples thereof include nitrogen, carbon dioxide, helium, and argon. These may be used alone or as a mixture of two or more kinds thereof. A firing temperature is preferably 250°C or higher and 450°C or lower.

[0048] [Method for Producing Methacrylic Acid]

A method for producing methacrylic acid according to the present invention is a method including producing a methacrylic acid production catalyst by the method according to the present invention and producing methacrylic acid by the gas phase catalytic oxidation of methacrolein with molecular oxygen in the presence of the methacrylic acid production catalyst. According to the method, methacrylic acid can

be produced with a high yield.

[0049] As a raw material, a raw material gas containing methacrolein and molecular oxygen is preferably used. A concentration of methacrolein in the raw material gas when the raw material gas is brought into contact with the catalyst produced by the method according to the present invention can be changed in a wide range, and is preferably 1 to 20% by volume and more preferably 3 to 10% by volume. A concentration of molecular oxygen in the raw material gas is preferably 0.5 to 4.0 mol and more preferably 1.0 to 3.0 mol with respect to 1 mol of methacrolein.

[0050] The raw material gas may be diluted by adding an inert gas such as nitrogen or carbon dioxide. In addition, the raw material gas preferably contains water vapor. When the reaction is performed in the presence of water, methacrylic acid can be produced with a higher yield. A concentration of water vapor in the raw material gas is preferably 0.1 to 50.0% by volume and more preferably 1.0 to 40.0% by volume. A reaction pressure is preferably from normal pressure (atmospheric pressure) to 5 atmosphere. A reaction temperature is preferably 230°C to 500°C and more preferably 250 to 400°C.

[0051] [Method for Producing Methacrylic Acid Ester]

A method for producing a methacrylic acid ester according to the present invention performs esterification of methacrylic acid produced by the method according to the present invention. According to the method, a methacrylic acid ester can be produced using methacrylic acid obtained from methacrolein. Examples of alcohol reacting with the methacrylic acid include methanol, ethanol, isopropanol, n-butanol, and isobutanol. Examples of the methacrylic acid ester thus produced include methyl methacrylate, ethyl methacrylate, propyl methacrylate, and butyl methacrylate. The reaction can be performed in the presence of an acidic catalyst such as a sulfonic acid-

type cation-exchange resin. A reaction temperature is preferably 50 to 200°C.

EXAMPLES

[0052] Hereinafter, the present invention is described in detail with preference to Examples and Comparative Examples; however, the present invention is not limited to these Examples. The unit "part(s)" in Examples and Comparative Examples means "part(s) by mass." A molar ratio of the catalyst composition was calculated on the basis of the amount of each raw material charged in the catalyst preparation. The quantitative analysis of the raw material gas and a product in the production of methacrylic acid was performed using gas chromatography. Incidentally, a reaction rate of methacrolein, selectivity of methacrylic acid thus produced, and a one pass yield of methacrylic acid are defined as follows.

[0053] Reaction rate (%) of methacrolein (MAL) = (B/A) × 100

Selectivity (%) of methacrylic acid (MAA) = (C/B) × 100

One pass yield (%) of methacrylic acid (MAA) = (C/A) × 100

Herein, 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] The drop powdering rate, which is an index of mechanical strength, was measured using following method. A stainless steel cylinder having an inner diameter of 27.5 mm and a length of 6 m was installed such that the longitudinal direction would be vertical, with the lower opening of the cylinder being closed with a stainless steel plate, and 100 g of the dried molded article was packed into the cylinder by dropping from the upper opening of the cylinder. The mass of the dried molded article not passing through a sieve having a mesh size of 1 mm among the dried molded articles

collected by opening the lower opening was designated as D g, and the drop powdering rate was calculated by the following equation. As the drop powdering rate was smaller, higher mechanical strength was obtained, and as the drop powdering rate was larger, lower mechanical strength was obtained. Incidentally, the drop powdering rate in Examples is an average value of the drop powdering rates which are measured with respect to each of dried molded articles obtained by producing a dried molded article ten times under the same conditions.

[0055] Drop powdering rate (%) = {(100 - D)/100} × 100

[0056] [Example 1]

In 4000 parts of pure water, 1000 parts of molybdenum trioxide, 54 parts of ammonium metavanadate, 67 parts of 85% by mass phosphoric acid aqueous solution, and 11 parts of cupric nitrate were dissolved, the temperature of the resulting solution was increased to 95°C under stirring, and the resulting solution was stirred for 3 hours while the liquid temperature was maintained at 95°C. After cooling to 90°C, a solution obtained by dissolving 135 parts of cesium nitrate and 6 parts of potassium nitrate in 200 parts of pure water was added under stirring using a rotary blade stirrer and the resultant mixture was stirred for 15 minutes. Subsequently, a solution obtained by dissolving 92 parts of ammonium carbonate in 200 parts of pure water was added and further stirred for 20 minutes. This catalyst raw material slurry was dried using a spray dryer to adjust the liquid content to 5.0% by mass or less, thereby producing a dried catalyst A. To 500 parts of the dried catalyst A obtained in this way, 25 parts of hydroxypropyl cellulose was added and dry-mixed. 40 parts of pure water and 60 parts of ethanol were mixed therewith and kneaded with a kneading machine until being in a clay state, thereby producing a kneaded product A. Thereafter, the kneaded product A having an irregular shape was subjected to extrusion molding using a piston-

type extruder having a cylinder and a die with 8 holes to produce a molded article A having a median diameter of 4359 μm. Further, at this time, the clogging of the die in the extrusion molding performed for 1 hour continuously was 0 hole. This molded article A was dried at 105°C for 2 hours under a nitrogen atmosphere to adjust the liquid content to 5.0% by mass or less, thereby producing a dried molded article A. This dried molded article A was pulverized using a shear-type crusher to produce a dried molded article pulverized product having a median diameter of 498 μm.

[0057] 497.5 parts of the dried catalyst A produced above, 24.87 parts of hydroxypropyl cellulose, and 2.63 parts of the dried molded article pulverized product were dry-mixed. Incidentally, the dried catalyst A and the dried molded article pulverized product correspond to the dried catalyst B. That is, the dried molded article pulverized product was used as a portion of the dried catalyst B. 40 parts of pure water and 60 parts of ethanol were mixed with the obtained mixture and kneaded with a kneading machine until being in a clay state, thereby producing a kneaded product B. Thereafter, the kneaded product B having an irregular shape was subjected to extrusion molding using a piston-type extruder having a cylinder to produce a molded article B having a median diameter of 4365 μm. Further, at this time, the clogging of the die in the extrusion molding performed for 1 hour continuously was 0 hole. This molded article B was dried at 105°C for 2 hours under a nitrogen atmosphere to produce a dried molded article B. As a result of measuring the drop powdering rate of the dried molded article B, the drop powdering rate was 0.28%. Subsequently, the produced dried molded article B was fired at 380°C for 5 hours under air circulation to produce a catalyst. The composition of the catalyst (excluding an oxygen atom) was $P_1Mo_{12}V_{0.8}Cu_{0.1}Cs_{1.2}K_{0.1}$.

[0058] The reaction was performed in such a way that the catalyst was packed in a

reactor and a mixed gas containing 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 therethrough at a reaction temperature of 300°C for a contact time of 3.4 sec. As a result, the reaction rate of methacrolein was 32.5%, the selectivity of methacrylic acid was 92.2%, and the one pass yield of methacrylic acid was 30.0%. The results are presented in Table 1. Incidentally, in Table 1, the number of clogging of die holes in extrusion molding performed for 1 hour continuously indicates the number of clogging of die holes in extrusion molding of the kneaded product B in Examples 1 to 8 and Comparative Example 2 and the number of clogging of die holes in extrusion molding of the kneaded product A in Comparative Example 1.

[0059] [Comparative Example 1]

In Example 1, the pulverization of the dried molded article A and the mixing of the dried molded article pulverized product were not carried out. That is, the dried molded article A in Example 1 was fired at 380°C for 5 hours under air circulation to produce a catalyst, and the reaction was performed. At this time, the clogging of the die in extrusion molding performed for 1 hour continuously was 0 hole. Further, as a result of measuring the drop powdering rate of the produced dried molded article A, the drop powdering rate was 0.12%. The results are presented in Table 1.

[0060] [Example 2]

A dried molded article B was produced by the same method as in Example 1, except that the mixing amounts of the dried catalyst A, hydroxypropyl cellulose, and the dried molded article pulverized product were changed to 495 parts, 24.75 parts, and 5.25 parts, respectively. At this time, the clogging of the die in extrusion molding performed for 1 hour continuously was 0 hole. Further, as a result of measuring the drop powdering rate of the produced dried molded article B, the drop powdering rate

was 0.16%. A catalyst was produced using the dried molded article B by the same method as in Example 1, and the reaction was performed. The results are presented in Table 1.

[0061] [Example 3]

A dried molded article B was produced by the same method as in Example 1, except that the mixing amounts of the dried catalyst A, hydroxypropyl cellulose, and the dried molded article pulverized product were changed to 485 parts, 24.25 parts, and 15.75 parts, respectively. At this time, the clogging of the die in extrusion molding performed for 1 hour continuously was 0 hole. Further, as a result of measuring the drop powdering rate of the produced dried molded article B, the drop powdering rate was 0.11%. A catalyst was produced using the dried molded article B by the same method as in Example 1, and the reaction was performed. The results are presented in Table 1.

[0062] [Example 4]

A dried molded article B was produced by the same method as in Example 1, except that the mixing amounts of the dried catalyst A, hydroxypropyl cellulose, and the dried molded article pulverized product were changed to 420 parts, 21 parts, and 84 parts, respectively. At this time, the clogging of the die in extrusion molding performed for 1 hour continuously was 0 hole. Further, as a result of measuring the drop powdering rate of the produced dried molded article B, the drop powdering rate was 0.24%. A catalyst was produced using the dried molded article B by the same method as in Example 1, and the reaction was performed. The results are presented in Table 1.

[0063] [Example 5]

A dried molded article B was produced by the same method as in Example 1,

except that the mixing amounts of the dried catalyst A, hydroxypropyl cellulose, and the dried molded article pulverized product were changed to 400 parts, 20 parts, and 105 parts, respectively. At this time, the clogging of the die in extrusion molding performed for 1 hour continuously was 0 hole. Further, as a result of measuring the drop powdering rate of the produced dried molded article B, the drop powdering rate was 0.29%. A catalyst was produced using the dried molded article B by the same method as in Example 1, and the reaction was performed. The results are presented in Table 1.

[0064] [Reference Example 1]

A dried molded article B was produced by the same method as in Example 1, except that the mixing amounts of the dried catalyst A, hydroxypropyl cellulose, and the dried molded article pulverized product were changed to 385 parts, 19.25 parts, and 120.75 parts, respectively. At this time, the clogging of the die in extrusion molding performed for 1 hour continuously was 0 hole. Further, as a result of measuring the drop powdering rate of the produced dried molded article B, the drop powdering rate was 0.48%. A catalyst was produced using the dried molded article B by the same method as in Example 1, and the reaction was performed. The results are presented in Table 1.

[0065] [Reference Example 2]

A dried molded article B was produced by the same method as in Example 1, except that the mixing amounts of the dried catalyst A, hydroxypropyl cellulose, and the dried molded article pulverized product were changed to 0 part, 0 part, and 525 parts, respectively. At this time, the clogging of the die in extrusion molding performed for 1 hour continuously was 1 hole. Further, as a result of measuring the drop powdering rate of the produced dried molded article B, the drop powdering rate was 0.36%. A

catalyst was produced using the dried molded article B by the same method as in Example 1, and the reaction was performed. The results are presented in Table 1.

[0066] [Example 8]

A dried molded article B was produced by the same method as in Example 1, except that the median diameter of the dried molded article pulverized product was changed to 2366 μm. At this time, the clogging of the die in extrusion molding performed for 1 hour continuously was 2 holes. Further, as a result of measuring the drop powdering rate of the produced dried molded article B, the drop powdering rate was 0.28%. A catalyst was produced using the dried molded article B by the same method as in Example 1, and the reaction was performed. The results are presented in Table 1.

[0067] [Comparative Example 2]

The dried molded article A was fired for 5 hours under air circulation to produce a fired molded article. This fired molded article was pulverized using a shear-type crusher to produce a fired molded article pulverized product having a median diameter of 498 μm. A dried molded article B was produced by the same method as in Example 1, except that the mixing amounts of the dried catalyst A, hydroxypropyl cellulose, and the fired molded article pulverized product were changed to 485 parts, 24.25 parts, and 15.75, respectively. At this time, the clogging of the die in extrusion molding performed for 1 hour continuously was 0 hole. Further, as a result of measuring the drop powdering rate of the produced dried molded article B, the drop powdering rate was 0.37%. A catalyst was produced using the dried molded article B by the same method as in Example 1, and the reaction was performed. The results are presented in Table 1.

[0068] [Table 1]

Examples and Comparative Examples	Dried molded article A use rate [% by mass]	Ratio of the median diameter of the dried molded article A after pulverization with respect to the median diameter before pulverization [%]	Number of clogging of die holes in extrusion molding performed for 1 hour continuously	Drop powdering rate [%]	MAL reaction rate [%]	MAA selectivity [%]	MAA one pass yield [%]
Example 1	0.5	11	0/8	0.28	32.5	92.2	30.0
Comparative Example 1	0.0	-	0/8	0.12	31.4	93.7	29.4
Example 2	1.0	11	0/8	0.16	33.7	93.1	31.4
Example 3	3.1	11	0/8	0.11	35.8	91.9	32.9
Example 4	16.7	11	0/8	0.24	35.6	93.1	33.1
Example 5	20.8	11	0/8	0.29	34.4	92.0	31.7
Reference Example 1	23.9	11	0/8	0.48	32.8	91.8	30.1
Reference Example 2	100.0	11	1/8	0.36	34.8	93.0	32.4
Example 8	0.5	54	2/8	0.28	32.2	92.5	29.8
Comparative Example 2	3.1 (Fired molded article)	11	0/8	0.37	31.5	92.5	29.1

[0069] In Examples in which the dried molded article was pulverized and a portion thereof was mixed with the dried catalyst and then used, as compared to Comparative Example 1 in which mixing of the dried molded article with the dried catalyst was not performed, it was possible to produce methacrylic acid with a high yield in all Examples. In addition, it was found that, in Comparative Example 2 in which the fired molded article was pulverized instead of the dried molded article and a portion thereof was mixed with the dried catalyst, the yield of methacrylic acid is lower than in Example, and by mixing a portion of the dried molded article with the dried catalyst, the yield of methacrylic acid is improved. In Examples 1 to 5 in which the dried molded article use rate is 0.3% by mass or more and 22.0% by mass or less, the yield of methacrylic acid was particularly high. On the other hand, it was found that Reference Example 1 in which the dried molded article use rate is more than 22.0% by mass has a higher drop powdering rate and a lower mechanical strength than Examples 1 to 5. In Reference Example 2 in which the dried molded article use rate is 100%, the yield of methacrylic acid was high, but the clogging of the die hole in extrusion molding occurred, and the catalyst was inferior to Examples 1 to 5 in moldability. Incidentally, also in Example 8 in which a ratio of the median diameter of the dried molded article pulverized product with respect to the median diameter before pulverization is more than 50%, the clogging of the die hole in extrusion molding occurred, and the catalyst was inferior to Example 1 in moldability.

[0070] This application claims priority from Japanese Patent Application No. 2016-122583 filed June 21, 2016, which is hereby incorporated by reference herein in its entirety.

[0071] Hereinbefore, the invention of the present application has been described with reference to the embodiments and the examples; however, the invention of the present

application is not limited to the embodiments and the examples described above. The configuration and details of the invention of the present application can be variously modified by those skilled in the art within the scope of the invention of the present application.

CLAIMS

1. A method for producing a methacrylic acid production catalyst that contains at least phosphorus and molybdenum and is used in the production of methacrylic acid by the gas phase catalytic oxidation of methacrolein with molecular oxygen, the method comprising the steps of:

(a) mixing and kneading a dried catalyst containing a catalyst component with a solvent to produce a kneaded product;

(b) molding the kneaded product to produce a molded article;

(c) drying the molded article to produce a dried molded article; and

(d) firing the dried molded article to produce the catalyst,

wherein molding in the step (b) is extrusion molding,

wherein at least a portion of the dried molded article produced in the step (c) is used as at least a portion of the dried catalyst in the step (a), and

wherein a dried molded article use rate is 0.3% by mass or more and 22.0% by mass or less:

Dried molded article use rate (% by mass) = (α/β) x 100, wherein α represents a solid content mass of the dried molded article produced in the step (c), and β represents a total solid content mass of the dried catalyst.

2. The method for producing a methacrylic acid production catalyst according to claim 1, wherein the dried molded article use rate is 0.3% by mass or more and 20.0% by mass or less

3. The method for producing a methacrylic acid production catalyst according to claim 1 or 2, wherein the methacrylic acid production catalyst contains a heteropoly

acid compound containing phosphorus and molybdenum.

4. The method for producing a methacrylic acid production catalyst according to claim 3, wherein the heteropoly acid compound has a composition represented by the following Formula (I):

$P_aMo_bV_cX_dY_eO_f$ (I)

(in Formula (I), P, Mo, V, and O each represent phosphorus, molybdenum, vanadium, and oxygen; X represents at least one element selected from the group consisting of antimony, bismuth, arsenic, germanium, zirconium, tellurium, copper, silver, selenium, silicon, tungsten, iron, zinc, chromium, magnesium, tantalum, cobalt, barium, gallium, lanthanum, and boron; Y represents at least one element selected from the group consisting of potassium, rubidium, and cesium; and a, b, c, d, e, and f represent an atomic ratio of each element, when b = 12, a = 0.1 to 3, c = 0.01 to 3, d = 0 to 3, e = 0.01 to 3, and f is an oxygen atomic ratio necessary for satisfying an atomic valence of the element.).

5. The method for producing a methacrylic acid production catalyst according to any one of claims 1 to 4, wherein a drying temperature in the step (c) is 20°C or higher and lower than 200°C.

6. The method for producing a methacrylic acid production catalyst according to any one of claims 1 to 5, wherein a firing temperature in the step (d) is 200°C or higher and 500°C or lower.

7. The method for producing a methacrylic acid production catalyst according to any one of claims 1 to 6, wherein, when at least a portion of the dried molded article produced in the step (c) is used as at least a portion of the dried catalyst in the step (a), the dried molded article is pulverized for use.

8. The method for producing a methacrylic acid production catalyst according to claim 7, wherein a median diameter of a pulverized product produced by pulverizing the dried molded article is 50% or less of a median diameter of the dried molded article before pulverization.

9. A method for producing methacrylic acid, the method comprising producing a methacrylic acid production catalyst by the method according to any one of claims 1 to 8 and producing methacrylic acid by the gas phase catalytic oxidation of methacrolein with molecular oxygen in the presence of the methacrylic acid production catalyst.

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