

DESCRIPTION

METHOD FOR PRODUCING CATALYST FOR (METH)ACRYLIC ACID PRODUCTION AND METHOD FOR PRODUCING (METH)ACRYLIC ACID

TECHNICAL FIELD

[0001] The present invention relates to a method for producing a catalyst for (meth)acrylic acid production and a method for producing (meth)acrylic acid.

BACKGROUND ART

[0002] Regarding a catalyst component for producing (meth)acrylic acid through gas phase catalytic oxidation of (meth)acrolein using molecular oxygen, heteropolyacid compounds represented by phosphomolybdic acid are known. Furthermore, in order to make the catalyst component effectively act on a gas phase catalytic oxidation reaction, many methods for forming a pore structure within the catalyst have been suggested.

[0003] For example, Patent Literature 1 proposes a method for producing a catalyst for methacrylic acid production, the method including a primary molding step of performing primary molding of a kneaded product; and a secondary molding step of molding the primary molded article to the final shape with a piston molding machine, characterized in that the relation of the secondary molding pressure P2 to the primary molding pressure P1 is such that P2 is in the range of $(P1 - 0.2)$ MPaG to $(P1 - 8)$ MPaG.

PRIOR ART DOCUMENT

PATENT DOCUMENT

[0004] Patent Document1: JP 2011-224482 A

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0005] However, on the occasion of industrial use, a catalyst production method that can reduce uneven quality in a catalyst molded product by a simpler operation is required.

[0006] It is an purpose of the present invention to provide a method for producing a catalyst for (meth)acrylic acid production, by which the uneven quality in a catalyst molded product of a catalyst for (meth)acrylic acid production can be reduced.

MEANS FOR SOLVING PROBLEMS

[0007] The method for producing a catalyst for (meth)acrylic acid production according to the present invention is a method for producing a (meth)acrylic acid production containing at least molybdenum and phosphorus as catalytic components, the catalyst for (meth)acrylic acid production being used for producing (meth)acrylic acid though gas phase catalytic oxidation of (meth)acrolein using molecular oxygen,

the method comprising:

(1) a step of mixing a contactant of a catalyst component-containing catalyst precursor, a liquid and a binder so as to produce a mixture;

(2) a step of molding the mixture so as to, produce a molded product; and

(3) a step of heat-treating the molded product,

wherein during a period after producing the contactant in Step (1) and before heat-treating the molded product in Step (3), at least one of the contactant, the mixture, and the molded product is kept for a total 2 hours or more at a temperature of 10°C or higher, and the liquid content in the mixture, which is calculated from the charged quantities in Step (1), is denoted by $\alpha\%$ and the liquid content in the mixture

immediately before carrying out the molding in Step (2) is denoted by $\beta\%$, the rate of change in the liquid content, as calculated using following Formula (I), is -10% to 10%.

$$[0008] \text{ Rate of change in liquid content (\%)} = (\alpha - \beta)/\alpha \times 100 \quad (I)$$

Wherein, α represents the liquid content on a wet basis, calculated using following Formula (II) from the mass a of the liquid charged into Step (1) and the total mass b of the catalyst precursor and the binder.

$$[0009] \alpha = a/(a + b) \times 100 \quad (II)$$

Furthermore, β represents the liquid content calculated using following Formula (III) from the mass c (g) obtainable after 10 g of the mixture in a state of immediately before carrying out the molded in Step (2) is dried at normal pressure and at 100°C for 30 minutes.

$$[0010] \beta = (10 - c)/10 \times 100 \quad (III)$$

In the method for producing (meth)acrylic acid according to the present invention, a catalyst for (meth)acrylic acid production is produced by the method described above, and producing (meth)acrylic acid through gas phase catalytic oxidation of (meth)acrolein using molecular oxygen in the presence of the catalyst.

EFFECTS OF THE INVENTION

[0011] According to the present invention, a method for producing a catalyst for (meth)acrylic acid production, by which the uneven quality in a catalyst molded product of a catalyst for (meth)acrylic acid production can be reduced, can be provided.

MODE(S) FOR CARRYING OUT THE INVENTION

[0012] [Method for producing catalyst for (meth)acrylic acid production]

The method for producing a catalyst for (meth)acrylic acid production according

to the present invention is a method for producing a catalyst for (meth)acrylic acid production containing at least molybdenum and phosphorus as catalyst components, which is used for producing (meth)acrylic acid through gas phase catalytic oxidation of (meth)acrolein using molecular oxygen, the method including the following Step (1) to Step (3):

(1) a step of mixing a contactant of a catalyst component-containing catalyst precursor, liquid and a binder so as to produce a mixture;

(2) a step of molding the mixture so as to produce a molded product; and

(3) a step of heat-treating the molded product.

[0013] In the method according to the present invention, during a period after producing the contactant in Step (1) and before heat-treating the molded product in Step (3), at least one of the contactant, the mixture, and the molded product is kept for a total 2 hours or more at a temperature of 10°C or higher. Furthermore, the rate of change in the liquid content, as calculated using Formula (I) described above (hereinafter, also denoted by rate of change in the liquid content) is from -10% to 10%. The rate of change in the liquid content is a value calculated using Formula (I) to Formula (III) that will be described below. In the method according to the present invention, the uneven quality in a catalyst molded product of a catalyst for (meth)acrylic acid production can be reduced by these characteristics. The details of the various steps will be explained below.

[0014] (Step (1))

In Step (1), a contactant of a catalyst component-containing catalyst precursor, a liquid and a binder is mixed, so as to produce a mixture.

[0015] The catalyst component-containing catalyst precursor can be obtained by, for example, dissolving or suspending raw material compounds of the catalyst components

containing at least molybdenum and phosphorus in an appropriately selected solvent, preparing a mixed solution or slurry containing at least molybdenum and phosphorus, and drying the mixed solution or slurry thus obtained.

[0016] The method for preparing the mixed solution or the slurry is not particularly limited, and the mixed solution or slurry can be prepared by, for example, a precipitation method or an oxide mixing method.

[0017] The raw material compounds of the catalyst components used for the preparation of the mixed solution or the slurry are not particularly limited, and nitrates, carbonates, acetates, ammonium salts, oxides, halides, oxo acids, oxo acid salts, and the like of the various constituent elements of the catalyst can be used alone or in combination of two or more kinds thereof. Examples of the raw material compounds for molybdenum include molybdenum oxides such as molybdenum trioxide; and ammonium molybdates such as ammonium paramolybdate and ammonium dimolybdate. Examples of the raw material compounds for phosphorus include phosphoric acid, phosphorus pentoxide, and ammonium phosphate. Examples of the raw material compounds for vanadium include ammonium metavanadate, vanadium pentoxide, and vanadyl oxalate.

Examples of the raw material compounds for copper include copper nitrate, copper oxide, copper carbonate, and copper acetate. In regard to the raw material compounds of the catalyst components, one kind may be used for each of the elements that constitute the catalyst components, or two or more kinds may be used in combination. The mixing ratio of the raw material compounds of the various constituent elements of the catalyst is preferably a mixing ratio that satisfies the composition represented by Formula (IV) that will be described below.

[0018] Examples of the solvent that is used for the preparation of the mixed solution or slurry include water, ethyl alcohol, and acetone. These may be used alone, or two or

more kinds thereof may be used in combination. Among these, it is preferable to use water.

[0019] The method of drying the mixed solution or the slurry is not particularly limited, and for example, a method of drying using a spray dryer; a method of drying using a slurry dryer; a method of drying using a drum dryer; or a method of performing evaporation to dryness, can be applied. Among these, since particles are obtained simultaneously with drying, and the shape of the particles thus obtainable is a highly regular spherical shape, a method of drying using a spray dryer is preferred.

[0020] The drying conditions may vary depending on the drying method; however, in the case of using a spray dryer, temperature at the feeding end of the dryer is preferably 200°C to 400°C, and more preferably 220°C to 370°C.

[0021] In the case of using a spray dryer, the average particle size of the catalyst precursor thus obtainable is preferably 1 to 250 μm . When the average particle size is 1 μm or more, a pore size required for the oxidation reaction of (meth)acrolein can be ensured, and (meth)acrylic acid is obtained with high yield. Furthermore, when the average particle size is 250 μm or less, the number of contact points between catalyst precursor particles per unit volume does not decrease, and sufficient mechanical strength of the catalyst is obtained. The average particle size of the catalyst precursor is more preferably 5 to 150 μm . Meanwhile, the average particle size means volume average particle size and is a value measured using a laser type particle size distribution analyzer.

[0022] The contacting method between sprayed liquid droplets and hot air may be any of a parallel-flow, a counter-flow, and a parallel/counter-flow (mixed flow), and drying can be achieved adequately in all cases.

[0023] The catalyst precursor obtained as described above may be produced into a

calcination product by performing a heat treatment (calcination) at 200°C to 500°C as necessary. The calcination conditions are not particularly limited; however, calcination is usually carried out under a flow of oxygen, air, or nitrogen. Furthermore, the calcination time is set as appropriate depending on the catalyst intended to be obtained. In the following description, an uncalcined catalyst precursor and the calcination product will be collectively described as catalyst precursor.

[0024] In the present step, the liquid to be mixed with the catalyst component-containing catalyst precursor is not particularly limited as long as the liquid has a function of wetting the catalyst precursor, and examples thereof include water, and alcohols having 1 to 4 carbon atoms, such as methyl alcohol, ethyl alcohol, propyl alcohol, and butyl alcohol. Among these, from the viewpoint that the particles of the catalyst precursor are not disintegrated, and pores effective for an oxidation reaction may be easily formed, ethyl alcohol and propyl alcohol are preferred. These may be used alone, or two or more kinds thereof may be used in combination. Meanwhile, in the case of using an alcohol as the liquid, it is preferable that the alcohol is of high purity; however, the alcohol may include a small amount of water. The liquid according to the present invention represents a compound that is liquid under the conditions of normal temperature (5°C to 40°C) and normal pressure (atmospheric pressure (0.1 MPa)).

[0025] The amount of use of the liquid is selected as appropriate according to the type or particle size of the catalyst precursor, the type of the liquid, or the like; however, it is preferable that the amount of use of the liquid is 10 to 80 parts by mass with respect to 100 parts by mass of the catalyst precursor. When the amount of use of the liquid is 10 parts by mass or more, since extruding can be achieved more smoothly, the particles of the catalyst precursor are not easily crushed, large voids, that is, large pores are formed

in the catalyst molded product thus obtainable, and the selectivity of (meth)acrylic acid tends to increase. On the other hand, when the amount of use of the liquid is 80 parts by mass or less, adhesiveness during the molding is reduced, and ease of handling is thereby enhanced. Furthermore, since the catalyst molded product becomes more compact, the strength of the catalyst molded product tends to increase. The amount of use of the liquid is more preferably 10 to 60 parts by mass, and even more preferably 15 to 50 parts by mass, with respect to 100 parts by mass of the catalyst precursor.

[0026] The binder is not particularly limited as long as the binder has a function of adhering the catalyst precursor, and for example, an organic binder or an inorganic binder can be used. Examples of the organic binder include a polymer compound such as polyvinyl alcohol; an α -glucan derivative, and a β -glucan derivative. These may be used alone, or two or more kinds thereof may be used in combination.

[0027] The α -glucan derivative according to the present invention implies that in a polysaccharide composed of glucose, glucose is bonded in an α -type structure, and derivatives such as α 1-4 glucan, α 1-6 glucan, and α 1-4/1-6 glucan may be listed as examples. Specific examples of these α -glucan derivatives include amylose, glycogen, amylopectin, pullulan, dextrin, and cyclodextrin. These may be used alone, or two or more kinds thereof may be used in combination.

[0028] The β -glucan derivative according to the present invention implies that in a polysaccharide composed of glucose, glucose is bonded in a β -type structure, and derivatives such as β 1-4 glucan, β 1-3 glucan, β 1-6 glucan, and β 1-3/1-6 glucan may be listed as examples. Examples of these β -glucan derivatives include cellulose derivatives such as methyl cellulose, ethyl cellulose, carboxymethyl cellulose, carboxymethyl cellulose sodium, hydroxyethyl cellulose, hydroxypropyl cellulose, hydroxypropylmethyl cellulose, hydroxyethylmethyl cellulose, hydroxybutylmethyl

cellulose, ethylhydroxyethyl cellulose, and hydroxypropyl cellulose; and β 1-3 glucans such as curdlan, laminaran, paramylon, callose, pachyman, and scleroglucan. These may be used alone, or two or more kinds thereof may be used in combination.

[0029] The organic binder may be used in an unpurified form, or may be used after being purified. However, in order to prevent impurities such as metal impurities and ignition residues from causing a decrease in catalyst performance, it is more preferable that the content of metal impurities and ignition residue is smaller.

[0030] Examples of the inorganic binder include inorganic compounds such as silica, alumina, silica-alumina, silicon carbide, titania, magnesia, graphite, and diatomaceous earth; and inert carriers such as ceramic balls, stainless steel, and inorganic fibers such as glass fibers, ceramic fibers, and carbon fibers. These may be used alone, or two or more kinds thereof may be used in combination. Furthermore, the organic binders and the inorganic binders can also be used as mixtures.

[0031] The amount of use of the binder is selected as appropriate according to the type or particle size of the catalyst precursor, the type of the liquid, or the like. However, the amount of use of the binder is preferably 0.05 to 15 parts by mass, more preferably 0.1 to 10 parts by mass, and 1 to 8 parts by mass, with respect to 100 parts by mass of the catalyst precursor.

[0032] The methods for contacting and mixing of the catalyst precursor, the liquid, and the binder are not particularly limited. Specific examples include a method of bringing a dry mixture of the catalyst precursor and the binder, into contact with the liquid, and mixing; and a method of bringing a solution or dispersion of the binder in the liquid, into contact with the catalyst precursor, and mixing. Among these, a method of bringing a dry mixture of the catalyst precursor and the binder, into contact with the liquid, and mixing is preferred. In a case in which a binder that is available in a state

of being dissolved or dispersed in the liquid is used, the amount of the liquid that is further added for mixing with the catalyst may be regulated according to the amount of the liquid in the solution or dispersion.

[0033] The contactant for the present step is a material obtainable by bringing a catalyst precursor, a liquid, and a binder into contact with each other, and this means a material before being mixed. Furthermore, the term mixing for the present step is an operation of mixing blended materials, and includes kneading. Kneading is an operation of mixing blended materials by kneading, and making the mixture uniform. In the present step, it is preferable that the catalyst precursor, the liquid, and the binder are introduced into a kneading machine to be brought into contact with each other, and a mixture is obtained by kneading the contactant.

[0034] The kneading machine is not particularly limited, and for example, a batch type kneading machine with a double-arm sigma blades, continuous type kneading machine with reciprocating rotary shafts, continuous type kneading machine with self-cleaning functions, can be used. However, a batch type kneading machine is preferred from the viewpoint that the condition of the kneaded product can be checked while kneading is under way. Furthermore, when to finish kneading is defined as a time point at which the material has been mixed until a state of being capable of extruding is reached.

[0035] (Step (2))

In Step (2), the mixture is molded, and thereby a molded product is produced. The method for molding the mixture is not particularly limited, and examples include methods such as extruding, tablet molding, and tumbling granulation. Among these, extruding is preferred from the viewpoint that disintegration of the catalyst precursor particles occurs less, and pores effective for a reaction are easily obtained. For the extruding, an extruding machine can be used, and for example, an Auger extruding

machine or a plunger extruding machine can be used. Among these, from the viewpoint that suitable kneading can be applied to the mixture, and the performance of the resulting catalyst is stable, it is preferable to use a plunger extruding machine. The shape of the molded product is not particularly limited, and the molded product can be produced into a shape such as, for example, annular, columnar, or star-shaped.

[0036] (Step (3))

In Step (3), the molded product is heat-treated. For example, after the molded product is dried to obtain a catalyst molded product, the catalyst molded product is calcined, and thus a catalyst for (meth)acrylic acid production can be obtained. The drying method is not particularly limited, and for example, methods such as hot air drying, drying using far-infrared rays, and microwave can be used. The drying conditions can be selected as appropriate as long as the intended water content can be obtained, and for example, drying can be carried out at 100°C or below. The calcination conditions are not particularly limited; however, the calcination temperature is preferably 200°C to 600°C, and more preferably 200°C to 500°C. For example, the molded product can be calcined at 300°C to 450°C for 1 to 24 hours. Furthermore, it is also acceptable that drying and calcination are successively carried out.

[0037] (Aging)

In the method according to the present invention, during a period after producing the contactant in Step (1) and before heat-treating the molded product in Step (3), at least one of the contactant, the mixture, and the molded product is kept for a total 2 hours or more at a temperature of 10°C or higher. Meanwhile, according to the present invention, keeping for a predetermined time at a predetermined temperature may be referred to as aging, and the object of aging may be referred to as aging material. During aging, the aging material may migrate, may have its shape changed, or may be

in a state of being left to stand; however, it is preferable that the aging material is in a state of migrating or being left to stand. In the present invention, it was found that uneven quality of the catalyst molded product can be reduced by aging the aging material for a total 2 hours or more at a temperature of 10°C or higher during a period after production the contactant in Step (1) and before heat-treating the molded product in Step (3).

[0038] This aging is carried out during a period after the contactant in Step (1) and before heat-treating the molded product in Step (3). The phrase "after the contactant in Step (1)" means a time after the time point at which the catalyst component-containing catalyst precursor is brought into contact with the liquid and the binder. Furthermore, the phrase "before heat-treating the molded product in Step (3)" means a time immediately before a time point at which the molded product is heat-treated. Within this range, the aging may be carried out at anytime.

[0039] The temperature of the aging material during aging is 10°C or higher, preferably 15°C or higher, more preferably 20°C or higher, and even more preferably 25°C.

When the temperature is 10°C or higher, the uneven quality of the catalyst molded product is reduced. The upper limit of the temperature is not particularly limited; however, the upper limit is preferably 40°C or lower, and more preferably 35°C or lower.

When the temperature is 40°C or lower, strength of the catalyst tends to increase. It is not clear why the uneven quality of the catalyst molded product is reduced when the temperature of the aging material during aging is 10°C or higher; however, it is speculated that since dispersion of the catalyst precursor and the binder in the liquid adequately proceeds, and a state of being settled to a certain extent is attained, dispersion uneven quality within the mixture is reduced, and the density uneven quality during molding is reduced. Meanwhile, it is not also clear why strength of the catalyst

tends to increase when the temperature of the aging material during aging is 40°C or lower; however, it is speculated to be because, when the temperature is higher than 40°C, dispersing of the catalyst precursor in the liquid proceeds excessively, and the particles of the catalyst precursor are significantly crushed, and therefore, the effect of adhesion by the binder may be reduced. In a case in which the temperature is changed within the range of 10°C or higher during aging, the temperature represents the average temperature of the aging material during a period after producing the contactant in Step (1) and before heat-treating the molded product in Step (3). In this case, the maximum of the changing temperature is preferably 40°C.

[0040] The method for controlling the temperature of the aging material during aging is not particularly limited; however, for example, a method of controlling the ambient temperature around the aging material to be within the range of the aging temperature by a method of adjusting the air-conditioning temperature of the room where aging is performed, a method of adjusting the jacket temperature of the container in which aging is performed, a method of circulating a temperature-controlled gas within the container in which aging is performed, or the like, can be applied.

[0041] The aging time in the present invention is a total 2 hours or more. When the aging time is a total 2 hours or more, the uneven quality of the catalyst molded product can be reduced. Meanwhile, for example, in a case in which the contactant is aged for 1.5 hours, and the mixture is aged for 1.5 hours, since the sum is 3 hours, this satisfies the requirement that the aging time is a total 2 hours or more. The sum of the aging time is preferably 2.5 hours or more, and more preferably 3 hours or more. The upper limit of the sum of the aging time is not particularly limited; however, the upper limit is preferably 48 hours or less, more preferably 36 hours or less, and even more preferably 30 hours or less. When the sum of the aging time is 48 hours or less, strength of the

catalyst tends to increase. It is not clear why the uneven quality of the catalyst molded product is reduced when the sum of the aging time is 2 hours or more; however, it is speculated that in a case in which the mixture is aged, since dispersing of the catalyst precursor and the binder in the liquid proceeds, and a state of being settled to a certain extent is attained, dispersion uneven quality in the mixture is reduced, and the density uneven quality during molding is reduced. On the other hand, it is also not clear why strength of the catalyst tends to increase when the sum of the aging time is 48 hours or less; however, it is speculated to be because, when the sum of the aging time is more than 48 hours, since dispersing of the catalyst precursor in the liquid proceeds excessively, and the particles of the catalyst precursor are significantly crushed, the effect of adhesion by the binder may be reduced. Aging may be performed continuously for 2 hours or more, or aging may be performed intermittently, and the total time may be adjusted to be 2 hours or more.

[0042] (Rate of change in liquid content)

In the method according to the present invention, the rate of change in the liquid content, as calculated using Formula (I) described above, is -10% to 10%, preferably 0% to 10%, more preferably 0% to 9%, even more preferably 0% to 8%, and particularly preferably 1% to 5%. When the rate of change in the liquid content is -10% to 10%, since the viscosity uneven quality within the mixture is reduced, the uneven quality of the catalyst molded product is reduced. Meanwhile, the rate of change in the liquid content is a value, as calculated using Formula (I) to Formula (III) that will be described below.

[0043] (Conveying process)

The method according to the present invention may include at least one conveying process between the various steps from Step (1) to Step (3). Conveyance

according to the present invention means moving a product produced in each step to the subsequent step. For example, the method according to the present invention can include the conveying process between Step (1) and Step (2), and in this case, for example, the mixture obtainable in Step (1) can be conveyed to a molding machine, and Step (2) can be carried out. During the conveyance, an operation of temporarily stopping conveyance and leaving the product to stand may also be included. Furthermore, an operation of changing the shape of the product may also be included. For example, when the mixture obtained in Step (1) is conveyed as described above, an operation such as crushing or preliminary molding may also be included in order to facilitate charging into the molding machine in Step (2).

[0044] The method for conveyance is not particularly limited, and for example, conveyance by a manual operation or conveyance by means of a conveying machine may be mentioned. However, from the viewpoint that the operation load can be reduced, and high productivity is obtained, conveyance by means of a conveying machine is preferred.

[0045] Examples of the conveying machine include a screw type conveying machine, a belt conveyor type conveying machine, a chain conveyor type conveying machine, a roller conveyor type conveying machine, a vibration type conveying machine, an extrusion type conveying machine, and a dropping type conveying machine. Furthermore, from the viewpoint of controlling the rate of change in the liquid content in the range of from -10% to 10%, it is preferable that the conveying machine has a structure of suppressing evaporation of the liquid.

[0046] In the case of performing the aging in the conveying process, a method of controlling the ambient temperature around the aging material within the range of the aging temperature by a method of adjusting the air-conditioning temperature of the

room where conveyance is performed, a method of adjusting the jacket temperature of the conveying machine, a method of circulating a temperature-controlled gas within the conveying machine, or the like, can be applied.

[0047] The catalyst for (meth)acrylic acid production produced by the method according to the present invention is used when (meth)acrylic acid is produced through gas phase catalytic oxidation of (meth)acrolein using molecular oxygen. The catalyst for (meth)acrylic acid production is not particularly limited as long as the catalyst contains at least molybdenum and phosphorus as catalytic components.

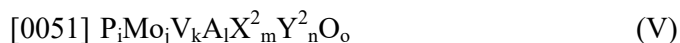
[0048] It is preferable that the catalyst for (meth)acrylic acid production for producing methacrylic acid through gas phase catalytic oxidation of (meth)acrolein is a composite oxide having the composition represented using following Formula (IV), from the viewpoints of activity and selectivity.



In Formula (IV), 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 ratios of the various elements, and when b = 12 is given, a = 0.1 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 represents the atomic ratio of oxygen required for satisfying the valences of the various elements.

[0050] Furthermore, it is preferable that the catalyst for acrylic acid production for

producing acrylic acid though gas phase catalytic oxidation of acrolein is a composite oxide having the composition represented using following Formula (V) from the viewpoints of activity and selectivity.



In Formula (V), P, Mo, V, and O represent phosphorus, molybdenum, vanadium, and oxygen, respectively. A represents at least one element selected from the group consisting of iron, cobalt, chromium, aluminum, and strontium. X^2 represents at least one element selected from the group consisting of germanium, boron, arsenic, selenium, silver, silicon, sodium, tellurium, lithium, antimony, potassium, and barium. Y^2 represents at least one element selected from the group consisting of magnesium, titanium, manganese, copper, zinc, zirconium, niobium, tungsten, tantalum, calcium, tin, and bismuth. i, j, k, l, m, n, and o represent the atomic ratios of the various elements, and when j = 12 is given, i = 0.01 to 10, k = 0.01 to 6, l = 0 to 5, m = 0 to 10, n = 0 to 5, and n represents the atomic ratio of oxygen required for satisfying the valences of the various components.

[0052] [Method for producing (meth)acrylic acid]

In the method for producing (meth)acrylic acid according to the present invention, a catalyst for (meth)acrylic acid production is produced by the method described above, and (meth)acrylic acid is produced though gas phase catalytic oxidation of (meth)acrolein using molecular oxygen in the presence of the catalyst for (meth)acrylic acid production.

[0053] The gas phase catalytic oxidation can be carried out in a fixed bed. The configuration of the catalyst layer is not particularly limited, and the catalyst layer may be an undiluted layer containing only the catalyst, or a diluted layer containing an inert carrier, or the catalyst layer may also be a single layer or a mixed layer composed of a

plurality of layers.

[0054] For the raw materials, it is preferable to use a raw material gas containing (meth)acrolein and molecular oxygen. The concentration of (meth)acrolein in the raw material gas is preferably 1% by volume or more, and more preferably 3% by volume or more. Furthermore, the concentration of (meth)acrolein 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, and more preferably 0.5 mol or more, with respect to 1 mol of (meth)acrolein. The concentration of the molecular oxygen is preferably 0.4 mol or more, and more preferably 0.5 mol or more, with respect to 1 mol of the (meth)acrolein. Furthermore, the concentration of the molecular oxygen is preferably 4 mol or less, and more preferably 3 mol or less, with respect to 1 mol of (meth)acrolein. It is cost effective to use air as an oxygen source; however, if necessary, air enriched with pure oxygen, or the like can also be used.

[0055] It is preferable that the raw material gas contains water (water vapor) in addition to (meth)acrolein and molecular oxygen. When the reaction is carried out in the presence of water, (meth)acrylic acid can be obtained with 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. This concentration is also preferably 50% by volume or less, and more preferably 40% by volume or less. The raw material gas may contain a small amount of impurities such as lower saturated aldehydes; however, it is preferable that the amount is as small as possible. Furthermore, the raw material gas may also contain an inert gas such as nitrogen or carbon dioxide.

[0056] The reaction pressure is preferably from normal pressure (atmospheric pressure) to 5 atmospheres. 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.

[0057] The flow rate of the raw material gas is not particularly limited and can be set as appropriate so as to obtain an appropriate contact time. The contact time is preferably 1.5 seconds or more, and more preferably 2 seconds or more. Furthermore, the contact time is preferably 15 seconds or shorter, and more preferably 10 seconds or shorter.

EXAMPLES

[0058] Hereinafter, the present invention is described in detail with reference to Examples and Comparative Examples; however, the present invention is not limited to these Examples. Meanwhile, the unit "parts" means "parts by mass".

[0059] (Standard deviation of packing density)

Regarding the uneven quality of the catalyst molded product, catalyst molded products were produced ten times under the same conditions, the packing density of the each catalyst molded product was measured, and the uneven quality was determined from the standard deviation of the packing density. Regarding the packing density, a molded product was packed in a graduated cylinder having an inner diameter of 27 mm up to the marking of 100 mL, and the packing density was calculated from its mass (B) using following formula.

[0060] Packing density (g/L) = $B \times 10$.

[0061] (Drop powdering rate)

The drop powdering rate, which is an index of mechanical strength, was measured using following method. A cylinder made of stainless steel and having an inner diameter of 27.5 mm and a length of 6 m was installed such that the longitudinal direction of the cylinder would be vertical, with the lower opening of the cylinder being

closed with a plate made of stainless steel, and 100 g of a catalyst molded product was packed into the cylinder by dropping from the upper opening of the cylinder. Among the pieces of the catalyst molded product collected by opening the lower opening, the mass of the pieces that were not screened through a sieve having a mesh size of 1 mm was denoted by C_g , and the drop powdering rate was calculated using following formula. As the powdering rate was smaller, higher mechanical strength was obtained, and as the powdering rate was larger, lower mechanical strength was obtained. Meanwhile, regarding the drop powdering rates given in Table 1, each catalyst molded product was produced ten times under the same conditions, and the average value of the drop powdering rates measured for the various samples of the catalyst molded product was determined as the drop powdering rate.

$$[0062] \text{ Drop powdering rate (\%)} = \{(100 - C)/100\} \times 100$$

$$[0063] \text{ (Rate of change in liquid content)}$$

The rate of change in the liquid content was calculated using following Formula (I).

$$[0064] \text{ Rate of change in liquid content (\%)} = (\alpha - \beta)/\alpha \times 100 \quad (I)$$

In Formula (I), α represents the liquid content on a wet basis, calculated using following Formula (II) from the mass a of the liquid charged into Step (1) and the total mass b of the catalyst precursor and the binder.

$$[0065] \alpha = a/(a + b) \times 100 \quad (II)$$

Furthermore, β represents the liquid content calculated using following Formula (III) from the mass c (g) obtainable after 10 g of the mixture in a state of immediately before carrying out the molded in Step (2) is dried at normal pressure and at 100°C for 30 minutes.

$$[0066] \beta = (10 - c)/10 \times 100 \quad (III)$$

[0067] [Example 1]

In 4,000 parts of pure water, 1,000 parts of molybdenum trioxide, 34 parts of ammonium metavanadate, 80 parts of a 85 mass% of phosphoric-acid solution, and 7 parts of copper nitrate were dissolved, and this solution was heated to 95°C while being stirred. While the liquid temperature was kept at 95°C, the solution was stirred for 3 hours. After the solution was cooled to 90°C, while the solution was stirred using a rotary-blade stirrer, a solution obtained by dissolving 124 parts of cesium hydrogen carbonate in 200 parts of pure water was added to the solution, and the mixture was stirred for 15 minutes. Next, a solution prepared by dissolving 92 parts of ammonium carbonate in 200 parts of pure water was added thereto, and the mixture was stirred for 20 minutes. A resultant mixed slurry containing the raw material compounds of the catalyst components was dried using a parallel-flow spray dryer under the conditions of 300°C temperature at the feeding end of the dryer and a rotating disc for spraying slurry being rotated at 18,000 rpm. Thus, a catalyst precursor was obtained. The average particle size of the catalyst precursor was 25 μm .

[0068] 100 parts of the catalyst precursor was brought into contact with 5 parts of hydroxypropyl cellulose and 20 parts of ethyl alcohol by charging the materials into a batch type kneading machine equipped with a double-arm sigma blades, such that the liquid content in the mixture calculated from the charged quantities would be 16.0%. The contactant was kneaded to attain a clay form, and thus a mixture was obtained.

[0069] The mixture was charged into a tank equipped with a screw type conveying machine in the lower part, and the inlet port was closed with a lid and was sealed. Next, the mixture was conveyed into a plunger extruding machine by discharging the mixture by the screw type conveying machine. The plunger extruding machine was equipped with a dice having 14 holes of 5.5 mm ϕ concentrically, and the inner diameter

of the plunger extruding machine was 120 mm ϕ . The amount of the mixture conveyed by the screw type conveying machine was an amount to be extruded once with the plunger extruding machine, and the remaining mixture was retained in the tank.

[0070] Here, during the mixture was conveyed by the screw type conveying machine, the mixture was aged for 3 hours at 25°C. At this time, the temperature of the aging material was controlled to be 25°C by adjusting the jacket temperature of the tank equipped with the screw type conveying machine to 25°C.

[0071] The mixture obtained after aging was extruded using the plunger extruding machine at a plunger movement speed of 100 mm/min. The extruded product discharged through the dice was cut by rotating a piano wire at the dice surface at a rate of 375 rpm, and thus a molded product was obtained.

[0072] The molded product was heat-treated at 90°C for 12 hours using a hot air dryer, and thereby a catalyst molded product was obtained. Furthermore, the mixture remaining in the tank was also similarly processed to produce a catalyst molded product, and the standard deviation of the packing density and the drop powdering rate were measured for these catalyst molded products. The liquid content in the mixture calculated from the charged quantities, the liquid content in the mixture measured immediately before performing molding, the rate of change in the liquid content, the standard deviation of the packing density, and the drop powdering rate are shown in Table 1. Meanwhile, the composition of the catalyst excluding oxygen, which is obtained after calcination the catalyst molded product, is $P_{1.2}Mo_{12}V_{0.5}Cu_{0.05}Cs_{1.1}$.

[0073] [Example 2]

A catalyst molded product was obtained by employing the same procedures described in Example 1, except that the aging time was changed to 25 hours, and the catalyst molded product was evaluated. The results are shown in Table 1.

[0074] [Example 3]

A catalyst molded product was obtained by employing the same procedures described in Example 1, except that the aging time was changed to 47 hours, and the catalyst molded product was evaluated. The results are shown in Table 1.

[0075] [Example 4]

A catalyst molded product was obtained by employing the same procedures described Example 1, except that the aging time was changed to 61 hours, and the catalyst molded product was evaluated. The results are shown in Table 1.

[0076] [Example 5]

A catalyst molded product was obtained by employing the same procedures described in Example 1, except that the aging time was changed to 25 hours and that the aging temperature was changed to 50°C, and the catalyst molded product was evaluated. The results are shown in Table 1.

[0077] [Example 6]

A catalyst molded product was obtained by employing the same procedures described in Example 1, except that the aging temperature was changed to 30°C, and that the conveying machine was changed to a belt conveyor conveying machine, and the catalyst molded product was evaluated. The results are shown in Table 1.

[0078] [Comparative Example 1]

A catalyst molded product was obtained by employing the same procedures described in Example 1, except that the aging time was changed to one hour, and the catalyst molded product was evaluated. The results are shown in Table 1.

[0079] [Comparative Example 2]

A catalyst molded product was obtained by employing the same procedures described in Example 1, except that the aging temperature was changed to 7°C, and the

catalyst molded product was evaluated. The results are shown in Table 1.

[0080] [Comparative Example 3]

A catalyst molded product was obtained by employing the same procedures described in Example 1, except that after the mixture was charged into a tank equipped with a screw type conveying machine in the lower part, the inlet port was not closed with a lid and was not sealed, and the catalyst molded product was evaluated. The results are shown in Table 1.

[0081] [Example 7]

A catalyst molded product was obtained by employing the same procedures described in Example 1, except that the aging time was changed to 30°C, and that the mixture was discharged into a polyethylene bag without using a conveying machine, and the mixture was manually conveyed and charged into a plunger extruding machine. Then, the catalyst molded product was evaluated. The results are Shown in Table 1. Meanwhile, in the method of Example 7, the uneven quality of the catalyst molded product was reduced; however, since the mixture was manually pulled out and conveyed, the operation load was large, and the number of workers needed for the operation was three times the number needed in the case of using a conveying machine.

[0082] [Example 8]

A catalyst molded product was obtained by employing the same procedures described in Example 1, except that the amount of ethyl alcohol used during mixing was changed to 24 parts, and the catalyst molded product was evaluated. The results are shown in Table 1.

[0083] [Comparative Example 4]

A catalyst molded product was obtained by employing the same procedures described in Example 8, except that the aging time was changed to one hour, and the

catalyst molded product was evaluated. The results are shown in Table 1.

[0084] [Example 9]

In 4,000 parts of pure water, 1,000 parts of molybdenum trioxide, 80 parts of a 85 mass% of phosphoric-acid solution, 42 parts of vanadium pentoxide, 9 parts of copper oxide, and 2 parts of iron oxide were dissolved, and this solution was heated to 95°C while being stirred. While the liquid temperature was kept at 95°C, the solution was stirred for 3 hours. After this liquid was cooled to 50°C, 374 parts of a 29 mass% ammonia water was dripped into the liquid, and the mixture was stirred for 15 minutes. Next, a solution prepared by dissolving 102 parts of cesium nitrate in 30 parts of pure water was dripped thereto, and the mixture was stirred for 15 minutes. A resultant mixed slurry containing the raw material compounds of the catalyst components was dried using a parallel-flow spray dryer under the conditions of 300°C temperature at the feeding end of the dryer and a rotating disc spraying being rotated at 18,000 rpm. Thus, a catalyst precursor was obtained. The average particle size of the catalyst precursor was 30 μm .

[0085] 100 parts of the catalyst precursor was brought into contact with 5 parts of hydroxypropyl cellulose and 30 parts of isopropyl alcohol by charging the materials into a batch type kneading machine equipped with a double-arm sigma blades, such that the liquid content in the mixture calculated from the charged quantities would be 22.2%. The contactant was kneaded to attain a clay form, and thus a mixture was obtained.

[0086] The mixture was charged into a tank equipped with a screw type conveying machine in the lower part, and the inlet port was closed with a lid and was sealed. Next, the mixture was conveyed into a plunger extruding machine by discharging the mixture by the screw type conveying machine. The plunger extruding machine was equipped with a dice having 14 holes of 5.5 mm ϕ concentrically, and the inner diameter

of the plunger extruding machine was 120 mm ϕ . The amount of the mixture conveyed by the screw type conveying machine was an amount to be extruded once with the plunger extruding machine, and the remaining mixture was retained in the tank.

[0087] Here, during the mixture was conveyed by the screw type conveying machine, the mixture was aged for 3 hours at 25°C. At this time, the temperature of the aging material was controlled to be 25°C by adjusting the jacket temperature of the tank equipped with the screw type conveying machine to 25°C.

[0088] The mixture obtained after aging was extruded using the plunger extruding machine at a plunger movement speed of 100 mm/min. The extruded product discharged through the dice was cut by rotating a piano wire at the dice surface at a rate of 375 rpm, and thus a molded product was obtained.

[0089] The molded product was heat-treated at 90°C for 12 hours using a hot air dryer, and thereby a catalyst molded product was obtained. Furthermore, the mixture remaining in the tank was also similarly processed to produce a catalyst molded product, and the standard deviation of the packing density and the drop powdering rate were measured for these catalyst molded products. The liquid content in the mixture calculated from the charged quantities, the liquid content in the mixture measured immediately before performing molding, the rate of change in the liquid content, the standard deviation of the packing density, and the drop powdering rate are shown in Table 1. Meanwhile, the composition of the catalyst excluding oxygen, which is obtained after calcination the catalyst molded product, is $P_{1.2}Mo_{12}V_{0.8}Cu_{0.2}Fe_{0.05}Cs_{0.9}$.

[0090] [Comparative Example 5]

A catalyst molded product was obtained by employing the same procedures described in Example 9, except that the aging time was changed to one hour, and the catalyst molded product was evaluated. The results are shown in Table 1.

[0091] [Example 10]

100 parts of a catalyst precursor, obtained by employing the same procedures described in Example 1, was brought into contact with 5 parts of hydroxypropyl cellulose and 20 parts of ethyl alcohol by charging the materials into a batch type kneading machine equipped with a double-arm sigma blades, such that the liquid content in the mixture calculated from the charged quantities would be 16.0%. Subsequently, the contactant was aged for 1.5 hours at 25°C. At this time, the temperature of the aging material was controlled to be 25°C by adjusting the jacket temperature of the kneading machine to 25°C. The contactant obtained after aging was kneaded with the kneading machine to attain a clay form, and thus a mixture was obtained.

[0092] The mixture was charged into a tank equipped with a screw type conveying machine in the lower part, and the inlet port was closed with a lid and was sealed. Next, the mixture was conveyed into a plunger extruding machine by discharging the mixture by the screw type conveying machine. The plunger extruding machine was equipped with a dice having 14 holes of 5.5 mm ϕ concentrically, and the inner diameter of the plunger extruding machine was 120 mm ϕ . The amount of the mixture conveyed by the screw type conveying machine was an amount to be extruded once with the plunger extruding machine, and the remaining mixture was retained in the tank.

[0093] Here, during the mixture was conveyed by the screw type conveying machine, the mixture was aged for 1.5 hours at 25°C. At this time, the temperature of the aging material was controlled to be 25°C by adjusting the jacket temperature of the tank equipped with the screw type conveying machine to 25°C.

[0094] Extrusion molding and heat treatments were carried out by employing the same procedures described in Example 1, using the mixture obtained after aging, and thereby

a catalyst molded product was obtained . The catalyst molded product was evaluated, and the results are shown in Table 1.

[0095] [Example 11]

100 parts of a catalyst precursor, obtained by employing the same procedures described in Example 1, was brought into contact with 5 parts of hydroxypropyl cellulose and 20 parts of ethyl alcohol by charging the materials into a batch type kneading machine equipped with a double-arm sigma blades, such that the liquid content in the mixture calculated from the charged quantities would be 16.0%. Subsequently, the contactant was aged for 3 hours at 25°C. At this time, the temperature of the aging material was controlled to be 25°C by adjusting the jacket temperature of the kneading machine to 25°C. The contactant obtained after aging was kneaded with the kneading machine to attain a clay form, and thus a mixture was obtained.

[0096] The mixture was charged into a tank equipped with a screw type conveying machine in the lower part, and the inlet port was closed with a lid and was sealed. Next, the mixture was conveyed into a plunger extruding machine by discharging the mixture by the screw type conveying machine. The plunger extruding machine was equipped with a dice having 14 holes of 5.5 mmφ concentrically, and the inner diameter of the plunger extruding machine was 120 mmφ. The amount of the mixture conveyed by the screw type conveying machine was an amount to be extruded once with the plunger extruding machine, and the remaining mixture was retained in the tank.

[0097] Extrusion molding and heat treatments were carried out by employing the same procedures described in Example 1, using the mixture obtained after aging, and thereby a catalyst molded product was obtained. The catalyst molded product was evaluated, and the results are shown in Table 1.

[0098] [Reference Example 1]

To 1,000 parts of pure water, 500 parts of ammonium paramolybdate, 12.4 parts of ammonium paratungstate, 2.3 parts of potassium nitrate, 27.5 parts of antimony trioxide, and 66.0 parts of bismuth trioxide were added, and the mixture was heated and stirred (Liquid A). Separately, to 1,000 parts of pure water, 114.4 parts of ferric nitrate, 274.7 parts of cobalt nitrate, and 35.1 parts of zinc nitrate were sequentially added, and the compounds were dissolved therein (Liquid B). Subsequently, Liquid B was added to Liquid A, and thus an aqueous slurry was obtained. A resultant mixed slurry containing the raw material compounds of the catalyst components was dried using a parallel-flow spray dryer under the conditions of 250°C temperature at the feeding end of the dryer and a rotating disc spraying being rotated at 13,000 rpm. Thus, a catalyst precursor was obtained. The average particle size of the catalyst precursor was 46 μm .

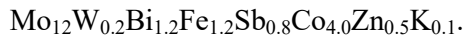
[0099] 100 parts of the catalyst precursor was brought into contact with 5 parts of hydroxypropyl cellulose and 30 parts of pure water by charging the materials into a batch type kneading machine equipped with a double-arm sigma blades, such that the liquid content in the mixture calculated from the charged quantities would be 22.2%. The contactant was kneaded to attain a clay form, and a mixture was obtained.

[0100] The mixture was charged into a tank equipped with a screw type conveying machine in the lower part, and the inlet port was closed with a lid and was sealed. Next, the mixture was conveyed into a plunger extruding machine by discharging the mixture by the screw type conveying machine. The plunger extruding machine was equipped with a dice having 14 holes of 5.5 mm ϕ concentrically, and the inner diameter of the plunger extruding machine was 120 mm ϕ . The amount of the mixture conveyed by the screw type conveying machine was an amount to be extruded once with the plunger extruding machine, and the remaining mixture was retained in the tank.

[0101] Here, during the mixture was conveyed by the screw type conveying machine, the mixture was aged for 7 hours at 25°C. At this time, the temperature of the aging material was controlled to be 25°C by adjusting the jacket temperature of the tank equipped with the screw type conveying machine to 25°C.

[0102] The mixture obtained after aging was extruded using the plunger extruding machine at a plunger movement speed of 100 mm/min. The extruded product discharged through the dice was cut by rotating a piano wire at the dice surface at a rate of 375 rpm, and thus a molded product was obtained.

[0103] The molded product was heat-treated at 90°C for 12 hours using a hot air dryer, and thereby a catalyst molded product was obtained. Furthermore, the mixture remaining in the tank was also similarly processed to produce a catalyst molded product, and the standard deviation of the packing density and the drop powdering rate were measured for these catalyst molded products. The liquid content in the mixture calculated from the charged quantities, the liquid content in the mixture measured immediately before performing molding, the rate of change in the liquid content, the standard deviation of the packing density, and the drop powdering rate are shown in Table 1. Meanwhile, the composition of the catalyst excluding oxygen, which is obtained after calcination the catalyst molded product, is



[0104] [Reference Example 2]

A catalyst molded product was obtained by employing the same procedures described in Reference Example 1, except that the aging time was changed to one hour, and the catalyst molded product was evaluated. The results are shown in Table 1.

[0105] [Table 1]

Examples and Comparative Examples	Conveying machine	Aging time (h)			Aging temperature (°C)	Liquid content of kneaded product calculated from charged quantities (%)	Liquid content of kneaded product immediately before performing molding (%)	Rate of change (%) in liquid content	Standard deviation of packing density (g/L)	Drop powdering rate (%)
		Step (1) (contactant)	Conveying process (mixture)	Total						
Example 1	Screw	0	3	3	25	16.0	15.5	3.1	6.6	0.2
Example 2	Screw	0	25	25	25	16.0	15.2	5.0	6.3	0.3
Example 3	Screw	0	47	47	25	16.0	15.1	5.6	7.1	0.2
Example 4	Screw	0	61	61	25	16.0	14.5	9.4	8.8	1.8
Example 5	Screw	0	25	25	50	16.0	14.7	8.1	7.8	1.5
Example 6	Belt conveyor	0	3	3	30	16.0	15.4	3.8	6.8	0.3
Comparative Example 1	Screw	0	1	1	25	16.0	15.8	1.3	14.3	0.5
Comparative Example 2	Screw	0	3	3	7	16.0	15.8	1.3	13.7	0.5
Comparative Example 3	Screw	0	3	3	25	16.0	14.2	11.3	17.9	0.6
Example 7	None	0	3	3	30	16.0	15.8	1.3	5.1	0.4
Example 8	Screw	0	3	3	25	18.6	18.0	3.2	5.9	0.3
Comparative Example 4	Screw	0	1	1	25	18.6	18.3	1.6	12.6	0.4
Example 9	Screw	0	3	3	25	22.2	21.4	3.6	6.9	0.5
Comparative Example 5	Screw	0	1	1	25	22.2	21.6	2.7	11.8	0.5
Example 10	Screw	1.5	1.5	3	25	16.0	15.5	3.1	7.8	0.3
Example 11	Screw	3	0	3	25	16.0	15.6	2.5	9.0	0.4
Reference Example 1	Screw	0	7	7	25	22.2	21.8	1.9	5.3	0.4
Reference Example 2	Screw	0	1	1	25	22.2	22.0	1.0	5.1	0.9

[0106] In Examples 1 to 11, in which the aging time, the aging temperature, and the rate of change in the liquid content were within the ranges of the present invention, the standard deviations of the packing density were small compared to Comparative Examples 1 to 5, and it was confirmed that the uneven quality of the catalyst molded products was reduced. Furthermore, in Example 4 in which the aging time was more than 48 hours, and in Example 5 in which the aging temperature was higher than 40°C, the standard deviations of the packing density were slightly higher than those of Examples 1 to 3, and also, it was confirmed that catalysts having a high drop powdering rate and low mechanical strength were produced. Thus, it was found that there are optimal ranges for the aging time and the aging temperature, respectively. Furthermore, even if the sum of the aging time and the aging temperature were the same, in Examples 10 and 11 in which a portion or the entirety of aging was applied to the contactant of Step (1), the standard deviations of the packing density were slightly higher compared to Example 1 in which the aging was applied to the mixture of the conveying process, and it was found that the uneven quality of the catalyst molded products can be further reduced by performing aging during the conveying process. Meanwhile, from Reference Examples 1 and 2, it was found that in a case in which phosphorus is not included as a catalyst component, even if the aging time, the aging temperature, and the rate of change in the liquid content were within the ranges of the present invention, an effect of reducing the uneven quality of the catalyst molded product cannot be obtained.

[0107] The present application based upon and claims the benefit of priority to Japanese Patent Application No. 2015-234745 filed on December 1, 2015, the entire contents of the application are incorporated herein by reference.

[0108] Thus, the present invention has been described with reference to the

embodiments and Examples; however, the present invention is not limited to those embodiments and Examples. Configuration and details of the present invention, it is possible to make various modifications that can be understood by those skilled in the art within the scope of the present invention.

CLAIMS

1. A method for producing a catalyst for (meth)acrylic acid production containing at least molybdenum and phosphorus as catalyst components, the catalyst for (meth)acrylic acid production being used for producing (meth)acrylic acid through gas phase catalytic oxidation of (meth)acrolein using molecular oxygen,

the method comprising:

(1) a step of mixing a contactant of a catalyst component-containing catalyst precursor, a liquid and a binder so as to produce a mixture;

(2) a step of molding the mixture so as to produce a molded product; and

(3) a step of heat-treating the molded product,

wherein during a period after producing the contactant in Step (1) and before producing the molded product

in Step (2), at least one of the contactant and the mixture is kept for a total 2 hours or more at a temperature of 10°C or higher, and

if the liquid content in the mixture, which is calculated from the charged quantities in Step (1), is denoted by $\alpha\%$ and the liquid content in the mixture immediately before carrying out the molding in Step (2) is denoted by $\beta\%$, the rate of change in the liquid content, as calculated using following Formula (I), is -10% to 10%:

$$\text{Rate of change in liquid content (\%)} = (\alpha - \beta)/\alpha \times 100 \quad (\text{I})$$

[wherein α represents the liquid content on a wet basis, calculated using following Formula (II) from the mass a of the liquid charged into Step (1) and the total mass b of the catalyst precursor and the binder:

$$\alpha = a/(a + b) \times 100 \quad (\text{II}); \text{ and}$$

β represents the liquid content calculated using following Formula (III) from the mass c (g) obtainable after 10 g of the mixture in a state of immediately before carrying

out the molded in Step (2) is dried at normal pressure and at 100°C for 30 minutes:

$$\beta = (10 - c)/10 \times 100 \quad \text{(III)].}$$

2. The method for producing a catalyst for (meth)acrylic acid production according to claim 1, wherein the rate of change in the liquid content calculated using Formula (I) is from 0% to 10%.

3. The method for producing a catalyst for (meth)acrylic acid production according to claim 1 or 2, wherein during a period after producing the contactant in Step (1) and before producing the molded product in Step (2), at least one of the contactant and the mixture is kept for a total 2 hours or more and 48 hours or less at a temperature of 10°C or higher.

4. The method for producing a catalyst for (meth)acrylic acid production according to claim 1 or 2, wherein during a period after producing the contactant in Step (1) and before producing the molded product in Step (2), at least one of the contactant and the mixture is kept for a total 2 hours or more at a temperature of 10°C or higher and 40°C or lower.

5. The method for producing a catalyst for (meth)acrylic acid production according to any one of claims 1 to 4, wherein at least one conveying process is included between the various steps from Step (1) to Step (3).

6. The method for producing a catalyst for (meth)acrylic acid production according to claim 5, wherein the conveying process is included between Step (1) and Step (2).

7. The method for producing a catalyst for (meth)acrylic acid production according to claim 5 or 6, wherein the conveying process is carried out using a conveying machine.

8. The method for producing a catalyst for (meth)acrylic acid production according to claim 7, wherein in the conveying process, conveyance is performed by means of a screw type conveying machine, a belt conveyor type conveying machine, a chain conveyor type conveying machine, a roller conveyor type conveying machine, a vibration type conveying machine, an extrusion type conveying machine, or a dropping type conveying machine.

9. The method for producing a catalyst for (meth)acrylic acid production according to any one of claims 1 to 8, wherein in Step (2), molding of the mixture is performed using an extruding machine.

10. The method for producing a catalyst for (meth)acrylic acid production according to any one of claims 1 to 9, wherein the catalyst for methacrylic acid production is a composite oxide having a composition represented using following Formula (IV):



[wherein in Formula (IV), 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 respectively represent the atomic ratios of the various elements; and when b = 12, a = 0.1 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 represents the atomic ratio of oxygen required for satisfying the valences of the various elements].

11. The method for producing a catalyst for (meth)acrylic acid production according to any one of claims 1 to 9, wherein the catalyst for acrylic acid production is a composite oxide having a composition represented using following Formula (V):



[wherein in Formula (V), P, Mo, V, and O represent phosphorus, molybdenum, vanadium, and oxygen, respectively; A represents at least one element selected from the group consisting of iron, cobalt, chromium, aluminum, and strontium; X² represents at least one element selected from the group consisting of germanium, boron, arsenic, selenium, silver, silicon, sodium, tellurium, lithium, antimony, potassium, and barium; Y² represents at least one element selected from the group consisting of magnesium, titanium, manganese, copper, zinc, zirconium, niobium, tungsten, tantalum, calcium, tin, and bismuth; i, j, k, l, m, n, and o respectively represent the atomic ratios of the various elements; and when j = 12, i = 0.01 to 10, k = 0.01 to 6, l = 0 to 5, m = 0 to 10, n = 0 to 5, and o represents the atomic ratio of oxygen required for satisfying the valences of the various components].

12. A method for producing (meth)acrylic acid, the method comprising producing a catalyst for (meth)acrylic acid production by the method for producing a catalyst for (meth)acrylic acid production according to any one of claims 1 to 11, and producing

(meth)acrylic acid through gas phase catalytic oxidation of (meth)acrolein using molecular oxygen in the presence of the catalyst.