DESCRIPTION

CATALYST FOR PRODUCING METHACRYLIC ACID, METHOD FOR PRODUCING THE SAME, AND METHOD FOR PRODUCING METHACRYLIC ACID

TECHNICAL FIELD

[0001]

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

BACKGROUND ART

[0002]

As a component of the catalyst for producing methacrylic acid through gas-phase catalytic oxidation of methacrolein with molecular oxygen, heteropoly acid compounds represented by phosphomolybdic acid are known. In addition, there have been many proposals of a method for forming pore structure in the catalyst in order to allow the catalyst component to act effectively on the gas-phase catalytic oxidation reaction.

[0003]

In Patent Document 1, there is proposed a method of catalyst preparation in which powder of a carbonic acid compound having an average particle size of 0.1 to 100 μm is

mixed with a dry powdery catalyst precursor and the resulting mixture is shaped and then subjected to heat treatment. In Patent Document 2, there is proposed a method in which an organic substance such as polyvinyl alcohol is added at the time of catalyst shaping and the resulting shaped article is subjected to heat treatment and then used as a finished catalyst. In Patent Document 3, there is proposed a method in which an organic polymer compound which decomposes into monomers and vaporizes at a relatively low temperature such as polymethyl methacrylate or polystyrene is added for shaping. In Patent Document 4, there is proposed a method of catalyst production in which particles of a dried material of a mixture solution or aqueous slurry containing catalyst components are allowed to have particle sizes that fall within a range of from 1 to 250 μm and shaped.

[0004]

In addition, in Patent Document 5, there is described a method in which an organic reducing material is added to a mixture solution or slurry containing raw material compounds for catalyst components for the purpose of reduction.

Patent Document 1: Japanese Patent Application Laid-Open No. Hei 10-244,160

Patent Document 2: Japanese Patent Application Laid-Open No. Sho 55-73,347

Patent Document 3: Japanese Patent Application Laid-Open No. Hei 04-367,737

Patent Document 4: Japanese Patent Application Laid-Open No. Hei 08-10,621

Patent Document 5: Japanese Patent Application Laid-Open No. Sho 58-51,943

DISCLOSURE OF INVENTION

PROBLEM TO BE SOLVED BY THE INVENTION

[0005]

However, a catalyst is desired which enables to further raise the yield of methacrylic acid to be produced by gas-phase catalytic oxidation of methacrolein.

[0006]

It is an object of the present invention to provide a catalyst for producing methacrylic acid in a high yield through gas-phase catalytic oxidation of methacrolein with molecular oxygen. Further objects of the present invention are to provide a method for producing the catalyst and to provide a method for producing methacrylic acid by use of the catalyst.

MEANS FOR SOLVING THE PROBLEM

[0007]

The present invention is a method for producing a catalyst for producing methacrylic acid through gas-phase catalytic oxidation of methacrolein with molecular oxygen, containing molybdenum and phosphorus as catalyst components, the method comprising the steps of:

(1) adding organic binder (B1) to a mixture solution or slurry containing raw material compounds for said catalyst components followed by drying the resulting mixture;

(2) kneading thus obtained dried materials, a liquid, and organic binder (B2); and

(3) subjecting thus obtained kneaded materials to extrusion molding.

Further, the present invention is a catalyst for producing methacrylic acid to be obtained by this method.

[0008]

Further, the present invention is a method for producing methacrylic acid through gas-phase catalytic oxidation of methacrolein with molecular oxygen in the presence of

the aforementioned catalyst.

EFFECT OF THE INVENTION

[0009]

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

BEST MODE FOR CARRYING OUT THE INVENTION

[0010]

The catalyst of the present invention is a catalyst for producing methacrylic acid through gas-phase catalytic oxidation of methacrolein with molecular oxygen, containing molybdenum and phosphorus as catalyst components and obtained by a method comprising the steps of:

(1) adding organic binder (B1) to a mixture solution or slurry containing raw material compounds for said catalyst components followed by drying the resulting mixture;

(2) kneading thus obtained dried materials, a liquid, and organic binder (B2); and

(3) subjecting thus obtained kneaded materials to extrusion molding.

[0011]

The composition of the catalyst components that constitute the catalyst of the present invention can be suitably selected depending on the performance of the target catalyst for producing methacrylic acid. Although the catalyst for producing methacrylic acid, which is the target of the present invention, is not particularly limited as long as it

contains molybdenum and phosphorus as catalyst components, it preferably has the composition represented by the following formula (1).

[0012]

$P_aMo_bV_cCu_dX_eY_fZ_gO_h$ (A)

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

[0013]

In the step (1) in the present invention, at first, raw material compounds for the catalyst components of the catalyst for producing methacrylic acid are dissolved or suspended in a solvent suitably selected, and a mixture solution or slurry thereof is prepared. The method for preparing the mixture solution or slurry is not particularly limited, and for example, conventional methods such as precipitation and oxides mixing can be recited.

[0014]

The raw materials for the catalyst to be used for the preparation of the mixture

solution or slurry are not particularly limited, and nitrates, carbonates, acetates, ammonium salts, oxides, halogenated compounds, oxo-acids, oxo-acid salts, and the like of each constituent element of the catalyst can be used in combination. Examples of a raw material for molybdenum include molybdenum oxides such as molybdenum trioxide; and ammonium molybdates such as ammonium paramolybdate and ammonium dimolybdate. Examples of a raw material compound for phosphorus include phosphoric acid, phosphorus pentoxide, and ammonium phosphate. Examples of a raw material compound for vanadium include ammonium metavanadate, vanadium pentoxide, and vanadyl oxalate. The raw material compounds for the catalyst components can be used alone or in a combination of two or more kinds with respect to each element constituting the catalyst components.

[0015]

As a solvent to be used, for example, water, ethyl alcohol, or acetone can be recited, and water is preferable.

[0016]

Then, organic binder (B1) is added to the mixture solution or slurry. Organic binder (B1) is not particularly limited, and for example, polymer compounds such as polyvinyl alcohol, α-glucan derivatives, and β-glucan derivatives can be recited. The polymer compounds may be water-soluble or water-dispersive. Among them, organic binders which are soluble in the solvent of the mixture solution or slurry and insoluble or poorly soluble in the liquid to be used in the step (2) are preferable because the dried materials do not collapse in the step (2) and thus pores effective for the oxidation reaction can easily be formed. For example, when the solvent of the mixture solution or slurry is water and the liquid to be used in the step (2) is ethyl alcohol, methyl cellulose,

polyvinyl alcohol, and pullulan are preferable which are poorly soluble or insoluble in ethyl alcohol and soluble in water.

[0017]

In the present invention, "poorly soluble or insoluble" in the solvent means that solubility in the solvent (dissolved amount (g) in 100 g of solvent) is 0 to 5, preferably 0 to 3, and more preferably 0 to 0.5. In addition, "soluble" in the solvent means that solubility in the solvent (dissolved amount (g) in 100 g of solvent) is more than 5 and preferably 8 or more.

[0018]

The α-glucan derivatives in the present invention mean polysaccharides constituted from α-glucose among polysaccharides constituted from glucose and exemplified by derivatives such as α-1,4 glucan, α-1,6 glucan, and α-1,4/1,6 glucan.

[0019]

Examples of such α-glucan derivatives include amylose, glycogen, amylopectin, pullulan, dextrin, and cyclodextrin.

[0020]

The β-glucan derivatives in the present invention mean polysaccharides constituted from β-glucose among polysaccharides constituted from glucose and exemplified by derivatives such as β-1,4 glucan, β-1,3 glucan, β-1,6 glucan, and β-1,3/1,6 glucan.

[0021]

Examples of such β-glucan derivatives include cellulose derivatives such as methyl cellulose, ethyl cellulose, carboxymethyl cellulose, sodium carboxymethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, hydroxypropyl methyl cellulose, hydroxyethyl methyl cellulose, hydroxybutyl methyl cellulose, and ethyl hydroxyethyl

cellulose; and β-1,3 glucans such as curdlan, laminaran, paramylon, callose, pachyman, and scleroglucan.

[0022]

One kind or a proper combination of two or more kinds of organic binder (B1) may be added to the mixture solution or slurry.

[0023]

The amount of organic binder (B1) to be added to the mixture solution or slurry is preferably 0.1 to 20 parts by mass relative to 100 parts by mass of raw material compounds as solid content, more preferably 0.5 to 15 parts by mass, and furthermore preferably 0.8 to 10 parts by mass.

[0024]

The method for adding organic binder (B1) to the mixture solution or slurry is not particularly limited and a method of directly adding the organic binder into the mixture solution or slurry to dissolve it or disperse it, a method of adding the organic binder after dissolving it or dispersing it in the solvent, or the like can be recited. The method for dissolving or dispersing the organic binder is not particularly limited and a method of dispersing organic binder (B1) in the solvent at a high temperature followed by cooling the resulting dispersion to a low temperature to dissolve the organic binder, or conversely, a method of dispersing organic binder (B1) in the solvent at a low temperature followed by heating the resulting dispersion to a high temperature to dissolve the organic binder, or the like can be recited. The timing of the addition is not particularly limited and a method of adding the organic binder during the preparation of the mixture solution or slurry, a method of adding the organic binder after the preparation of the mixture solution or slurry, or the like can be recited.

[0025]

Then, the mixture solution or slurry thus obtained as mentioned above is dried. The drying method is not particularly limited and a method for drying with a spray dryer, a method for drying with a slurry dryer, a method for drying with a drum dryer, or a method for drying by evaporation to dryness can be applied. Among them, the method with a spray dryer is preferable because particles can be obtained at the same time with drying and the shape of the particles thus obtained is regularly spherical.

[0026]

Although the drying condition varies with the drying method, in the case where the spray dryer is used, a hot air temperature at the dryer inlet is preferably 200 to 400°C and more preferably 220 to 370°C.

[0027]

In the case where the spray dryer is used, an average particle size of the dried particles thus obtained is preferably 1 to 250 μm. When the average particle size is less than 1 μm, there is a case where the yield of the target reaction product is lowered because a proper pore size necessary for the catalytic oxidation of the present invention cannot be obtained. By contrast, when the average particle size is more than 250 μm, there is a case where mechanical strength of the catalyst is lowered because a number of contact points among the dried particles per unit volume is reduced. An average particle size of the dried particles is preferably 1 to 150 μm. Note that the average particle size means volume average particle size and can be measured with, for example, a laser particle size distribution analyzer.

[0028]

In addition, the contact mode of sprayed liquid drops with the hot air may be any one

of co-current, counter current, and co-counter current (mixed current), and the drying can be carried out preferably in any one of these modes.

[0029]

Then, in the step (2), a mixture of dried materials obtained in the step (1) and at least a liquid and organic binder (B2) is kneaded. The apparatus to be used for kneading is not particularly limited and, for example, a batch type kneader with double stirring blades, or a continuous kneader such as one having a rotating reciprocating screw or one having a self-cleaning function can be used, and the batch type kneader is preferable because the kneading can be carried out while the state of the kneaded material is checked. In addition, the end point of the kneading can usually be judged by visual inspection or the touch. The method for mixing the aforementioned dried materials, the liquid, and organic binder (B2) is not particularly limited. Specifically, a method in which the dried materials and organic binder (B2) is dry-mixed and the resulting mixture is mixed with the liquid, a method in which organic binder (B2) is dissolved or dispersed in the liquid and then mixed with the dried materials, or the like can be exemplified, and among them, the method in which the dried materials and organic binder (B2) is dry-mixed and the resulting mixture is mixed with the liquid is preferable.

[0030]

The liquid to be used in the step (2) is not particularly limited as long as it has a function of wetting the dried materials obtained in the step (1), and for example, water and lower alcohols having 1 to 4 carbon atoms such as methyl alcohol, ethyl alcohol, propyl alcohol, and butyl alcohol can be recited. Among them, ethyl alcohol and propyl alcohol are preferable because the dried materials do not collapse in the step (2) and

thus pores effective for the oxidation reaction can easily be formed. The lower alcohols are preferably those of high-purity, but may contain a small amount of water.

[0031]

The amount of the liquid to be used is suitably selected depending on the kind or size of the dried materials, the kind of the liquid, or the like, but it is usually 10 to 80 parts by mass relative to 100 parts by mass of the dried materials obtained in the step (1). When the amount of the liquid to be used becomes large, the resulting mixture can be extrusion-molded more smoothly and hence the dried materials become hard to collapse and large voids, namely large pores, are formed in the resulting molded article after being dried and calcined and thus the selectivity tends to be improved. Therefore, the amount of the liquid to be used is preferably 40 parts by mass or more relative to 100 parts by mass of the dried materials and more preferably 45parts by mass or more. On the other hand, when the amount of the liquid to be used becomes smaller, adhesive property at the time of molding is reduced and hence handling property is improved. In addition, when the amount of the liquid to be used becomes small, the resulting molded article becomes dense and hence strength of the molded article tends to be improved. Therefore, the amount of the liquid to be used is preferably 70 parts by mass or less relative to 100 parts by mass of the dried materials and more preferably 65parts by mass or less.

[0032]

Organic binder (B2) to be used in the step (2) is not particularly limited, and for example, polymer compounds such as polyvinyl alcohol, α-glucan derivatives, and β-glucan derivatives can be recited. It is preferable that, among them, at least one organic binder which can be dissolved in the liquid to be used in the step (2) be

contained in organic binder (B2) because the strength of the resulting molded article is improved. For example, when the liquid to be used in the step (2) is ethyl alcohol, it is preferable that organic binder (B2) contain an organic binder soluble in ethyl alcohol. In the case where an organic binder soluble in the liquid to be used in the step (2) and an organic binder not soluble in the liquid to be used in the step (2) are jointly used, the organic binder soluble in the liquid to be used in the step (2) is preferably 10 to 95 parts by mass in 100 parts by mass of the total of these binders and more preferably 50 to 85 parts by mass.

[0033]

As organic binder (B2) to be used in the step (2), hydroxypropyl methylcellulose is more preferable. One kind or a proper combination of two or more kinds of organic binder (B2) may be used in the step (2).

[0034]

Although organic binder (B2) may be used without purification or after purification thereof, smaller amounts of metals or residue on ignition as impurities are better for avoiding deterioration of the catalyst performance.

[0035]

The amount of organic binder (B2) to be used in the step (2) is suitably selected depending on the kind or size of the dried materials, the kind of the liquid, or the like, but it is usually 0.05 to 15 parts by mass relative to 100 parts by mass of the dried materials obtained in the step (1) and preferably 0.1 to 10 parts by mass. As the amount of organic binder (B2) to be added is increased, moldability tends to be improved, and as the amount is decreased, post-treatment after molding such as heat treatment tends to become easy.

[0036]

In addition, an inert carrier such as inorganic compound like silica, alumina, silica-alumina, silicon carbide, titania, magnesia, graphite, or diatomaceous earth; glass fiber; ceramic ball or stainless steel; or inorganic fiber like ceramic fiber or carbon fiber can be added in the present invention. The addition thereof may be carried out at the time of kneading in the step (2).

[0037]

Then, in the step (3), kneaded materials obtained in the step (2) is extrusion-molded. When extrusion molding is carried out after the dried materials containing raw material compounds for the catalyst components, organic binder (B2), and the liquid are kneaded, for example, an auger extrusion molding machine or a piston extrusion molding machine can be used.

[0038]

The shape of molded article obtained by extrusion molding is not particularly limited, and it can be, for example, any shape such as ring, cylinder, or star.

[0039]

Then, a molded article of catalyst precursor thus obtained in the step (3) is dried and then calcined, and a catalyst (product) can be obtained.

[0040]

The method for drying is not particularly limited, and for example, a conventional method such as hot air drying, humidity drying, far infrared drying, or microwave drying can properly be used. The drying condition can be properly selected as long as the target moisture content is secured.

[0041]

The calcination condition is not particularly limited and a conventional calcination condition can be applied. Usually, the calcination is carried out at a temperature range of from 200 to 600°C. Usually, the calcination is carried out at 200 to 500°C and preferably at 300 to 450°C, for 1 to 24 hours.

[0042]

In the next place, the method for producing methacrylic acid of the present invention will be explained. The method for producing methacrylic acid of the present invention is the one in which methacrylic acid is produced through gas-phase catalytic oxidation of methacrolein with molecular oxygen in the presence of the catalyst for producing methacrylic acid thus obtained as mentioned above.

[0043]

The gas-phase catalytic oxidation is usually carried out in a fixed bed. The catalyst layer thereof is not particularly limited and may be either a non-diluted layer composed of only the catalyst or a diluted layer containing an inert carrier, and may be either a single layer or multilayer composed of a plurality of layers.

[0044]

It is preferable to use a feed gas containing methacrolein and molecular oxygen in the reaction.

[0045]

Although the concentration of methacrolein in the feed gas can be changed in a wide range, it is preferably 1% by volume or more and more preferably 3% by volume or more. In addition, the concentration of methacrolein in the feed gas is preferably 20% by volume or less and more preferably 10% by volume or less.

[0046]

The concentration of molecular oxygen in the feed gas is preferably 0.4 mol or more relative to 1 mol of methacrolein and more preferably 0.5 mol or more. In addition, the concentration of molecular oxygen in the feed gas is preferably 4 mol or less relative to 1 mol of methacrolein and more preferably 3 mol or less. As a source of molecular oxygen, air is economical, but air enriched with pure oxygen can also be used, if necessary.

[0047]

The feed gas preferably contains water (water vapor) besides methacrolein and molecular oxygen. Methacrylic acid can be obtained in a higher yield when the reaction is carried out in the presence of water. The concentration of water vapor in the feed gas is preferably 0.1% by volume or more and more preferably 1% by volume or more. In addition, the concentration of water vapor in the feed gas is preferably 50% by volume or less and more preferably 40% by volume or less. Although the feed gas may contain a small amount of impurities such as lower saturated aldehyde, it is preferable that the amount be as small as possible. In addition, the feed gas may contain an inert gas such as nitrogen or carbon dioxide.

[0048]

The reaction pressure of the gas-phase catalytic oxidation reaction is preferably from normal pressure (atmospheric pressure) to 5 atm. The reaction temperature is preferably 230°C or higher and more preferably 250°C or higher. In addition, the reaction temperature is preferably 450°C or lower and more preferably 400°C or lower.

[0049]

The flow rate of the feed gas is not particularly limited and suitably controlled in such a way that a proper contact time can be obtained. The contact time is preferably 1.5

seconds or longer and more preferably 2 seconds or longer. In addition, the contact time is preferably 15 seconds or shorter and more preferably 10 seconds or shorter.

EXAMPLES

[0050]

Hereinafter, the present invention will be explained specifically with reference to Examples and Comparative Examples, but the present invention is not limited to these Examples. In the following Examples and Comparative Examples, "part" means part by mass.

[0051]

Analyses of the feed gas and the product were carried out by use of gas chromatography. Note that rate of reaction of methacrolein, selectivity to methacrylic acid and per pass yield of methacrylic acid to be produced are defined as follows.

Rate of reaction of methacrolein (%) = (B/A) × 100

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

Yield of methacrylic acid (%) = (C/A) × 100

In the above formulae, A represents a number of moles of methacrolein supplied, B represents a number of moles of methacrolein reacted, and C represents a number of moles of methacrylic acid produced.

[0052]

Solubility of an organic binder in ethyl alcohol was measured as follows. To 500 parts of ethyl alcohol having a purity of 99.5% by mass and a temperature of 20°C, 50 parts of an organic binder was introduced little by little with stirring in such a way that unmixed-in lump of flour of the organic binder was not formed, and the resulting

mixture was stirred for 1 hour. Subsequently, the stirring was finished and the mixture was left to stand for 8 hours and thus an insoluble portion was precipitated. One hundred parts of a homogeneous solution, which is the supernatant of the solution thus obtained, were dried in a vacuum dryer at an ordinary temperature for 12 hours and solubility in ethyl alcohol was calculated from a mass of the resulting dried materials as follows.

Solubility in ethyl alcohol (dissolved amount in g per 100 g of ethyl alcohol) = (D/E) × 100

Wherein D represents mass of the dried materials and E represents a remainder obtained by subtraction of the mass of the dried materials from mass of the homogeneous solution.

[0053]

Example 1

In 400 parts of pure water, 100 parts of molybdenum trioxide, 3.1 parts of ammonium metavanadate, 7.3 parts of 85% by mass aqueous phosphoric acid solution, and 1.1parts of copper nitrate were dissolved, and the resulting solution was heated to 95°C while being stirred, and the stirring was continued for 3 hours while the temperature of the solution was kept at 95°C. Then, the solution was cooled to 40°C, and a solution obtained by dissolution of 13.5 parts of cesium bicarbonate in 20 parts of pure water was added thereto with stirring by a rotating blade stirrer, and the stirring was continued for 15 minutes. Then, a solution obtained by dissolution of 11.6 parts of ammonium nitrate in 20 parts of pure water was added thereto and the stirring was continued for 20 minutes.

[0054]

To a thus obtained mixture slurry containing the raw material compounds for catalyst components, 2.0 parts of pullulan (having a solubility in ethyl alcohol of 0.1) relative to 100 parts of the raw material compounds as solid content were added in the form of 5% by mass aqueous solution and then dried with a co-current spray dryer under the conditions of a dryer inlet temperature of 270°C and a rotational frequency of a rotary disk for spraying slurry of 16,000 rpm. The particle sizes of dried particles thus obtained were measured with a laser particle size distribution analyzer to fall within the range of from 5 to 150 μm and the average particle diameter thereof was measured to be 40 μm.

[0055]

To 100 parts of the dried particles thus obtained, 5 parts of hydroxypropyl methylcellulose (having a solubility in ethyl alcohol of 10) were added and dry-mixed. To the resulting mixture, 45 parts of ethyl alcohol was added and mixed, and kneaded with a kneader until the resulting mixture became clayey, and then the mixture was molded with a piston extrusion molding machine and ring-shaped molded articles having an outer diameter of 6 mm, an inner diameter of 3 mm, and an average length of 4 mm were obtained.

[0056]

The molded articles were dried at 60°C for 16 hours and then subjected to heat treatment of 380°C for 5 hours under air flow and a catalyst was obtained. The elemental composition other than oxygen (hereinafter, expressed in the same way) of the catalyst thus obtained was as follows.

[0057]

$Mo_{12}V_{0.45}P_{1.1}Cu_{0.08}Cs_{1.2}$

This catalyst was loaded in a reactor and a feed gas composed of 5% by volume of

methacrolein, 10% by volume of oxygen, 30% by volume of water vapor, 55% by volume of nitrogen was caused to react at a reaction temperature of 290°C, a reaction pressure of 1 atm (absolute pressure), and a contact time of 3.6 seconds, and gas-phase catalytic oxidation of methacrolein was carried out. The products were collected and analyzed by gas chromatography and rate of reaction of methacrolein, selectivity to methacrylic acid, and yield of methacrylic acid were obtained. The results are shown in Table 1.

[0058]

Example 2

The same procedure as in Example 1 was carried out except that the amount of pullulan to be added to the mixture slurry containing the raw material compounds for the catalyst components was changed to 0.5 part relative to 100 parts of the raw material compounds as solid content, a catalyst was obtained, and gas-phase catalytic oxidation of methacrolein was carried out. The results are shown in Table 1.

[0059]

Example 3

The same procedure as in Example 1 was carried out except that the organic binder to be added to the mixture slurry containing the raw material compounds for the catalyst components was changed from pullulan to polyvinyl alcohol (having a solubility in ethyl alcohol of 0.1), a catalyst was obtained, and gas-phase catalytic oxidation of methacrolein was carried out. The results are shown in Table 1.

[0060]

Example 4

The same procedure as in Example 1 was carried out except that the organic binder to

be added to the mixture slurry containing the raw material compounds for the catalyst components was changed from pullulan to hydroxypropyl methylcellulose (having a solubility in ethyl alcohol of 10), a catalyst was obtained, and gas-phase catalytic oxidation of methacrolein was carried out. The results are shown in Table 1.

[0061]

Comparative Example 1

The same procedure as in Example 1 was carried out except that pullulan was not added to the mixture slurry containing the raw material compounds for the catalyst components, a catalyst was obtained, and gas-phase catalytic oxidation of methacrolein was carried out. The results are shown in Table 1.

[0062]

Table 1

	Organic binder (B1)		Solvent	Organic binder (B2)		Liquid	Rate of reaction of methacrolein [%]	Selectivity to methacrylic acid [%]	Yield of methacrylic acid [%]
	Kind	Amount of addition		Kind	Amount of addition				
Ex. 1	Pullulan	2.0	Water	HPMC	5	Ethyl alcohol	86.8	91.0	79.0
Ex. 2	Pullulan	0.5	Water	HPMC	5	Ethyl alcohol	85.2	90.8	77.4
Ex. 3	PVA	2.0	Water	HPMC	5	Ethyl alcohol	86.2	90.7	78.2
Ex. 4	HPMC	2.0	Water	HPMC	5	Ethyl alcohol	85.3	89.8	76.6
Comp. Ex. 1	None	-	Water	HPMC	5	Ethyl alcohol	84.0	89.7	75.3

* The amount of addition of binder (B1) is expressed in part by mass relative to 100 parts by mass of the raw material compounds as solid content
* The amount of addition of binder (B2) is expressed in part by mass relative to 100 parts by mass of dried particles
* PVA: polyvinyl alcohol, HPMC: hydroxypropyl methylcellulose

[0063]

Example 5

In 400 parts of pure water, 100 parts of molybdenum trioxide, 3.4 parts of ammonium

metavanadate, 7.3 parts of 85% by mass aqueous phosphoric acid solution, 7.5 parts of 60% by mass arsenic acid, and 1.4 parts of copper nitrate were dissolved, and the resulting solution was heated to 95°C while being stirred, and the stirring was continued for 3 hours while the temperature of the solution was kept at 95°C. Then, the solution was cooled to 50°C, and a solution in which a solution obtained by dissolution of 12.4 parts of cesium bicarbonate in 20 parts of pure water and a solution obtained by dissolution of 11.6 parts of ammonium nitrate in 20 parts of pure water were dissolved in 20 parts of pure water was added thereto with stirring by a rotating blade stirrer, and the stirring was continued for 20 minutes.

[0064]

To a thus obtained mixture slurry containing the raw material compounds for the catalyst components, 2.0 parts of pullulan (having a solubility in ethyl alcohol of 0.1) relative to 100 parts of the raw material compounds as solid content were added in the form of 5% by mass aqueous solution and then the resulting slurry was dried with a co-current spray dryer under the conditions of a dryer inlet temperature of 300°C and a rotational frequency of a rotary disk for spraying slurry of 18,000 rpm. The particle sizes of dried particles thus obtained were measured with a laser particle size distribution analyzer and found to fall within the range of from 5 to 150 μm and the average particle diameter thereof was measured to be 30 μm.

[0065]

To 100 parts of the dried particles thus obtained, 3 parts of hydroxypropyl methylcellulose (having a solubility in ethyl alcohol of 10) and 1 part of curdlan (having a solubility in ethyl alcohol of 1) were added and dry-mixed. To the resulting mixture, 50 parts of ethyl alcohol was added and mixed, and kneaded with a kneader until the

resulting mixture became clayey, and then the mixture was molded with a piston extrusion molding machine and pellet-shaped molded articles having an outer diameter of 5 mm and an average length of 5 mm were obtained.

[0066]

The molded articles were dried at 60°C for 16 hours, then subjected to heat treatment of 380°C for 5 hours under air flow, and a catalyst was obtained. The elemental composition other than oxygen (hereinafter, expressed in the same way) of the catalyst thus obtained was as follows.

[0067]

$Mo_{12}V_{0.5}P_{1.1}As_{0.55}Cu_{0.1}Cs_{1.1}$

This catalyst was loaded in a reactor and a feed gas composed of 5% by volume of methacrolein, 10% by volume of oxygen, 10% by volume of water vapor, 75% by volume of nitrogen was caused to react at a reaction temperature of 290°C, a reaction pressure of 1 atm (absolute pressure), and a contact time of 4.0 seconds, and gas-phase catalytic oxidation of methacrolein was carried out. The products were collected, analyzed by gas chromatography, and rate of reaction of methacrolein, selectivity to methacrylic acid, and yield of methacrylic acid were obtained. The results are shown in Table 2.

[0068]

Example 6

The same procedure as in Example 5 was carried out except that the amount of pullulan to be added to the mixture slurry containing the raw material compounds for the catalyst components was changed to 0.5 part relative to 100 parts of the raw material compounds as solid content, a catalyst was obtained, and gas-phase catalytic oxidation

of methacrolein was carried out. The results are shown in Table 2.

[0069]

Example 7

The same procedure as in Example 5 was carried out except that the amount of pullulan to be added to the mixture slurry containing the raw material compounds for the catalyst components was changed to 0.3 part relative to 100 parts of the raw material compounds as solid content, a catalyst was obtained, and gas-phase catalytic oxidation of methacrolein was carried out. The results are shown in Table 2.

[0070]

Example 8

The same procedure as in Example 5 was carried out except that the amount of pullulan to be added to the mixture slurry containing the raw material compounds for the catalyst components was changed to 0.1 part relative to 100 parts of the raw material compounds as solid content, a catalyst was obtained, and gas-phase catalytic oxidation of methacrolein was carried out. The results are shown in Table 2.

[0071]

Example 9

The same procedure as in Example 5 was carried out except that the organic binder to be added to the mixture slurry containing the raw material compounds for the catalyst components was changed from pullulan to polyvinyl alcohol (having a solubility in ethyl alcohol of 0.1), a catalyst was obtained, and gas-phase catalytic oxidation of methacrolein was carried out. The results are shown in Table 2.

[0072]

Example 10

The same procedure as in Example 5 was carried out except that the organic binder to be added to the mixture slurry containing the raw material compounds for the catalyst components was changed from pullulan to methylcellulose (having a solubility in ethyl alcohol of 1.5), a catalyst was obtained, and gas-phase catalytic oxidation of methacrolein was carried out. The results are shown in Table 2.

[0073]

Example 11

The same procedure as in Example 5 was carried out except that 50 parts of ethyl alcohol to be added at the time of kneading were changed to 50 parts of propyl alcohol, a catalyst was obtained, and gas-phase catalytic oxidation of methacrolein was carried out. The results are shown in Table 2.

[0074]

Example 12

The same procedure as in Example 5 was carried out except that the organic binder to be added to the mixture slurry containing the raw material compounds for the catalyst components was changed from pullulan to hydroxypropyl methylcellulose (having a solubility in ethyl alcohol of 10), a catalyst was obtained, and gas-phase catalytic oxidation of methacrolein was carried out. The results are shown in Table 2.

[0075]

Example 13

The same procedure as in Example 5 was carried out except that hydroxypropyl methylcellulose to be added to the dried particles was changed to pullulan (having a solubility in ethyl alcohol of 0.1), a catalyst was obtained, and gas-phase catalytic oxidation of methacrolein was carried out. The results are shown in Table 2.

[0076]

Example 14

The same procedure as in Example 5 was carried out except that 50 parts of ethyl alcohol to be added at the time of kneading were changed to 50 parts of pure water, a catalyst was obtained, and gas-phase catalytic oxidation of methacrolein was carried out. The results are shown in Table 2.

[0077]

Example 15

The same procedure as in Example 5 was carried out except that the drying method of the mixture slurry containing the raw material compounds for the catalyst components and the organic binder was changed from the method using a co-current spray dryer to the one using a drum dryer, a catalyst was obtained, and gas-phase catalytic oxidation of methacrolein was carried out. The results are shown in Table 2.

[0078]

Comparative Example 2

The same procedure as in Example 5 was carried out except that pullulan was not added to the mixture slurry containing the raw material compounds for the catalyst components, a catalyst was obtained, and gas-phase catalytic oxidation of methacrolein was carried out. The results are shown in Table 2.

[0079]

Comparative Example 3

The same procedure as in Example 5 was carried out except that hydroxypropyl methylcellulose and curdlan were not added to the dried particles for preparation of the catalyst, but the extrusion-molded article from the piston extrusion molding machine

was easy to collapse and molded articles having a constant size could not be obtained.

[0080]

Comparative Example 4

The same procedure as in Example 5 was carried out except that tablet making was carried out after hydroxypropyl methylcellulose and curdlan were dry-mixed with the dried particles, a catalyst was obtained, and gas-phase catalytic oxidation of methacrolein was carried out. The results are shown in Table 2.

[0081]

Comparative Example 5

The same procedure as in Example 5 was carried out except that the material to be added to the mixture slurry containing the raw material compounds for the catalyst components was changed from 2 part of pullulan to 2 part of ethylene glycol, a catalyst was obtained, and gas-phase catalytic oxidation of methacrolein was carried out. The results are shown in Table 2.

[0082]

Table 2

	Organic binder (B1)		Solvent	Organic binder (B2)		Liquid	Rate of reaction of methacrolein [%]	Selectivity to methacrylic acid [%]	Yield of methacrylic acid [%]
	Kind	Amount of addition		Kind	Amount of addition				
Ex. 5	Pullulan	2.0	Water	HPMC Curdlan	3 1	Ethyl alcohol	87.4	91.0	79.5
Ex. 6	Pullulan	0.5	Water	HPMC Curdlan	3 1	Ethyl alcohol	87.3	90.3	78.8
Ex. 7	Pullulan	0.3	Water	HPMC Curdlan	3 1	Ethyl alcohol	87.0	89.6	78.0
Ex. 8	Pullulan	0.1	Water	HPMC Curdlan	3 1	Ethyl alcohol	86.9	89.5	77.8
Ex. 9	PVA	2.0	Water	HPMC Curdlan	3 1	Ethyl alcohol	87.2	90.9	79.3
Ex. 10	Methyl cellulose	2.0	Water	HPMC Curdlan	3 1	Ethyl alcohol	87.2	90.6	79.0
Ex. 11	Pullulan	2.0	Water	HPMC Curdlan	3 1	Propyl alcohol	87.4	90.9	79.4
Ex. 12	HPMC	2.0	Water	HPMC Curdlan	3 1	Ethyl alcohol	86.3	89.7	77.4
Ex. 13	Pullulan	2.0	Water	Pullulan Curdlan	3 1	Ethyl alcohol	86.2	89.8	77.4
Ex. 14	Pullulan	2.0	Water	HPMC Curdlan	3 1	Water	86.1	89.8	77.3
Ex. 15	Pullulan	2.0	Water	HPMC Curdlan	3 1	Ethyl alcohol	85.8	89.9	77.1
Comp. Ex. 2	None	-	Water	HPMC Curdlan	3 1	Ethyl alcohol	84.3	89.5	75.4
Comp. Ex. 3	Pullulan	2.0	Water	None	-	Ethyl alcohol	-	-	-
Comp. Ex. 4	Pullulan	2.0	Water	HPMC Curdlan	3 1	None	83.5	89.7	74.9
Comp. Ex. 5	None	-	Water	HPMC Curdlan	3 1	Ethyl alcohol	84.5	89.5	75.6

* The amount of addition of binder (B1) is expressed in part by mass relative to 100 parts by mass of the raw material compounds as solid content
* The amount of addition of binder (B2) is expressed in part by mass relative to 100 parts by mass of dried particles
* PVA: polyvinyl alcohol, HPMC: hydroxypropyl methylcellulose

What is claimed is:

1. A method for producing a catalyst for producing methacrylic acid through gas-phase catalytic oxidation of methacrolein with molecular oxygen, the catalyst containing molybdenum and phosphorus as catalyst components, the method comprising the steps of:

(1) adding organic binder (B1) to a mixture solution or slurry containing raw material compounds for said catalyst components followed by drying the resulting mixture;

(2) kneading thus obtained dried materials, a liquid, and organic binder (B2); and

(3) subjecting thus obtained kneaded materials to extrusion molding.

2. The method for producing a catalyst for producing methacrylic acid according to claim 1, wherein both the aforementioned binders (B1) and (B2) are selected from the group consisting of polymer compounds, α-glucan derivatives, and β-glucan derivatives.

3. The method for producing a catalyst for producing methacrylic acid according to claim 1 or 2, wherein the aforementioned binder (B1) is poorly soluble or insoluble in the aforementioned liquid and soluble in a solvent of the aforementioned mixture solution or slurry.

4. The method for producing a catalyst for producing methacrylic acid according to claim 3, wherein the aforementioned binder (B1) is selected from pullulan, polyvinyl alcohol, and methyl cellulose.

5. The method for producing a catalyst for producing methacrylic acid according to any one of claims 1 to 4, wherein at least one kind of the aforementioned binder (B2) is soluble in the aforementioned liquid.

6. The method for producing a catalyst for producing methacrylic acid according to any one of claims 1 to 5, wherein the aforementioned liquid is selected from the group consisting of water and an alcohol having 1 to 4 carbon atoms.

7. The method for producing a catalyst for producing methacrylic acid according to claim 6, wherein the aforementioned liquid is an alcohol having 1 to 4 carbon atoms.

8. The method for producing a catalyst for producing methacrylic acid according to claim 7, wherein the aforementioned liquid is at least one of ethyl alcohol and propyl alcohol.

9. The method for producing a catalyst for producing methacrylic acid according to any one of claims 1 to 8, wherein a spray dryer is used in the aforementioned step (1).

10. A catalyst for producing methacrylic acid produced by the method according to any one of claims 1 to 9.

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