

DESCRIPTION

TITLE OF THE INVENTION:

MOLDED CATALYST BODY, AND METHOD FOR PRODUCING UNSATURATED ALDEHYDE AND UNSATURATED CARBOXYLIC ACID USING SAME

TECHNICAL FIELD

[0001]

The present invention relates to a catalyst molded body and a method for producing an unsaturated aldehyde and/or an unsaturated carboxylic acid using the same.

BACKGROUND ART

[0002]

In the process for producing an unsaturated aldehyde and an unsaturated carboxylic acid, a catalyst is generally molded into a spherical molded body having a diameter of about 2 to 20 mm, or a columnar or cylindrical molded body having a diameter of about 2 to 10 mm and a length of about 2 to 20 mm, and is used in the reaction.

[0003]

As a method for improving a method for producing a catalyst molded body and improving a yield of an unsaturated aldehyde or an unsaturated carboxylic acid, for example, Patent Document 1 proposes a method for producing a catalyst in which a catalyst component containing molybdenum and bismuth, and a scaly inorganic material having an average particle diameter of 10 μ m to 2 mm and an average thickness of 0.005 to 0.3 times the average particle diameter are mixed and molded.

[0004]

In addition, Patent Document 2 proposes a method for producing a catalyst for producing methacrylic acid, including: a step of producing a dried material having an apparent density (X) of 1.00 to 1.80 kg/L by drying an aqueous mixed solution containing at least molybdenum and phosphorus as catalyst components and containing the raw material compound of the catalyst components, and a step of producing a catalyst molded body having a molded body density (Y) of 1.60 to 2.40 kg/L and a ratio (X/Y) of the apparent density (X) to the molded body density (Y) of 0.50 to 0.80 by molding the dried material or a mixture containing the dried material.

PRIOR-ART DOCUMENT

PATENT DOCUMENT

[0005]

[Patent Document 1] JP 2007-000803 A

[Patent Document 2] WO 2012/141076 A1

SUMMARY OF THE INVENTION

TECHNICAL PROBLEMS

[0006]

However, in terms of improving the yield of an unsaturated aldehyde and an unsaturated carboxylic acid, even when the catalyst molded body improved by the above method is used, it cannot be said that it is still sufficient. Therefore, further improvement in yield is desired.

An object of the present invention is to provide a catalyst molded body capable of producing an unsaturated aldehyde or an unsaturated carboxylic acid in a high yield. Further, an object of the present invention is to provide a method for producing an unsaturated aldehyde, an unsaturated carboxylic acid, and an unsaturated carboxylic acid ester using this catalyst molded body.

MEANS FOR SOLVING THE PROBLEMS

[0007]

As a result of extensive studies in view of the above problems, the present inventors have found that the above problems can be solved by using a catalyst molded body having a specific molded body density and surface characteristic, and have completed the present invention.

That is, the present invention includes the following [1] to [10].

[1] A catalyst molded body used in producing an unsaturated aldehyde and/or an unsaturated carboxylic acid by an oxidation reaction, wherein the catalyst molded body simultaneously satisfies the following requirements (A) and (B):

(A) A molded body density of the catalyst molded body is 2.25 g/mL or less in a state before being filled into a reactor;

(B) The catalyst molded body satisfies at least one of the following requirements (B-1) and (B-2):

(B-1) An arithmetic average roughness (Ra) defined by JIS B-0601-2001 of a surface of the catalyst molded body is 3.0 μm or less;

(B-2) A maximum height (Rz) defined by JIS B-0601-2001 of a surface of the catalyst molded body is 15 μm or less.

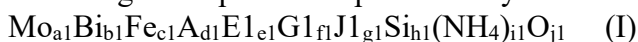
[2] The catalyst molded body according to [1], wherein the catalyst molded body has a coating layer of organic polymer compounds on at least a part of the surface.

[3] The catalyst molded body according to [2], wherein the organic polymer compounds are contained in an amount of 0.001 to 2% by mass.

[4] The catalyst molded body according to any one of [1] to [3], wherein the molded body is an extruded molded body.

[0008]

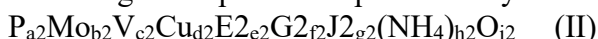
[5] The catalyst molded body according to any one of [1] to [4], including a catalyst component having a composition represented by the following formula (I):



(In formula (I), Mo, Bi, Fe, Si, NH_4 , and O represent molybdenum, bismuth, iron, silicon, ammonium species, and oxygen, respectively; A represents at least one element selected from the group consisting of cobalt and nickel; E1 represents at least one element selected from the group consisting of chromium, lead, manganese, calcium, magnesium, niobium, silver, barium, tin, thallium, tantalum, and zinc; G1 represents at least one element selected from the group consisting of phosphorus, boron, sulfur, selenium, tellurium, cerium, tungsten, antimony, and titanium; J1 represents at least one element selected from the group consisting of lithium, sodium, potassium, rubidium, and cesium; and a_1 , b_1 , c_1 , d_1 , e_1 , f_1 , g_1 , h_1 , i_1 , and j_1 represent a molar ratio of each component, and when $a_1 = 12$, $b_1 = 0.01\text{--}3$, $c_1 = 0.01\text{--}5$, $d_1 = 0.01\text{--}12$, $e_1 = 0\text{--}8$, $f_1 = 0\text{--}5$, $g_1 = 0.001\text{--}2$, $h_1 = 0\text{--}20$, $i_1 = 0\text{--}30$, and j_1 is a molar ratio of oxygen required to satisfy the valence of each above component.).

[0009]

[6] The catalyst molded body according to any one of [1] to [4], including a catalyst component having a composition represented by the following formula (II):



(In formula (II), P, Mo, V, Cu, NH_4 , and O represent phosphorus, molybdenum, vanadium, copper, ammonium species, and oxygen, respectively; E2 represents at least one element selected from the group consisting of antimony, bismuth, arsenic, germanium, zirconium, tellurium, silver, selenium, silicon, tungsten, and boron; G2 represents at least one element selected from the group consisting of iron, zinc, chromium, magnesium, calcium, strontium, tantalum, cobalt, nickel, manganese, barium, titanium, tin, thallium, lead, niobium, indium, sulfur, palladium, gallium, cerium, and lanthanum; J2 represents at least one element selected from the group consisting of potassium, rubidium, and cesium; and a_2 , b_2 , c_2 , d_2 , e_2 , f_2 , g_2 , h_2 , and i_2 represent a molar ratio of each

component, and when $b_2 = 12$, $a_2 = 0.1-3$, $c_2 = 0.01-3$, $d_2 = 0.01-2$, $e_2 = 0-3$, $f_2 = 0-3$, $g_2 = 0.01-3$, $h_2 = 0-30$, and i_2 is a molar ratio of oxygen required to satisfy the valence of each above component.).

[0010]

[7] A method for producing an unsaturated aldehyde and an unsaturated carboxylic acid, wherein propylene, isobutylene, primary butyl alcohol, tertiary butyl alcohol or methyl tertiary butyl ether is subjected to a gas phase catalytic oxidation with molecular oxygen in the presence of the catalyst molded body according to [5].

[8] A method for producing an unsaturated carboxylic acid, wherein (meth)acrolein is subjected to a gas phase catalytic oxidation with molecular oxygen in the presence of the catalyst molded body according to [6].

[0011]

[9] A method for producing an unsaturated carboxylic acid ester, wherein the unsaturated carboxylic acid produced by the method according to [7] or [8] is esterified.

[10] A method for producing an unsaturated carboxylic acid ester, including the steps of: producing an unsaturated carboxylic acid by the method according to [7] or [8]; and esterifying the unsaturated carboxylic acid.

EFFECT OF THE INVENTION

[0012]

According to the present invention, it is possible to provide a catalyst molded body capable of producing an unsaturated aldehyde and/or an unsaturated carboxylic acid in a high yield.

DETAILED DESCRIPTION OF THE PRESENT INVENTION

[0013]

[Catalyst Molded Body]

One aspect of a catalyst molded body of the present invention is a catalyst molded body used in producing an unsaturated aldehyde and/or an unsaturated carboxylic acid by an oxidation reaction, wherein a molded body density of the catalyst molded body is 2.25 g/mL or less in a state before being filled into a reactor, and an arithmetic average roughness (R_a) defined by JIS B-0601-2001 of a surface of the catalyst molded body is 3.0 μm or less.

Further, another aspect of the catalyst molded body of the present invention is a catalyst molded body used in producing an unsaturated aldehyde and/or an unsaturated carboxylic acid by an oxidation reaction, wherein a molded body density of the catalyst molded body is 2.25 g/mL or less in a state before being filled into a reactor, and a maximum height (R_z) defined by JIS B-0601-2001 of a surface of the catalyst molded body is 15 μm or less.

In addition, yet another aspect of the catalyst molded body of the present invention is a catalyst molded body used in producing an unsaturated aldehyde and/or an unsaturated carboxylic acid by an oxidation reaction, wherein a molded body density of the catalyst molded body is 2.25 g/mL or less in a state before being filled into a reactor, an arithmetic average roughness (R_a) defined by JIS B-0601-2001 of a surface of the catalyst molded body is 3.0 μm or less, and a maximum height (R_z) defined by JIS B-0601-2001 is 15 μm or less.

When such a catalyst molded body is filled into the reactor, the number of catalyst molded bodies which can be filled per unit volume increases, so that the amount of catalytically active component per unit volume in the reactor increases. As a result, the reaction activity in the production of an unsaturated aldehyde and/or an unsaturated carboxylic acid is improved, and the yield of the obtained target product is improved. Further, an effect of increasing the continuous reaction time is also obtained by increasing the amount of the catalytically active component per unit volume.

[0014]

(Requirement A: Molded Body Density of Catalyst Molded Body)

The molded body density of the catalyst molded body of the present invention is 2.25 g/mL or less in a state before being filled into the reactor. As a result, many pores are formed inside the catalyst molded body, and the selectivity of the target product is improved. The molded body density is more preferably 2.20 g/mL or less, and further preferably 2.15 g/mL or less. The molded body density of the molded body is usually 1.0 g/mL or more.

Here, the molded body density is a value obtained by dividing the mass (g) per catalyst molded body by the volume (mL), and performing this on 100 catalyst molded bodies, and calculating the value from the arithmetic average thereof.

[0015]

(Requirement (B): Arithmetic Average Roughness (Ra) and Maximum Height (Rz) of Surface of Catalyst Molded Body)

As described above, when the molded body density of the catalyst molded body is 2.25 g/mL or less, the selectivity of the target product is improved. On the other hand, the amount of the catalytically active component per catalyst molded body decreases and the reaction activity decreases due to the fact that more pores are formed inside the catalyst molded body. In other words, in the case where the same number of catalyst molded bodies having the same shape and size are used, when the reaction is carried out by filling a catalyst molded body having the molded body density of 2.25 g/mL or less, and when the reaction is carried out by filling a catalyst molded body having the molded body density of more than 2.25 g/mL, although the former improves the selectivity of the target product, the reaction rate of the raw material is lowered because the reaction activity is low. Further, since the total amount of the catalytically active component is reduced, there is also a problem that the continuous reaction time is shorter than that of the conventional catalyst molded body.

[0016]

To solve the above problems, the present inventors have focused on the surface characteristics of the catalyst molded body and found that, in addition to the molded body density of the catalyst molded body being 2.25 g/mL or less, when the arithmetic average roughness (Ra) of a surface of the catalyst molded body is 3.0 μm or less (Requirement (B-1)) or when the maximum height (Rz) of a surface is 15 μm or less (Requirement (B-2)) in a state before being filled into the reactor, the number of catalyst molded bodies that can be filled per unit volume can be increased, thereby solving the problem that the total amount of the catalytically active component that can be filled into the reactor is small. More particularly, it has been discovered that, in the case where the molded body density of the catalyst molded body is larger than 2.25 g/mL, when the catalyst molded body is filled into the reactor, it is densely filled by its own weight. On the other hand, in the case where the molded body density of the catalyst molded body is 2.25 g/mL or less, the catalyst molded body is light and cannot be densely filled by its own weight. However, it has been found that, when having specific surface characteristics as described above, the catalyst molded body can be densely filled and the number of catalyst molded bodies filled into the reactor increases. Thus, both the effect of improving the selectivity and improving the yield is achieved, and further, the problem regarding the reaction duration can be solved.

From the viewpoint of the number of catalyst molded bodies that can be filled per unit volume, it is preferable that the arithmetic average roughness (Ra) of the surface of the catalyst molded body is 3.0 μm or less and the maximum height (Rz) of the surface is 15 μm or less. Further, the upper limit of the arithmetic average roughness (Ra) of the surface of the catalyst molded body is preferably 2.8 μm or less, more preferably 2.6 μm or less. It is noted that the arithmetic average roughness (Ra) of the surface is usually 0.5 μm or more. In addition, the upper limit of the maximum height (Rz) of the surface is preferably 14 μm or less, and more preferably 13 μm or less. It is noted that the maximum height (Rz) of the surface is usually 3 μm or more.

[0017]

Here, the arithmetic average roughness (Ra) represents the average of the absolute values at the reference length. The maximum height (Rz) represents a sum of the height of the highest

peak and the depth of the deepest valley in a contour curve at the reference length. Both can be measured according to JIS B-0601-2001 standards.

[0018]

Regarding the measurement positions of the arithmetic average roughness (Ra) and the maximum height (Rz) of the surface of the catalyst molded body according to the present invention, the measurement is performed on the surface having the largest surface area among the surfaces that can come into contact with other molded bodies when the molded body has a shape having a plurality of surfaces. For example, in the case of a columnar catalyst molded body, the surface area of the circular portion and the surface area of the side surface portion are compared, and the measurement is performed on the surface having a large surface area. If the cylindrical catalyst molded body, as a surface that can come into contact with the other molded bodies, the surface area of the ring-shape portion and the cylindrical side surface portion are compared, and the measurement is performed on a surface having a large surface area. This is performed on 10 catalyst molded bodies, and is calculated from the arithmetic average thereof.

[0019]

(Surface of Catalyst Molded Body)

The catalyst molded body of the present invention may be one in which the surface is treated as necessary to adjust the arithmetic average roughness (Ra) and the maximum height (Rz). From the viewpoint of the mechanical strength of the surface of the catalyst molded body, it is preferable to have a coating layer of organic polymer compounds on at least a part of the surface. In addition, by forming the coating layer, the arithmetic average roughness (Ra) and the maximum height (Rz) of the surface of the catalyst molded body can be adjusted to desired values.

[0020]

Specific examples of the organic polymer compounds include saccharides and synthetic resins. Examples of the saccharides include monosaccharides such as threose, arabinose, xylose, galactose, ribose, glucose, sorbose, fructose, and mannose; disaccharides such as sucrose, lactose, maltose, trehalose, cellobiose, isomaltose, isotrehalose, neotrehalose, neolactose, turanose, and palatinose; and polysaccharides such as starch, glycogen, pullulan, water-soluble cellulose, and water-insoluble cellulose. Examples of synthetic resins include polyvinyl alcohol, polyethylene, polypropylene, polystyrene, phenol resin, and epoxy resin and the like. These may be used alone, or in combination of two or more thereof. The molecular weight of the organic polymer compounds is preferably 20,000 to 400,000, more preferably 30,000 or more at the lower limit and 300,000 or less at the upper limit.

[0021]

From the viewpoint of the mechanical strength of the catalyst molded body, it is more preferable to have a coating layer of a saccharide on at least a part of the surface of the catalyst molded body, and it is further preferable to have a coating layer of a polysaccharide, and it is particularly preferable to have at least one coating layer selected from pullulan and water-soluble cellulose.

Specific examples of the water-soluble cellulose include methyl cellulose, carboxymethyl cellulose, sodium carboxymethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, hydroxypropyl methyl cellulose, hydroxyethyl methylcellulose, hydroxybutyl methyl cellulose, ethyl hydroxyethyl cellulose, and salts thereof and the like. These may be used alone, or in combination of two or more thereof.

In addition, it is preferable that the catalyst molded body contains 0.001 to 2% by mass of the organic polymer compounds. When the content of the organic polymer compounds is 0.001% by mass or more, the mechanical strength of the catalyst molded body increases. Further, when the content of the organic polymer compounds is 2% by mass or less, the catalytically active component contained in the catalyst molded body becomes a sufficient amount. The upper limit of the content of the organic polymer compounds is more preferably 1.5% by mass or less, and further preferably 1% by mass or less.

[0022]

(Type and Shape of Catalyst Molded Body)

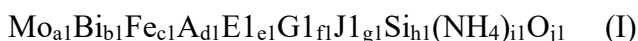
The type of the catalyst molded body is not particularly limited, and for example, an extruded molded body, a tablet molded body, a carrier molded body, a rolling granulated body, and the like can be cited. Among them, an extruded molded body is preferred in view of easy adjustment of the molded body density. Here, the extruded molded body indicates a product formed into a fixed shape by extruding a catalyst placed in a mold by applying pressure thereto. The shape of the catalyst molded body is not particularly limited, and for example, including a shape such as spherical, columnar, cylindrical (ring-shape), and star-shape, among them, spherical, columnar or cylindrical is preferred in view of high mechanical strength.

[0023]

(Catalyst Component in Catalyst Molded Body for Producing Unsaturated Aldehyde and Unsaturated Carboxylic Acid)

It is preferable that the catalyst molded body used in producing an unsaturated aldehyde and an unsaturated carboxylic acid according to the present invention contains a catalyst component having a composition represented by the following formula (I) from the viewpoint of unsaturated aldehyde and unsaturated carboxylic acid yields. Note that the molar ratio of each element is a value obtained by analyzing a component in which the catalyst component is dissolved in ammonia water by an ICP atomic emission spectrometry method. In addition, the molar ratio of ammonium species is defined as a value obtained by analyzing the catalyst component by the Kjeldahl method.

[0024]



In formula (I), Mo, Bi, Fe, Si, NH_4 , and O represent molybdenum, bismuth, iron, silicon, ammonium species, and oxygen, respectively; A represents at least one element selected from the group consisting of cobalt and nickel; E1 represents at least one element selected from the group consisting of chromium, lead, manganese, calcium, magnesium, niobium, silver, barium, tin, thallium, tantalum, and zinc; G1 represents at least one element selected from the group consisting of phosphorus, boron, sulfur, selenium, tellurium, cerium, tungsten, antimony, and titanium; J1 represents at least one element selected from the group consisting of lithium, sodium, potassium, rubidium, and cesium; and a_1 , b_1 , c_1 , d_1 , e_1 , f_1 , g_1 , h_1 , i_1 , and j_1 represent a molar ratio of each component, and when $a_1 = 12$, $b_1 = 0.01-3$, $c_1 = 0.01-5$, $d_1 = 0.01-12$, $e_1 = 0-8$, $f_1 = 0-5$, $g_1 = 0.001-2$, $h_1 = 0-20$, $i_1 = 0-30$, and j_1 is a molar ratio of oxygen required to satisfy the valence of each above component.

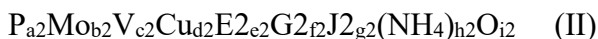
It is noted that, in the present application, the term "ammonium species" is a generic term for ammonia (NH_3) which can be ammonium ion (NH_4^+) and ammonium contained in ammonium-containing compounds such as ammonium salt.

[0025]

(Catalyst Component in Catalyst Molded Body for Producing Unsaturated Carboxylic Acid)

It is preferable that the catalyst molded body used in producing an unsaturated carboxylic acid according to the present invention contains a catalyst component having a composition represented by the following formula (II) from the viewpoint of unsaturated carboxylic acid yield.

[0026]



In formula (II), P, Mo, V, Cu, NH_4 , and O represent phosphorus, molybdenum, vanadium, copper, ammonium species, and oxygen, respectively; E2 represents at least one element selected from the group consisting of antimony, bismuth, arsenic, germanium, zirconium, tellurium, silver, selenium, silicon, tungsten, and boron; G2 represents at least one element selected from the group consisting of iron, zinc, chromium, magnesium, calcium, strontium, tantalum, cobalt, nickel, manganese, barium, titanium, tin, thallium, lead, niobium, indium, sulfur, palladium, gallium,

cerium, and lanthanum; J2 represents at least one element selected from the group consisting of potassium, rubidium, and cesium; and a2, b2, c2, d2, e2, f2, g2, h2, and i2 represent a molar ratio of each component, and when $b2 = 12$, $a2 = 0.1-3$, $c2 = 0.01-3$, $d2 = 0.01-2$, $e2 = 0-3$, preferably $0.01-3$, $f2 = 0-3$, $g2 = 0.01-3$, $h2 = 0-30$, and i2 is a molar ratio of oxygen required to satisfy the valence of each above component.

[0027]

[Method for Producing Catalyst Molded Body]

The catalyst molded body of the present invention can be produced according to a known method for producing a catalyst molded body, provided that the molded body density is 2.25 g/mL or less, and the arithmetic average roughness (Ra) of the surface is 3.0 μm or less, or the molded body density is 2.25 g/mL or less, and the maximum height (Rz) of the surface is 15 μm or less in a state before being filled into the reactor, but is preferably produced by a method including the following steps (i) to (iii):

(i) A step of mixing raw material compounds of a catalyst component with a solvent to prepare a catalyst raw material liquid;

(ii) A step of drying the catalyst raw material liquid to obtain a catalyst dried body;

(iii) A step of molding the catalyst dried body and, if necessary, surface-treating the catalyst molded body to obtain a catalyst molded body.

[0028]

(Step (i))

In step (i), raw material compounds of a catalyst component are mixed with a solvent to prepare a catalyst raw material liquid. For example, in the production of a catalyst for producing an unsaturated aldehyde and an unsaturated carboxylic acid, raw material compounds of the catalyst component of a catalyst for producing an unsaturated aldehyde and an unsaturated carboxylic acid are mixed with an appropriately selected solvent to prepare a catalyst raw material liquid containing at least molybdenum and bismuth. In addition, in the production of a catalyst for producing an unsaturated carboxylic acid, raw material compounds of the catalyst component of a catalyst for producing an unsaturated carboxylic acid are mixed with an appropriately selected solvent to prepare a catalyst raw material liquid containing at least molybdenum and phosphorus.

[0029]

The raw material compounds used for preparing the catalyst raw material liquid is not particularly limited, and organic acid salts such as oxides, sulfates, nitrates, carbonates, hydroxides, and acetates of each constituent element of the catalyst, ammonium salts, halides, oxoacids, oxoacid salts, alkali metal salts, and the like can be used alone or in combination of two or more thereof. Examples of the raw material compounds of molybdenum include molybdenum oxide such as molybdenum trioxide; ammonium molybdate such as ammonium paramolybdate and ammonium dimolybdate; molybdic acid, and molybdenum chloride. Examples of the raw material compounds of bismuth include bismuth nitrate, bismuth oxide, bismuth acetate, and bismuth hydroxide. Examples of the raw material compounds of phosphorus include, for example, phosphoric acid, phosphorous pentoxide, and phosphate such as ammonium phosphate. Examples of the raw material compounds of vanadium include ammonium vanadate, ammonium metavanadate, vanadium pentoxide, vanadium chloride, and vanadyl oxalate. As the raw material compounds, only one kind may be used for each element constituting the catalyst component, or two or more kinds may be used in combination.

[0030]

Examples of the solvent include water, ethyl alcohol, and acetone, but water is preferably used from an industrial viewpoint.

[0031]

In the production of the catalyst for producing an unsaturated carboxylic acid, it is preferable that the catalyst raw material liquid includes a Keggin-type heteropoly acid containing at least molybdenum and phosphorus from the viewpoint of unsaturated carboxylic acid selectivity.

For example, a Keggin-type heteropoly acid can be stably formed by adjusting the pH of the catalyst raw material liquid to 4 or less, preferably 3 or less, by a method such as appropriately selecting the amount of the raw material compounds to be added, and appropriately adding nitric acid, oxalic acid, or the like. Note that the structure of the obtained heteropoly acid can be judged from infrared absorption analysis using a NICOLET6700FT-IR (product name, manufactured by Thermo electron Co., Ltd.). When the heteropoly acid salt has a Keggin-type structure, the infrared absorption spectrum obtained has characteristic peaks in the vicinity of 1060, 960, 870, and 780 cm^{-1} .

[0032]

(Step (ii))

In step (ii), the catalyst raw material liquid obtained in step (i) is dried to obtain a catalyst dried body. The method of drying the catalyst raw material liquid 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, a method of evaporating to dryness, and the like can be applied. Among these, a method of drying using a spray dryer is preferred because particles are obtained simultaneously with drying and the shape of the obtained particles is a well-shaped spherical shape. Although the drying conditions vary depending on the drying method, when a spray dryer is used, the dryer inlet temperature is preferably 100 to 500 °C. The lower limit is more preferably 200 °C or more, and further preferably 220 °C or more. The upper limit is more preferably 400 °C or less, further preferably 370 °C or less. The lower limit of the dryer outlet temperature is preferably 100 °C or more, further preferably 105 °C or more. The upper limit is preferably 200 °C or less. The drying is preferably performed so that the moisture content of the obtained catalyst dried body is 0.1 to 4.5% by mass. It is to be noted that these conditions can be appropriately selected depending on the shape and size of the desired catalyst.

[0033]

When the spray dryer is used, the average particle diameter of the obtained catalyst dried body is preferably 1 to 250 μm . When the average particle diameter is 1 μm or more, pores having a preferable diameter for producing the target product are formed in step (iii) described later, and the target product is obtained in a high yield. Further, when the average particle diameter is 250 μm or less, the number of contact points between the catalyst dried body particles per unit volume can be maintained, and the mechanical strength of the catalyst molded body obtained in the step (iii) described later is improved. The lower limit of the average particle diameter of the catalyst dried body is more preferably 5 μm or more, and the upper limit is more preferably 150 μm or less. The average particle diameter means the volume average particle diameter, which is a value measured by a laser type particle size distribution measuring apparatus.

[0034]

In addition, the contact method between the sprayed droplets and the hot air may be any one of a co-current flow, a counter-current flow, and a co-counter-current flow (mixed flow), and in any case, the liquid droplets can be suitably dried.

[0035]

(Step (iii))

In step (iii), the catalyst dried body obtained in step (ii) is molded to obtain a catalyst molded body. The catalyst molded body may be subjected to surface treatment if necessary.

<Molding of Catalyst Dried Body>

The catalyst dried body is preferably mixed with a solvent and then molded from the viewpoint of adjusting the molded body density of the catalyst molded body. The amount of the solvent to be used is appropriately selected depending on the type of the catalyst dried body, the shape of the particles, and the type of the solvent. By reducing the amount of the solvent to be used for the catalyst dried body, the molded body density of the obtained catalyst molded body increases, and by increasing the amount of the solvent to be used for the catalyst dried body, the molded body density of the obtained catalyst molded body decreases. The amount of the solvent to be used is

preferably adjusted in the range of 10 to 70 parts by mass with respect to 100 parts by mass of the catalyst dried body. When the amount of the solvent to be used with respect to 100 parts by mass of the catalyst dried body is 10 parts by mass or more, moldability is improved, and pores effective for producing methacrylic acid tend to increase in the obtained catalyst molded body. Further, when the amount of the solvent to be used is 70 parts by mass or less, adhesiveness at the time of molding is reduced and handleability is improved. It is more preferable that the lower limit of the amount of the solvent to be used with respect to 100 parts by mass of the catalyst dried body is adjusted in a range of 15 parts by mass or more, and the upper limit is adjusted in a range of 60 parts by mass or less.

The type of the solvent is not particularly limited, but water or an organic solvent is preferred. Examples of the organic solvent include lower alcohols such as methyl alcohol, ethanol, propyl alcohol, butyl alcohol, and isopropanol, acetone, dimethyl ether, diethyl ether, methyl ethyl ketone, and ethyl acetate and the like. These solvents may be used alone, or in combination of two or more thereof. It is preferable that the solvent contains at least an organic solvent.

In addition, at the time of molding, polyvinyl alcohol, α -glucan derivative, β -glucan derivative, stearic acid, ammonium nitrate, graphite, water, alcohol, and the like, which are commonly used as molding aids, can be used as necessary.

The molding method of the catalyst dried body is not particularly limited. For example, known methods such as extrusion molding, tablet molding, carrier molding, rolling granulation, and the like can be cited. Among them, extrusion molding is preferred from the viewpoint of easily adjusting the molded body density of the catalyst molded body. As the extruder, for example, an auger type extruder, a plunger type extruder, or the like can be used, and preferably, a plunger type extruder can be used.

In extrusion molding, the molded body density of the catalyst molded body obtained increases by increasing the extrusion pressure, and the molded body density of the catalyst molded body obtained decreases by decreasing the extrusion pressure. The extrusion pressure is preferably adjusted in a range of 0.1 to 30 MPa (G). Here, (G) means gauge pressure. When the extrusion pressure is 0.1 MPa (G) or more, the catalyst molded body can be stably produced. In addition, when the extrusion pressure is 30 MPa or less, the pores effective for producing methacrylic acid tend to be increased in the obtained catalyst molded body. The lower limit of the extrusion pressure is more preferably 0.5 MPa (G) or more, further preferably 1 MPa (G) or more, and particularly preferably 2 MPa (G) or more. The upper limit of the extrusion pressure is more preferably 20 MPa (G) or less, further preferably 15 MPa (G) or less, and particularly preferably 10 MPa (G) or less.

[0036]

<Surface Treatment of Catalyst Molded Body>

The surface of the catalyst molded body of the present invention may be treated as necessary to adjust the arithmetic average roughness (Ra) and the maximum height (Rz). Examples of the method of surface treatment of the catalyst molded body include a method of coating the surface with organic polymer compounds, and a method of spraying a solvent on the surface and drying the surface. From the viewpoint of imparting the mechanical strength and adjusting the arithmetic average roughness (Ra) and the maximum height (Rz) of the surface of the catalyst molded body, it is preferable to use the method of coating the surface of the catalyst molded body with organic polymer compounds, and it is more preferable to use the method of coating with organic polymer compounds and then further spraying a solvent on the surface and drying the surface.

[0037]

Examples of the method of coating the surface of the catalyst molded body with organic polymer compounds include a method in which a coating liquid obtained by dissolving the above-mentioned organic polymer compounds in a solvent is sprayed in a spray form and adhered to the catalyst molded body, and at the same time, the solvent is vaporized and evaporated. According to

this method, it can be easily and uniformly coated.

Examples of the solvent used in the coating liquid and the solvent to be further sprayed after coating include water, an alcohol, an alkaline solution, and the like, and water is preferable. The concentration of the organic polymer compounds in the coating liquid is preferably set to 10% by mass or less. Thus, adhesion between the catalyst molded bodies is reduced, which is advantageous in operation. It is noted that, the concentration of the organic polymer compounds in the coating liquid is usually 0.1% by mass or more. Further, the amount of the solvent to be further sprayed after spraying of the coating liquid is preferably 0.1 to 3% by mass, more preferably 0.2% by mass or more at the lower limit and 2% by mass or less at the upper limit, with respect to the catalyst molded body.

[0038]

As the coating apparatus, a container called a pan such as a coating pan to which a rotation mechanism is added is preferable in terms of simplicity. By using such an apparatus, while rolling the catalyst molded body, the coating liquid is sprayed in a spray form to adhere to the catalyst molded body, and at the same time, hot air is blown to remove the solvent. As the coating apparatus, a dragee processing machine, a coating machine, or the like of tablets used in the pharmaceutical industry and the food industry may be used.

[0039]

[Method for Producing Unsaturated Aldehyde and/or Unsaturated Carboxylic Acid]

In the production of an unsaturated aldehyde and/or an unsaturated carboxylic acid, it is preferable to calcine the catalyst molded body obtained in step (iii) and use it, from the viewpoint of the yield of the target product. Incidentally, calcination may be performed on the catalyst dried body obtained in the step (ii). The calcination temperature is usually 200 to 600 °C, and the lower limit is preferably 300 °C or more and the upper limit is preferably 500 °C or less. Although the calcination conditions are not particularly limited, calcination is usually performed under oxygen, air or nitrogen flow. The calcination time is appropriately set depending on the target catalyst, but is preferably 0.5 to 40 hours, more preferably 1 hour or more at the lower limit, and 40 hours or less at the upper limit.

[0040]

(Method for Producing Unsaturated Aldehyde and Unsaturated Carboxylic Acid)

In the method for producing an unsaturated aldehyde and an unsaturated carboxylic acid according to the present invention, propylene, isobutylene, primary butyl alcohol, tertiary butyl alcohol or methyl tertiary butyl ether is subjected to a gas phase catalytic oxidation with molecular oxygen in the presence of the catalyst molded body used in producing an unsaturated aldehyde and an unsaturated carboxylic acid according to the present invention. According to these methods, unsaturated aldehydes and unsaturated carboxylic acids can be produced in high yields.

[0041]

Unsaturated aldehydes and unsaturated carboxylic acids produced correspond to propylene, isobutylene, primary butyl alcohol, tertiary butyl alcohol or methyl tertiary butyl ether, respectively. For example, the unsaturated aldehyde corresponding to propylene is acrolein, and the unsaturated carboxylic acid corresponding to propylene is acrylic acid. The unsaturated aldehyde corresponding to isobutylene, primary butyl alcohol, tertiary butyl alcohol and methyl tertiary butyl ether is methacrolein, and the unsaturated carboxylic acid corresponding to isobutylene, primary butyl alcohol, tertiary butyl alcohol and methyl tertiary butyl ether is methacrylic acid.

[0042]

From the viewpoint of yield of the target product, the unsaturated aldehyde and the unsaturated carboxylic acid are preferably methacrolein and methacrylic acid, respectively.

[0043]

Hereinafter, a method for producing methacrolein and methacrylic acid by the gas phase catalytic oxidation of isobutylene with molecular oxygen in the presence of the catalyst molded

body produced by the method according to the present invention as a representative example will be described.

[0044]

In the above method, methacrolein and methacrylic acid are produced by bringing a raw material gas containing isobutylene and molecular oxygen into contact with the catalyst molded body according to the present invention. A fixed-bed reactor can be used in this reaction. A reaction can be carried out by filling the catalyst molded body into a reactor and supplying the raw material gas to the reactor. The catalyst molded body layer may be one layer, and a plurality of catalyst molded bodies having different activities may be divided into a plurality of layers and filled, respectively. In addition, in order to control the activity, the catalyst molded body may be diluted with an inert carrier and filled.

[0045]

The concentration of isobutylene in the raw material gas is not particularly limited, but is preferably 1 to 20% by volume, more preferably 3% by volume or more at the lower limit and 10% by volume or less at the upper limit.

[0046]

The concentration of molecular oxygen in the raw material gas is preferably 0.1 to 5 mol, more preferably 0.5 mol or more at the lower limit and 3 mol or less at the upper limit, with respect to 1 mol of isobutylene. Note that air is preferred as the molecular oxygen source from the viewpoint of economic efficiency. If necessary, a gas obtained by enriching molecular oxygen by adding pure oxygen to air may be used.

[0047]

The raw material gas may be obtained by diluting isobutylene and molecular oxygen with an inert gas such as nitrogen or carbon dioxide gas. Further, water vapor may be added to the raw material gas.

[0048]

The contact time between the raw material gas and the catalyst molded body is preferably 0.5 to 10 seconds, more preferably 1 second or more at the lower limit and 6 seconds or less at the upper limit. The reaction pressure is preferably 0.1 to 1 MPa (G). Here, (G) means gauge pressure. The reaction temperature is preferably 200 to 420 °C, more preferably 250 °C or more at the lower limit and 400 °C or less at the upper limit.

[0049]

(Method for Producing Unsaturated Carboxylic Acid)

In the method for producing an unsaturated carboxylic acid according to the present invention, (meth) acrolein is subjected to a gas phase catalytic oxidation with molecular oxygen in the presence of the catalyst molded body used in producing an unsaturated carboxylic acid according to the present invention. According to these methods, unsaturated carboxylic acids can be produced in high yields.

[0050]

The unsaturated carboxylic acid to be produced is an unsaturated carboxylic acid in which an aldehyde group of (meth)acrolein is changed to a carboxyl group, and specifically, (meth)acrylic acid is obtained.

[0051]

Note that "(meth)acrolein" indicates acrolein and methacrolein, and "(meth)acrylic acid" indicates acrylic acid and methacrylic acid. From the viewpoint of yield of the target product, the (meth)acrolein and the (meth)acrylic acid are preferably methacrolein and methacrylic acid, respectively.

[0052]

Hereinafter, as a representative example, a method for producing methacrylic acid by the gas phase catalytic oxidation of methacrolein with molecular oxygen in the presence of the catalyst molded body produced by the method according to the present invention will be described.

[0053]

In the above method, methacrylic acid is produced by bringing a raw material gas containing methacrolein and molecular oxygen into contact with the catalyst molded body according to the present invention. A fixed-bed reactor can be used in this reaction. A reaction can be carried out by filling the catalyst molded body into a reactor and supplying a raw material gas to the reactor. The catalyst molded body layer may be one layer, and a plurality of catalyst molded bodies having different activities may be divided into a plurality of layers and filled, respectively. In addition, in order to control the activity, the catalyst molded body may be diluted with an inert carrier and filled.

[0054]

The concentration of the methacrolein in the raw material gas is not particularly limited, but is preferably 1 to 20% by volume, more preferably 3% by volume or more at the lower limit and 10% by volume or less at the upper limit. The raw material, methacrolein may also contain small amounts of impurities such as lower saturated aldehydes which do not substantially affect the reaction.

[0055]

The concentration of molecular oxygen in the raw material gas is preferably 0.4 to 4 mol, more preferably 0.5 mol or more at the lower limit and 3 mol or less at the upper limit, with respect to 1 mol of methacrolein. Note that air is preferred as the molecular oxygen source from the viewpoint of economic efficiency. If necessary, a gas obtained by enriching molecular oxygen by adding pure oxygen to air may be used.

[0056]

The raw material gas may be obtained by diluting methacrolein and molecular oxygen with an inert gas such as nitrogen or carbon dioxide gas. Further, water vapor may be added to the raw material gas. By carrying out the reaction in the presence of water vapor, methacrylic acid can be obtained in a high yield. The concentration of water vapor in the raw material gas is preferably 0.1 to 50% by volume, more preferably 1% by volume or more at the lower limit and 40% by volume at the upper limit.

[0057]

The contact time between the raw material gas and the catalyst for producing methacrylic acid is preferably 1.5 to 15 seconds, more preferably 2 seconds or more at the lower limit and 10 seconds or less at the upper limit. The reaction pressure is preferably 0.1 to 1 MPa (G). Here, (G) means gauge pressure. The reaction temperature is preferably 200 to 450 °C, more preferably 250 °C or more at the lower limit and 400 °C or less at the upper limit.

[0058]

[Method for Producing Unsaturated Carboxylic Acid Ester]

In a method for producing an unsaturated carboxylic acid ester according to the present invention, an unsaturated carboxylic acid produced by the method according to the present invention is esterified. In other words, a method for producing an unsaturated carboxylic acid ester according to the present invention includes a step of producing an unsaturated carboxylic acid by the method according to the present invention and a step of esterifying the unsaturated carboxylic acid. According to these methods, an unsaturated carboxylic acid ester can be obtained using an unsaturated carboxylic acid obtained by the gas phase catalytic oxidation of propylene, isobutylene, primary butyl alcohol, tertiary butyl alcohol or methyl tertiary butyl ether, or the gas phase catalytic oxidation of (meth)acrolein.

[0059]

The alcohol to be reacted with the unsaturated carboxylic acid is not particularly limited, and examples thereof include methanol, ethanol, isopropanol, n-butanol, and isobutanol. Examples of the obtained unsaturated carboxylic acid ester include methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, and butyl (meth)acrylate. The reaction can be carried out in the presence of an acidic catalyst, such as a sulfonic acid type cation exchange resin. The reaction

temperature is preferably 50 to 200 °C.

EXAMPLES

[0060]

Hereinafter, the present invention will be specifically described using Examples and Comparative Examples, but the present invention is not limited to these Examples. Note that "parts" indicates "parts by mass".

(Composition Ratio of Catalyst Component)

The molar ratio of each element was determined by analyzing the component in which the catalyst component was dissolved in ammonia water by ICP atomic emission spectrometry. In addition, the molar ratio of ammonium ions was determined by analyzing the catalyst component by the Kjeldahl method.

(Content Ratio of Organic Polymer Compounds)

The content ratio of the organic polymer compounds in the coated catalyst molded body was calculated from the mass M2 of the coated catalyst molded body and the mass M3 of the organic polymer compounds used in the coating liquid by the following formula.

$$\text{Content Ratio of Organic Polymer Compounds [\% by mass]} = (M3/M2) \times 100$$

Note that M2 is the sum of the charge amount of the catalyst molded body used in the coating and the charge amount of the organic polymer compounds used in the coating liquid. Here, the charge amount of the catalyst molded body used in the coating was set to be in a state in which the liquid was removed by a known drying method such as natural drying or hot air drying, and the liquid content of the catalyst molded body became 1% by mass or less. In addition, M3 is a charge amount of the organic polymer compounds used for the coating liquid.

(Molded Body Density of Catalyst Molded Body)

The molded body density of the catalyst molded body was calculated from the mass M1 (g) per catalyst molded body and the volume V1 (mL) per catalyst molded body by the following formula.

$$\text{Molded Body Density of Catalyst Molded Body (g/mL)} = M1/V1$$

Note that the molded body density of the catalyst molded body is an average value calculated with respect to 100 catalyst molded bodies produced under the same conditions.

[0061]

(Arithmetic Average Roughness (Ra) and Maximum Height (Rz))

The surface roughness of the catalyst molded body was measured using "SURFCOM1900SD" (trade name) manufactured by TOKYO SEIMITSU Co., Ltd. The measurement position was a side surface when the molded body was columnar, and a cylindrical side surface when the molded body was cylindrical, and the measurement was performed in the axial direction under the conditions of a measurement distance of 4.0 mm, a cutoff of 0.8 mm, and 4λ. This was performed on 10 catalyst molded bodies and calculated from the arithmetic average thereof.

(Powdering Rate at Dropping of Catalyst Molded Body)

As an index of the mechanical strength of the catalyst molded body, the powdering rate at dropping of the catalyst molded body was used. The smaller the powdering rate at dropping, the higher the mechanical strength, and the higher the powdering rate at dropping, the lower the mechanical strength. The powdering rate at dropping of the catalyst molded body was measured by the following method. From an upper opening of a stainless-steel cylinder having an inner diameter of 27.5 mm and a length of 6 m, which was installed so that the longitudinal direction is vertical and the lower opening of which was closed with a stainless-steel plate, 100 g of the catalyst molded body was dropped and filled in the cylinder. Among the catalyst molded body collected by opening the lower opening, the mass of the catalyst molded body which did not pass through the sieve with a 1-mm aperture was set to M4 g, and the powdering rate at dropping was calculated by the following formula. Note that the powdering rate at dropping in Examples is an

average value of the powdering rate at dropping measured for each catalyst molded body after the catalyst molded body was manufactured 10 times under the same conditions.

Powdering Rate at Dropping (%) = $\{(100 - M4)/100\} \times 100$
 (Number of Catalyst Molded Bodies Filled into Reactor)

The number of catalyst molded bodies filled into the reactor was calculated from the mass M1 (g) per catalyst molded body, the mass M5 (g) of the catalyst molded body filled into the reactor, and the filling volume V2 (mL) of the reactor according to the following formula.

Number of Catalyst Molded Bodies Filled into Reactor [number/mL] = $M5/M1/V2$
 [0062]

(Analysis of Raw Material Gas and Product)

Analysis of the raw material gas and the product was performed using a gas chromatography (instrument: GC-2014 manufactured by Shimadzu Corporation, column: DB-FFAP manufactured by J&W Co., Ltd., 30 m × 0.32 mm, film thickness of 1.0 μm). In Example 1 and Comparative Example 1, the total yield of methacrolein and methacrylic acid produced was calculated by the following formula.

[0063]
 Total Yield of Methacrolein and Methacrylic acid (%) = $(N2 + N3)/N1 \times 100$

Here, N1 is the number of moles of isobutylene supplied, N2 is the number of moles of methacrolein produced, and N3 is the number of moles of methacrylic acid produced.

[0064]

In Example 1 and Comparative Example 1, only the case where the raw material is isobutylene is shown, but even when tertiary butyl alcohol is used as the raw material, it is rapidly dehydrated to isobutylene at the inlet of the reactor, and the same result as in the case where isobutylene is used as the raw material can be obtained.

[0065]

In addition, in Examples 2 to 5 and Comparative Example 2, the yield of methacrylic acid produced was calculated by the following formula.

Yield of Methacrylic Acid (%) = $(N5/N4) \times 100$

Where N4 is the number of moles of methacrolein supplied, and N5 is the number of moles of methacrylic acid produced.

[0066]

[Example 1]

To 1000 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, 114.4 parts of ferric nitrate, 274.7 parts of cobalt nitrate and 35.1 parts of zinc nitrate were sequentially added to 1000 parts of pure water and dissolved (Liquid B). The catalyst raw material liquid obtained by adding the liquid B to the liquid A was dried using a co-current type spray dryer under conditions of a dryer inlet temperature of 250 °C and a rotating disk for spraying a slurry of 15,000 rpm to obtain a catalyst dried body having an average particle diameter of 42 μm. The composition of the catalyst excluding oxygen of the catalyst dried body was $\text{Mo}_{12}\text{W}_{0.2}\text{Bi}_{1.2}\text{Fe}_{1.2}\text{Sb}_{0.8}\text{Co}_{4.0}\text{Zn}_{0.5}\text{K}_{0.1}(\text{NH}_4)_{12.3}$.

[0067]

With respect to 100 parts of the catalyst dried body, 4 parts of hydroxypropyl methyl cellulose and 45 parts of pure water were added and kneaded in a batch type kneader equipped with a twin-arm type sigma blade until they became clay-like to obtain a mixture.

[0068]

The resulting mixture was extruded using a plunger type extruder, and molded into a cylindrical shape having an outer diameter of 6 mm, an inner diameter of 2 mm, and a length of 5.5 mm, and then dried in a hot air dryer at 90 °C for 14 hours to obtain a catalyst molded body.

[0069]

Next, the obtained catalyst molded body was filled into a coating pan, the catalyst molded body was rolled by rotation of the coating pan, and a coating liquid prepared as a 4% by mass aqueous solution of methyl cellulose by adding 0.5 parts of methyl cellulose was sprayed onto 100 parts of the catalyst molded body, and then 1 part of pure water was sprayed onto 100 parts of the catalyst molded body while applying hot air at 95 °C. Table 1 shows the measurement results of the molded body density, the arithmetic average roughness (Ra) and the maximum height (Rz) of the surface, and the powdering rate at dropping of the coated catalyst molded body.
[0070]

Subsequently, the coated catalyst molded body was filled so that the filling volume in the reactor was 2500 mL, and calcined under air flow at 450 °C for 5 hours. Then, a gas phase catalytic oxidation reaction of isobutylene was carried out by using and passing a raw material gas of 5% by volume of isobutylene, 12% by volume of oxygen, 10% by volume of water vapor and 73% by volume of nitrogen at a reaction temperature of 320 °C, and a contact time of 2.9 seconds. The total yield of methacrolein and methacrylic acid was determined by collecting the products and analyzing them by a gas chromatography. The number of the coated catalyst molded bodies filled into the reactor and the reaction results are shown in Table 1.

[0071]

[Comparative Example 1]

A catalyst molded body was produced in the same manner as in Example 1. Incidentally, the step of spraying the coating liquid and pure water on the catalyst molded body in the coating pan was not carried out. Table 1 shows the measurement results of the molded body density, the arithmetic average roughness (Ra) and the maximum height (Rz) of the surface, and the powdering rate at dropping of the catalyst molded body.

[0072]

Subsequently, the catalyst molded body was filled into the reactor in the same manner as in Example 1, and calcination and a gas phase catalytic oxidation reaction of isobutylene were performed. The number of the catalyst molded bodies filled into the reactor and the reaction results are shown in Table 1.

[0073]

Table 1

	Content of Organic Polymer Compounds [% by mass]	Molded Body Density of Catalyst Molded Body [g/mL]	Arithmetic Average Roughness (Ra) of Catalyst Molded Body [μm]	Maximum Height (Rz) of Catalyst Molded Body [μm]	Powdering Rate at Dropping of Catalyst Molded Body [%]	Number of Catalyst Molded Bodies Filled into Reactor [number/mL]	Total Yield of Methacrolein and Methacrylic acid [%]
Example 1	0.5	1.10	2.9	13.1	0.2	4.09	88.2
Comparative Example 1	0.0	1.10	4.1	25.5	0.8	3.86	86.8

[0074]

[Example 2]

To 4000 parts of pure water, 1000 parts of molybdenum trioxide, 34 parts of ammonium metavanadate, 80 parts of 85% by mass aqueous phosphoric acid and 7 parts of copper nitrate were added and dissolved, and the temperature was raised to 95 °C with stirring. And the mixture was stirred for 3 hours while keeping the liquid temperature at 95 °C. After cooling to 90 °C, a solution prepared by dissolving 124 parts of cesium bicarbonate in 200 parts of pure water was added while stirring using a rotary blade stirrer and the mixture was stirred for 15 minutes. Then, a solution obtained by dissolving 92 parts of ammonium carbonate in 200 parts of pure water was added, and the mixture was further stirred for 20 minutes to obtain a catalyst raw material liquid including a Keggin-type heteropoly acid containing molybdenum and phosphorus. The catalyst raw material liquid was dried using a co-current type spray dryer under the conditions of a dryer inlet temperature of 300 °C and a rotating disk for spraying a slurry of 18,000 rpm to obtain a catalyst dried body having an average particle diameter of 25 μm. The composition of the catalyst excluding the oxygen of the catalyst dried body is $P_{1.2}Mo_{12}V_{0.5}Cu_{0.05}Cs_{1.1}(NH_4)_{3.8}$.

[0075]

With respect to 100 parts of the catalyst dried body, 4 parts of hydroxypropyl methyl cellulose and 18 parts of ethyl alcohol were added and kneaded in a batch type kneader equipped with a twin-arm type sigma blade until they became clay-like to obtain a mixture.

[0076]

The resulting mixture was extruded using a plunger type extruder, and molded into a columnar shape having an outer diameter of 5.5 mm and a length of 5.5 mm, and then dried in a hot air dryer at 90 °C for 8 hours to obtain a catalyst molded body.

[0077]

Next, the obtained catalyst molded body was filled into a coating pan, the catalyst molded body was rolled by rotation of the coating pan, and a coating liquid prepared as a 4% by mass aqueous solution of methyl cellulose by adding 0.5 parts of methyl cellulose was sprayed onto 100 parts of the catalyst molded body, and then 2 parts of pure water was sprayed onto 100 parts of the catalyst molded body while applying hot air at 95 °C. Table 2 shows the measurement results of the molded body density, the arithmetic average roughness (Ra) and the maximum height (Rz) of the surface, and the powdering rate at dropping of the coated catalyst molded body.

[0078]

Subsequently, the coated catalyst molded body was filled so that the filling volume in the reactor was 2500 mL, and calcined under air flow at 380 °C for 11 hours. Then, a gas phase catalytic oxidation reaction of methacrolein was carried out by using and passing a raw material gas of 6% by volume of methacrolein, 12% by volume of oxygen, 10% by volume of water vapor and 72% by volume of nitrogen at a reaction temperature of 290 °C, and a contact time of 2.9 seconds. The yield of methacrylic acid was determined by collecting the product and analyzing it by a gas chromatography. The number of the coated catalyst molded bodies filled into the reactor and the reaction results are shown in Table 2.

[0079]

[Example 3]

A coated catalyst molded body was produced in the same manner as in Example 2, except that the amount of methyl cellulose used in the coating liquid was changed to 0.3 parts with respect to 100 parts of the catalyst molded body. Table 2 shows the measurement results of the molded body density, the arithmetic average roughness (Ra) and the maximum height (Rz) of the surface, and the powdering rate at dropping of the coated catalyst molded body.

[0080]

Subsequently, the coated catalyst molded body was filled into the reactor in the same manner as in Example 2, and calcination and a gas phase catalytic oxidation reaction of

methacrolein were performed. The number of the coated catalyst molded bodies filled into the reactor and the reaction results are shown in Table 2.

[0081]

[Example 4]

A coated catalyst molded body was produced in the same manner as in Example 2, except that the amount of methyl cellulose used in the coating liquid was changed to 0.2 parts with respect to 100 parts of the catalyst molded body. Table 2 shows the measurement results of the molded body density, the arithmetic average roughness (Ra) and the maximum height (Rz) of the surface, and the powdering rate at dropping of the coated catalyst molded body.

[0082]

Subsequently, the coated catalyst molded body was filled into the reactor in the same manner as in Example 2, and calcination and a gas phase catalytic oxidation reaction of methacrolein were performed. The number of the coated catalyst molded bodies filled into the reactor and the reaction results are shown in Table 2.

[0083]

[Example 5]

The catalyst molded body obtained in the same manner as in Example 2 was filled into a coating pan, the catalyst molded body was rolled by rotation of the coating pan, a coating liquid prepared as a 4% by mass aqueous solution of pullulan by adding 0.3 parts of pullulan was sprayed onto 100 parts of the catalyst molded body, and then 1 part of pure water was sprayed onto 100 parts of the catalyst molded body while applying hot air at 95 °C. Table 2 shows the measurement results of the molded body density, the arithmetic average roughness (Ra) and the maximum height (Rz) of the surface, and the powdering rate at dropping of the coated catalyst molded body.

[0084]

Subsequently, the coated catalyst molded body was filled into the reactor in the same manner as in Example 2, and calcination and a gas phase catalytic oxidation reaction of methacrolein were performed. The number of the coated catalyst molded bodies filled into the reactor and the reaction results are shown in Table 2.

[0085]

[Comparative Example 2]

A catalyst molded body was produced in the same manner as in Example 2. Incidentally, the step of spraying the coating liquid and pure water onto the catalyst molded body in the coating pan was not carried out. Table 2 shows the measurement results of the molded body density, the arithmetic average roughness (Ra) and the maximum height (Rz) of the surface, and the powdering rate at dropping of the catalyst molded body.

Subsequently, the catalyst molded body was filled into the reactor in the same manner as in Example 2, and calcination and a gas phase catalytic oxidation reaction of methacrolein were performed. The number of the catalyst molded bodies filled into the reactor and the reaction results are shown in Table 2.

[0086]

[Comparative Example 3]

A catalyst dried body was produced in the same manner as in Example 2.

Three parts of graphite were mixed with respect to 100 parts of the catalyst dried body, and formed into a columnar shape having an outer diameter of 5.5 mm and a length of 5.5 mm by a tablet molding machine to obtain a catalyst molded body.

Next, the obtained catalyst molded body was filled into a coating pan, the catalyst molded body was rolled by rotation of the coating pan, and a coating liquid prepared as a 4% by mass aqueous solution of methyl cellulose by adding 0.5 parts of methyl cellulose was sprayed onto 100 parts of the catalyst molded body, and then 2 parts of pure water was sprayed onto 100 parts of the catalyst molded body while applying hot air at 95 °C. Table 2 shows the measurement results of the molded body density, the arithmetic average roughness (Ra) and the maximum height (Rz) of

the surface, and the powdering rate at dropping of the coated catalyst molded body.

Subsequently, the coated catalyst molded body was filled into the reactor in the same manner as in Example 2, and calcination and a gas phase catalytic oxidation reaction of methacrolein were performed. The number of the coated catalyst molded bodies filled into the reactor and the reaction results are shown in Table 2.

[0087]

[Comparative Example 4]

A catalyst molded body was produced in the same manner as in Comparative Example 3. Incidentally, the step of spraying the coating liquid and pure water onto the catalyst molded body in the coating pan was not carried out. Table 2 shows the measurement results of the molded body density, the arithmetic average roughness (Ra) and the maximum height (Rz) of the surface, and the powdering rate at dropping of the catalyst molded body.

Subsequently, the catalyst molded body was filled into the reactor in the same manner as in Example 2, and calcination and a gas phase catalytic oxidation reaction of methacrolein were performed. The number of the catalyst molded bodies filled into the reactor and the reaction results are shown in Table 2.

[0088]

Table 2

	Type of Molded Body	Content of Organic Polymer Compounds [% by mass]	Molded Body Density of Catalyst Molded Body [g/mL]	Arithmetic Average Roughness (Ra) of Catalyst Molded Body [μm]	Maximum Height (Rz) of Catalyst Molded Body [μm]	Powdering Rate at Dropping of Catalyst Molded Body [%]	Number of Catalyst Molded Bodies Filled into Reactor [number/mL]	Yield of Methacrylic acid [%]
Example 2	extruded molded body	0.5	2.07	1.5	8.5	0.0	4.73	70.4
Example 3	extruded molded body	0.3	2.07	1.7	9.3	0.0	4.73	70.2
Example 4	extruded molded body	0.2	2.04	2.2	12.5	0.1	4.69	69.6
Example 5	extruded molded body	0.3	2.05	2.0	10.8	0.0	4.70	70.3
Comparative Example 2	extruded molded body	0.0	2.04	3.5	19.8	0.3	4.50	68.4
Comparative Example 3	tablet molded body	0.5	2.31	1.4	7.0	0.2	4.74	68.1
Comparative Example 4	tablet molded body	0.0	2.30	1.5	7.3	0.5	4.72	68.0

[0089]

As shown in Table 1, in the case of containing a catalyst component having a composition ratio of $\text{Mo}_{12}\text{W}_{0.2}\text{Bi}_{1.2}\text{Fe}_{1.2}\text{Sb}_{0.8}\text{Co}_{4.0}\text{Zn}_{0.5}\text{K}_{0.1}(\text{NH}_4)_{12.3}$, in Example 1, in which the molded body density and the arithmetic average roughness (Ra) and the maximum height (Rz) of the surface of the catalyst molded body are values within the specified range, the number of catalyst molded bodies filled into the reactor increased as compared with Comparative Example 1, in which the arithmetic average roughness (Ra) and the maximum height (Rz) of the surface of the catalyst molded body exceed the specified range, and the total yield of methacrolein and methacrylic acid was high. Further, it can be said that increasing the number of catalyst molded bodies filled into the reactor is also advantageous from the viewpoint of continuous reaction time.

[0090]

Similarly, as shown in Table 2, in the case of containing a catalyst component having a composition ratio of $\text{P}_{1.2}\text{Mo}_{12}\text{V}_{0.5}\text{Cu}_{0.05}\text{Cs}_{1.1}(\text{NH}_4)_{3.81}$, in Examples 2 to 5, in which the molded body density and the arithmetic average roughness (Ra) and maximum height (Rz) of the surface of the catalytic molded body are values within the specified range, the number of catalyst molded bodies filled into the reactor increased as compared with Comparative Example 2, in which the arithmetic average roughness (Ra) and the maximum height (Rz) of the surface of the catalyst molded body exceed the specified range, and the yield of methacrylic acid was high. Further, it can be said that increasing the number of catalyst molded bodies filled into the reactor is also advantageous from the viewpoint of continuous reaction time.

In addition, in Comparative Examples 3 and 4, the arithmetic average roughness (Ra) and the maximum height (Rz) of the surface of the catalyst molded body were within the specified range, but the molded body density exceeded the specified range. In this case, the number of the catalyst molded bodies filled into the reactor was similar to that of Examples 2 to 5, but the yield of methacrylic acid was lower than that of Examples 2 to 5. It is considered that this is because the pores, which are advantageous for producing methacrylic acid, in the catalyst molded body are reduced.

[0091]

Note that, a methacrylic acid ester can be obtained by esterifying the methacrylic acid obtained in the Examples.

CLAIMS

1. A catalyst molded body used in producing an unsaturated aldehyde and/or an unsaturated carboxylic acid by an oxidation reaction, wherein the catalyst molded body simultaneously satisfies the following requirements (A) and (B):

(A) A molded body density of the catalyst molded body is 2.25 g/mL or less in a state before being filled into a reactor;

(B) The catalyst molded body satisfies the following requirements (B-1) and (B-2):

(B-1) An arithmetic average roughness (Ra) defined by JIS B-0601-2001 of a surface of the catalyst molded body is 3.0 μm or less;

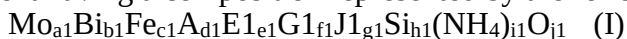
(B-2) A maximum height (Rz) defined by JIS B-0601-2001 of a surface of the catalyst molded body is 15 μm or less.

2. The catalyst molded body according to claim 1, wherein the catalyst molded body has a coating layer of organic polymer compounds on at least a part of the surface.

3. The catalyst molded body according to claim 2, wherein the organic polymer compounds are contained in an amount of 0.001 to 2% by mass.

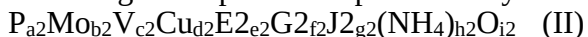
4. The catalyst molded body according to any one of claims 1 to 3, wherein the molded body is an extruded molded body.

5. The catalyst molded body according to any one of claims 1 to 4, comprising a catalyst component having a composition represented by the following formula (I):



(In formula (I), Mo, Bi, Fe, Si, NH_4 , and O represent molybdenum, bismuth, iron, silicon, ammonium species, and oxygen, respectively; A represents at least one element selected from the group consisting of cobalt and nickel; E1 represents at least one element selected from the group consisting of chromium, lead, manganese, calcium, magnesium, niobium, silver, barium, tin, thallium, tantalum, and zinc; G1 represents at least one element selected from the group consisting of phosphorus, boron, sulfur, selenium, tellurium, cerium, tungsten, antimony, and titanium; J1 represents at least one element selected from the group consisting of lithium, sodium, potassium, rubidium, and cesium; and a_1 , b_1 , c_1 , d_1 , e_1 , f_1 , g_1 , h_1 , i_1 , and j_1 represent a molar ratio of each component, and when $a_1 = 12$, $b_1 = 0.01\text{-}3$, $c_1 = 0.01\text{-}5$, $d_1 = 0.01\text{-}12$, $e_1 = 0\text{-}8$, $f_1 = 0\text{-}5$, $g_1 = 0.001\text{-}2$, $h_1 = 0\text{-}20$, $i_1 = 0\text{-}30$, and j_1 is a molar ratio of oxygen required to satisfy the valence of each above component.)

6. The catalyst molded body according to any one of claims 1 to 4, comprising a catalyst component having a composition represented by the following formula (II):



(In formula (II), P, Mo, V, Cu, NH_4 , and O represent phosphorus, molybdenum, vanadium, copper, ammonium species, and oxygen, respectively; E2 represents at least one element selected from the group consisting of antimony, bismuth, arsenic, germanium, zirconium, tellurium, silver, selenium, silicon, tungsten, and boron; G2 represents at least one element selected from the group consisting of iron, zinc, chromium, magnesium, calcium, strontium, tantalum, cobalt, nickel, manganese, barium, titanium, tin, thallium, lead, niobium, indium, sulfur, palladium, gallium, cerium, and lanthanum; J2 represents at least one element selected from the group consisting of potassium, rubidium, and cesium; and a_2 , b_2 , c_2 , d_2 , e_2 , f_2 , g_2 , h_2 , and i_2 represent a molar ratio of each component, and when $b_2 = 12$, $a_2 = 0.1\text{-}3$, $c_2 = 0.01\text{-}3$, $d_2 = 0.01\text{-}2$, $e_2 = 0\text{-}3$, $f_2 = 0\text{-}3$, $g_2 = 0.01\text{-}3$, $h_2 = 0\text{-}30$, and i_2 is a molar ratio of oxygen required to satisfy the valence of each above

component).

7. A method for producing an unsaturated aldehyde and an unsaturated carboxylic acid, wherein propylene, isobutylene, primary butyl alcohol, tertiary butyl alcohol or methyl tertiary butyl ether is subjected to a gas phase catalytic oxidation with molecular oxygen in the presence of the catalyst molded body according to claim 5.

8. A method for producing an unsaturated carboxylic acid, wherein (meth)acrolein is subjected to a gas phase catalytic oxidation with molecular oxygen in the presence of the catalyst molded body according to claim 6.

9. A method for producing an unsaturated carboxylic acid ester, wherein the unsaturated carboxylic acid produced by the method according to claim 7 or 8 is esterified.

10. A method for producing an unsaturated carboxylic acid ester, comprising the steps of: producing an unsaturated carboxylic acid by the method according to claim 7 or 8; and esterifying the unsaturated carboxylic acid.