DESCRIPTION

CATALYST MOLDED 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 containing a catalyst and a cellulose nanofiber, and a method for producing an unsaturated aldehyde and/or unsaturated carboxylic acid using the same.

BACKGROUND ART

[0002]

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

[0003]

For example, Patent Document 1 proposes a catalyst for synthesizing unsaturated aldehydes and unsaturated carboxylic acids by gas phase catalytic oxidation of propylene, isobutylene, tertiary butyl alcohol or methyl tertiary butyl ether with molecular oxygen, comprising a catalyst component containing molybdenum and bismuth and a scaly inorganic having an average particle diameter of 10 μm to 2 mm and an average thickness of 0.005 to 0.3 times the average particle diameter.

[0004]

Patent Document 2 proposes an oxide catalyst containing molybdenum, bismuth, cobalt and iron used for producing methacrolein, wherein a crystalline cellulose having a specific surface area of 0.5 m^2/g or more is mixed with a catalyst precursor powder and molded, and the obtained molded body is heat-treated to remove the crystalline cellulose.

PRIOR-ART LITERATURE

PATENT DOCUMENT

[0005]

Patent Document 1: JP 2011-224482A

Patent Document 2: JP 2007-061763A

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0006]

From an industrial viewpoint, however, further improvement in mechanical strength of the catalyst molded body is desired. An object of the present invention is to provide a catalyst molded body having high yield and high mechanical strength.

MEANS FOR SOLVING THE PROBLEMS

[0007]

The present invention includes the following [1] to [13].

[1] A catalyst molded body including a catalyst component capable of producing an unsaturated aldehyde and/or an unsaturated carboxylic acid by gas phase catalytic oxidation with molecular oxygen, and a cellulose nanofiber having an average fiber diameter of 1 to 300 nm.

[2] The catalyst molded body according to [1], wherein, when the mass of the catalyst molded body is M1 [g] and the mass of the cellulose nanofiber is M2 [g], the cellulose nanofiber content calculated by the following formula (III) is 0.1 to 5% by mass:

$$\text{Cellulose nanofiber content [\% by mass]} = (M2/M1) \times 100 \quad \text{(III)}.$$

[3] The catalyst molded body according to [1] or [2], further including a binder.

[4] The catalyst molded body according to [3], wherein the binder is water-soluble.

[5] The catalyst molded body according to [3], wherein the binder is a water-soluble organic binder.

[6] A catalyst molded body obtained by calcining the catalyst molded body according to any one of [1] to [5].

[7] The catalyst molded body according to any one of [1] to [6], which is produced by a process including extrusion molding.

[0008]

[8] The catalyst molded body according to any one of [1] to [7], wherein the catalyst component has a composition represented by the following formula (I), and is a catalyst

for producing an unsaturated aldehyde and an unsaturated carboxylic acid by which propylene, isobutylene, primary butyl alcohol, tertiary butyl alcohol or methyl tertiary butyl ether is subjected to a gas-phase catalytic oxidation with molecular oxygen:

$$Mo_{a1}Bi_{b1}Fe_{c1}A_{d1}E1_{e1}G1_{f1}J1_{g1}Si_{h1}(NH_4)_{i1}O_{j1} \quad (I)$$

(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 a1, b1, c1, d1, e1, f1, g1, h1, i1, and j1 represent the molar ratio of each component, and when a1 = 12, b1 = 0.01-3, c1 = 0.01-5, d1 = 0.01-12, e1 = 0-8, f1 = 0-5, g1 = 0.001-2, h1 = 0-20, i1 = 0-30, and j1 is the molar ratio of oxygen necessary to satisfy the valence of each above component.)

[0009]

[9] The catalyst molded body according to any one of [1] to [7], wherein the catalyst component has a composition represented by the following formula (II), and is a catalyst for producing an unsaturated carboxylic acid by a gas-phase catalytic oxidation of (meth)acrolein with molecular oxygen:

$$P_{a2}Mo_{b2}V_{c2}Cu_{d2}E2_{e2}G2_{f2}J2_{g2}(NH_4)_{h2}O_{i2} \quad (II)$$

(In Formula (II), P, Mo, V, Cu, NH_4 and O represent phosphorus, 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 the molar ratio of each component, when b2 = 12, a2 = 0.1-3, c2 = 0.01-3, d2 = 0.01-2, e2 = 0-3, f2 = 0-3, g2 = 0.01-3, h2 = 0-30, and

i2 is the molar ratio of oxygen necessary to satisfy the valence of each above component.)

[0010]

[10] 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 [8].

[11] 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 a catalyst molded body according to [9].

[12] A method for producing an unsaturated carboxylic acid ester, in which the unsaturated carboxylic acid produced by the method according to [10] or [11] is esterified.

[13] A method for producing an unsaturated carboxylic acid ester including a step of producing an unsaturated carboxylic acid by the method according to [10] or [11] and a step of esterifying the unsaturated carboxylic acid.

EFFECT OF INVENTION

[0011]

According to the present invention, it is possible to provide a catalyst molded body having high yield and high mechanical strength. Further, it is possible to provide a method for producing an unsaturated aldehyde and an unsaturated carboxylic acid capable of maintaining a high yield in a long period of time.

DETAILED DESCRIPTION OF THE INVENTION

[0012]

The catalyst molded body of the present invention includes cellulose nanofibers having an average fiber diameter of 1 to 300 nm. In addition, the catalyst molded body of the present invention includes a catalyst component capable of producing an unsaturated aldehyde and/or an unsaturated carboxylic acid by gas phase catalytic oxidation with molecular oxygen, particularly, a catalyst component used in gas phase catalytic oxidation of propylene, isobutylene, primary butyl alcohol, tertiary butyl alcohol or methyl tertiary butyl ether with molecular oxygen to produce an unsaturated aldehyde and an unsaturated carboxylic acid corresponding to each of them, or a catalyst

component used in gas phase catalytic oxidation of (meth)acrolein with molecular oxygen to produce an unsaturated carboxylic acid.

Since the catalyst molded body of the present invention includes cellulose nanofibers having a specific fiber diameter, it is possible to achieve both high yield of the target product and high mechanical strength. As a result, in the long-term continuous operation of the industrial process, the increase in the differential pressure can be suppressed because powdering and cracking of the catalyst are small, and the high yield can be maintained for a long period of time. Therefore, the catalyst life is long, and the frequency of replacement of the catalyst can be reduced.

The mechanical strength of the catalyst molded body can be evaluated by, for example, a powdering rate at dropping measured by the following method. The catalyst molded body is filled by dropping 100 g of the catalyst molded body from the upper opening of a stainless-steel cylinder so as to be placed the longitudinal direction of the stainless-steel cylinder vertically, wherein the cylinder has an inner diameter of 27.5mm and a length of 6 meters, and its lower opening is closed with a sheet made of stainless steel. Among the catalyst molded body collected by opening the lower opening, the mass of the catalyst molded body that does not pass through the sieve with a 1-mm aperture is set to α g, and the powdering rate at dropping is calculated by the following equation. The smaller the powdering rate at dropping, the higher the mechanical strength, and the larger the powdering rate, the lower the mechanical strength.

$$\text{Powdering rate at dropping (\%)} = \{(100-\alpha)/100\} \times 100$$

[0013]

[Cellulose Nanofibers]

The cellulose nanofibers used in the present invention have an average fiber diameter of 1 to 300 nm. The lower limit of the average fiber diameter is preferably 2 nm or more, more preferably 3 nm or more. Further, the upper limit of the average fiber diameter is preferably 100 nm or less, more preferably 50 nm or less. Note that the cellulose nanofibers denote fibrous celluloses having an average aspect ratio of 100 or more. The average aspect ratio is preferably from 100 to 10,000, more preferably from 100 to 2,000. The average aspect ratio means the ratio of the average fiber length and the average fiber diameter of the cellulose nanofibers (average fiber length/average fiber diameter).

[0014]

In the present invention, the average fiber diameter and the average fiber length of the cellulose nanofibers are determined for the cellulose nanofibers in a dry state. The average fiber diameter and the average fiber length of the cellulose nanofibers in the dried state in the present invention can be measured by scanning electron microscopy or transmission electron microscopy (with electron staining). For example, a dispersion solution having a content of cellulose nanofibers of 0.05 to 0.1% by mass is cast on a substrate such as a Si wafer and dried, and then observed by scanning electron microscopy. Assuming an axis of an image width arbitrarily in vertical and horizontal directions in the observation field, an image is obtained by adjusting the sample, magnification, and the like so that 20 to 100 fibers intersect the axis. After the image is obtained, two random axes at vertical and horizontal directions are drawn per image, and the values of the fiber diameter and the fiber length are read for arbitrary 20 pieces from the fibers crossing each axis. In this manner, three non-overlapping surface images are photographed by scanning electron microscopy, and the values of the fiber diameter and the fiber length of 20 fibers crossing each other in the two axes are read. That is, information on the fiber diameter and fiber length of 120 fibers as a total of 20 fibers × 2 axes × 3 sheets are obtained. The average fiber diameter is calculated from the arithmetic average of the obtained fiber diameters, and the average fiber length can be calculated from the arithmetic average of the fiber lengths. Note that, for the branched fibers, if the length of the branched portion is 50 nm or more, the portion is incorporated into the calculation of the fiber diameter as a 1 fiber. At this time, the length of the longest portion of the fiber is defined as the fiber length.

The average aspect ratio in the present invention may be calculated by a method other than the above as long as it can obtain a value equivalent to that obtained by scanning electron microscopy or transmission electron microscopy (with electron staining). In the present invention, the dry state is a state in which a liquid is removed by a conventionally known method such as natural drying or vacuum-freeze drying, and a liquid content of cellulose nanofibers becomes 1% by mass or less.

[0015]

The cellulose nanofiber used in the present invention is not particularly limited, and commercially available products or those produced by a known manufacturing

method can be used. Generally, a cellulose fiber-containing material is fibrillated or refined by grinding or beating with a refiner, high pressure homogenizer, medium stirring mill, stone mill, grinder, or the like. Further, it can also be produced by a known method such as the method described in, for example, JP 2005-42283A. It can also be produced utilizing microorganisms (e.g., acetic acid bacteria (Acetobacter)). In addition, commercial products can be used. The cellulose fiber-containing material is known to be derived from plants (e.g., wood, bamboo, hemp, jute, kenaf, agricultural waste residues, cloth, pulp, recycled pulp, waste paper), animals (e.g., ascidians), algae, microorganisms (e.g., acetic acid bacteria (Acetobacter)), microbial products, and the like, but any of them can be used in the present invention. Preferably, it is a cellulose nanofiber derived from a plant or a microorganism, and more preferably a cellulose nanofiber derived from a plant.

[0016]

As the cellulose nanofibers used in the present invention, so-called modified cellulose nanofibers subjected to some chemical modification, such as those described in JP 2013-181167A and JP 2010-216021A may be used, and for example, so-called unmodified cellulose nanofibers produced by the method described in JP 2011-056456A or unmodified cellulose nanofibers commercially available products may be used. Commercial products of unmodified cellulose nanofibers include, for example, the Bionanofiber "BiNFi-s" series of Sugino Machine Ltd., the "CELISH" series of Daicel Miraizu Ltd. (old name: Daicel Fine Chem Ltd.), and the "CNF" series of Chuetsu Pulp & Paper Co., Ltd. These cellulose nanofibers may be used alone or as a mixture of 2 or more thereof.

[0017]

[Catalyst for Producing Unsaturated Aldehydes and Unsaturated Carboxylic Acid]

It is preferable that the catalyst for producing an unsaturated aldehyde and an unsaturated carboxylic acid according to the present invention have a composition represented by the following formula (I) from the viewpoint of a yield of the unsaturated aldehyde and unsaturated carboxylic acid. Note that the molar ratio of each element is a value obtained by analyzing a component in which a catalyst component is dissolved in aqueous ammonia by an ICP atomic emission spectroscopy. In addition, the molar ratio of ammonium species is a value obtained by analyzing the catalyst component by the

Kjeldahl method.

$$Mo_{a1}Bi_{b1}Fe_{c1}A_{d1}E1_{e1}G1_{f1}J1_{g1}Si_{h1}(NH_4)_{i1}O_{j1} \quad (I)$$

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 a1, b1, c1, d1, e1, f1, g1, h1, i1, and j1 represent the molar ratio of each component, and when a1 = 12, b1 = 0.01-3, c1 = 0.01-5, d1 = 0.01-12, e1 = 0-8, f1 = 0-5, g1 = 0.001-2, h1 = 0-20, i1 = 0-30, and j1 is the molar ratio of oxygen necessary to satisfy the valence of each above component.

More preferably, the molar ratio of each component is b1 = 0.05-2, c1 = 0.1-4, d1 = 0.1-10, e1 = 0-5, f1 = 0-3, g1 = 0.01-1, h1 = 0-10, and i1 = 0-20. The term "ammonium species" as used herein is a generic term for ammonium, that can be ammonium ions (NH_4^+), contained in ammonia (NH_3) and an ammonium-containing compound such as an ammonium salt.

[0018]

[Catalyst for Unsaturated Carboxylic Acid Production]

It is preferable that the catalyst for producing an unsaturated carboxylic acid according to the present invention has a composition represented by the following formula (II) from the viewpoint of unsaturated carboxylic acid yield.

$$P_{a2}Mo_{b2}V_{c2}Cu_{d2}E2_{e2}G2_{f2}J2_{g2}(NH_4)_{h2}O_{i2} \quad (II)$$

In Formula (II), P, Mo, V, Cu, NH_4 and O represent phosphorus, 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 the molar ratio of each component, when b2 = 12, a2 = 0.1-3, c2 = 0.01-3, d2 = 0.01-2, e2 = 0-3, f2 = 0-3, g2 = 0.01-3, h2 = 0-30, and i2 is the molar ratio of oxygen necessary to satisfy the valence of each above component.

More preferably, the molar ratio of each component is a2 = 0.5-2, c2 = 0.05-2, d2 = 0.05-1.5, e2 = 0.01-2, f2 = 0-2, g2 = 0.05-2, and h2 = 0-20.

[0019]

[Catalyst Molded Body]

As for the content of cellulose nanofibers in the catalyst molded body, when the mass of the catalyst molded body is defined as M1 [g] and the mass of the cellulose nanofibers is defined as M2 [g], it is preferable that the cellulose nanofiber content calculated by the following formula (III) is 0.1 to 5% by mass. Note that M1 and M2 are masses calculated from the charged amount. For example, M1 is the mass of the total of the catalyst molded body containing cellulose nanofibers, and is calculated from the sum of the catalyst dried body, the binder, and other solid contents described later.

$$\text{Cellulose nanofiber content [mass \%]} = (M2/M1) \times 100 \qquad \text{(III)}$$

By setting the value of the cellulose nanofiber content to 0.1% by mass or more, the mechanical strength of the catalyst molded body can be further increased. Further, since the value of the cellulose nanofiber contain is 5% by mass or less, a sufficient amount of the catalyst component can be filled in the reactor, so that a high yield can be maintained over a long period of time in continuous operation. Therefore, the catalyst life is long, and the frequency of replacement of the catalyst can be reduced. The lower limit of the cellulose nanofiber content is more preferably 0.2% by mass or more, and still more preferably 0.3% by mass or more. In the meantime, the upper limit of the cellulose nanofiber content is more preferably 4% by mass or less, still more preferably 2% by mass or less, and particularly preferably 1% by mass or less.

[0020]

It is also preferable that the catalyst molded body further contains a binder in addition to cellulose nanofibers. When the catalyst molded body contains both cellulose nanofibers and a binder, moldability is improved in a molding process described later, and a molded body having a desired shape can be stably obtained. When the mass of the binder is M3 [g], the binder content calculated by the following formula (IV) is preferably

0.05 to 10% by mass. The lower limit is more preferably 0.1% by mass or more, and still more preferably 1% by mass or more. In addition, the upper limit is more preferably 8% by mass or less, and still more preferably 5% by mass or less.

$$\text{Binder content [mass \%]} = (M3/M1) \times 100 \qquad \text{(IV)}$$

[0021]

The binder is not particularly limited as long as it has a function of adhering a catalyst dried body or a catalyst after calcination, and a water-soluble binder or a non-water-soluble binder can be used.

Examples of the water-soluble binder include a water-soluble polymer compound such as polyvinyl alcohol, an organic binder such as a water-soluble α glucan derivative and a water-soluble β glucan derivative, and an inorganic binder such as a water-soluble silicic acid compound and an ammonium salt of an inorganic acid. These may be used singly or in combination of 2 or more kinds thereof.

[0022]

In the present invention, an α glucan derivative indicates a polysaccharide composed of glucose in which glucose is bonded in a structure of an α-type. Specific examples of the water-soluble α glucan derivative include amylose, glycogen, pullulan, dextrin, and cyclodextrin. These may be used singly, or in combination of two or more thereof. In addition, in the present invention, a β glucan derivative indicates a polysaccharide composed of glucose in which glucose is bound by a β-type structure. Examples of the water-soluble β-glucan derivative include methylcellulose, carboxymethylcellulose, sodium carboxymethylcellulose, hydroxyethylcellulose, hydroxypropylcellulose, hydroxypropylmethylcellulose, hydroxyethylmethylcellulose, hydroxybutylmethylcellulose, ethylhydroxyethylcellulose, scleroglucan, and the like.

[0023]

Specific examples of the water-soluble silicic acid compound include sodium silicate, potassium silicate, sodium metasilicate, potassium metasilicate, lithium silicate, ammonium silicate, and alkyl silicate. Examples of the ammonium salt of the inorganic acid include ammonium sulfate, ammonium nitrate, ammonium phosphate, ammonium chlorite, ammonium hydrogencarbonate, ammonium thiosulfate, ammonium hyposulfite, and ammonium chlorate. These may be used singly, or in combination of two or more thereof.

[0024]

Examples of the water-insoluble binder include an organic binder such as a water-insoluble α glucan derivative and a non-water-soluble β glucan derivative, and an inorganic binder such as a water-insoluble inorganic compound and a water-insoluble inert carrier. These may be used singly, or in combination of two or more thereof.

Specific examples of the water-insoluble α glucan derivative include amylopectin and the like. Examples of the water-insoluble β glucan derivative include ethyl cellulose, crystalline cellulose, curdlan, and paramylon. These may be used singly, or in combination of two or more thereof.

[0025]

Examples of the water-insoluble inorganic compound include silica, alumina, silica-alumina, silicon carbide, titania, magnesia, graphite, and siliceous earth. Further, specific examples of the water-insoluble inert carrier include ceramic balls, stainless steel, and inorganic fibers such as glass fibers, ceramic fibers, and carbon fibers. These may be used singly, or in combination of two or more thereof.

[0026]

From the viewpoint of mechanical strength of the catalyst molded body, the binder is preferably water-soluble, more preferably a water-soluble organic binder, and particularly preferably a water-soluble β glucan derivative. In the present invention, water solubility indicates a property of dissolving 5 g or more in 100 g of water at 20° C

[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, except that cellulose nanofibers are contained.

The method of incorporating cellulose nanofibers into the catalyst molded body is not particularly limited, and examples thereof include a method of adding cellulose nanofibers to a catalyst raw material liquid in a catalyst raw material liquid preparation step described later, a method of adding and molding cellulose nanofibers to a catalyst dried body in a molding step described later, and a method of using these methods in combination.

[0028]

(Preparation Step of Catalyst Raw Material Liquid)

In the present invention, a method of preparing catalyst components is not particularly limited, and various conventionally well-known methods such as a precipitation method and an oxide mixing method can be used unless there is a significant uneven distribution of components. For example, in the production of a catalyst for producing an unsaturated aldehyde and an unsaturated carboxylic acid, it is preferable that raw material compounds of catalyst components of a catalyst for producing an unsaturated aldehyde and an unsaturated carboxylic acid is dissolved or suspended in an appropriately selected solvent to prepare a solution or a slurry containing at least molybdenum and bismuth (hereinafter, also referred to as a catalyst raw material liquid). In addition, in the production of a catalyst for producing an unsaturated carboxylic acid, it is preferable that raw material compounds of catalyst components of the catalyst for producing an unsaturated carboxylic acid is dissolved or suspended in 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 are 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, oxoacids, alkali metal salts, and the like can be used alone or in combination of 2 or more. 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 for phosphorus include, for example, phosphate such as phosphoric acid, phosphorous pentoxide, and ammonium phosphate. Examples of the raw material compound of vanadium include ammonium vanadate, ammonium metavanadate, vanadium pentoxide, vanadium chloride, and vanadyl oxalate. The raw material compounds may be used only 1 kind for each element constituting the catalyst component or in combination two or more kinds for each element.

Examples of the solvent include water, ethyl alcohol, and acetone, but water is

preferably used.

[0030]

(Drying Step)

In the drying step, the catalyst raw material liquid obtained in the preparation step of the catalyst raw material liquid 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 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 still more preferably 220° C or more. The upper limit is more preferably 400° C or less, more preferably 370 ° C. or less. The dryer outlet temperature is preferably 100 to 200° C, and the lower limit is more preferably 105° C or more. 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.

When a spray dryer is used, the average particle diameter of the obtained catalyst dried body is preferably 1 to 250 μm. By having an average particle diameter of 1 μm or more, pores having a preferable diameter for producing a target product are formed, and a target product is obtained in high yield. In the meantime, when the average particle diameter is 250 μm or less, the number of contact points between the catalyst dry body particles per unit volume can be maintained, and a sufficient mechanical strength of the catalyst can be obtained. 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 measurement by a laser type particle size distribution measuring apparatus.

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.

[0031]

(Molding Step)

In the molding step, the catalyst dried body obtained in the drying step is molded to obtain a catalyst molded body. When the catalyst dried body contains cellulose nanofibers, it may be molded as it is, and the additional cellulose nanofibers may be added and then molded. When the catalyst dried body does not contain cellulose nanofibers, cellulose nanofibers are added and molded to obtain a catalyst molded body. Note that the molding may be performed, after adding the cellulose nanofibers to the catalyst dried body after the calcination step described later.

The catalyst dried body obtained in the drying step exhibits catalytic performance, and a product obtained by molding the catalyst dried body can be used as a catalyst molded body, but is preferable because the performance as a catalyst is improved by performing calcination. In the present invention, it is generically referred to as a catalyst molded body including those after calcination.

The molding method is not particularly limited, and for example, known methods such as extrusion molding, tablet molding, carrier molding, rolling granulation, and the like can be cited. Among them, tablet molding and extrusion molding are preferred from the viewpoint of productivity of the catalyst, and extrusion molding is more preferred from the viewpoint of forming pores advantageous for producing the target product in the catalyst molded body. The shape of the catalyst molded body is not particularly limited, for example, including a shape such as spherical, columnar, ring-shaped (cylindrical), and star-shaped, among them, spherical, columnar or ring-shaped is preferred in view of high mechanical strength.

In the catalyst molded body of the present invention, by further containing a binder in addition to cellulose nanofibers, moldability is improved, and a molded body having a desired shape can be stably obtained.

[0032]

(Calcination Step)

It is preferable from the viewpoint of yield of the target product to calcine the catalyst dried body obtained in the drying step or the catalyst molded body obtained in the molding step. 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. The calcination condition is not particularly limited, and the calcination is usually performed under oxygen, air or nitrogen flow. The calcination time is appropriately set by the target catalyst, but is preferably 0.5 to 40 hours, more preferably 1 to 40 hours.

[0033]

[Method for Producing Unsaturated Aldehydes and Unsaturated Carboxylic Acids]

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 gas phase catalytic oxidation with molecular oxygen in the presence of a catalyst molded body containing a catalyst for 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.

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 aldehydes corresponding to isobutylene, primary butyl alcohol, tertiary butyl alcohol and methyl tertiary butyl ether are methacrolein, and the unsaturated carboxylic acids corresponding to isobutylene, primary butyl alcohol, tertiary butyl alcohol and methyl tertiary butyl ether are methacrylic acid.

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

[0034]

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

In the above method, methacrolein and methacrylic acid are produced by bringing a source gas containing methacrolein and molecular oxygen into contact with a catalyst according to the present invention. A fixed-bed reactor can be used in this

reaction. The reaction can be carried out by filling the catalyst in a reaction tube and supplying the source gas to the reactor. The catalyst may be filled as one layer, and a plurality of catalysts having different activities may be divided into a plurality of layers and filled, respectively. In addition, the catalyst may be diluted and filled with an inert carrier to control the activity.

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

[0035]

The concentration of molecular oxygen in the source gas is preferably 0.1 to 5 moles, and the lower limit is more preferably 0.5 moles or more and the upper limit is more preferably 3 moles or less, based on 1 mole 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.

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 source gas.

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

[0036]

[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 gas phase catalytic oxidation with molecular oxygen in the presence of a catalyst molded body containing a catalyst for producing an unsaturated carboxylic acid according to the present invention. According to these methods, unsaturated carboxylic acids can be produced in high yields.

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.

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.

[0037]

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

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

[0038]

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

The concentration of molecular oxygen in the source gas is preferably 0.4 to 4 moles, and the lower limit is more preferably 0.5 moles or more and the upper limit is more preferably 3 moles or less, based on 1 mole 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.

The source 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 source gas. By carrying out the reaction in the presence of water vapor, methacrylic acid can be obtained with high yield. The concentration of water vapor in the source gas is preferably 0.1 to 50% by volume, the lower limit is more preferably 1% by volume or more, and the upper limit is more preferably 40% by volume or less.

The contact time between the source gas and the catalyst is preferably 1.5 to 15 seconds. The reaction pressure is preferably from 0. 1 MPa(G) to 1 MPa(G). Here, (G) means a gauge pressure. The reaction temperature is preferably 200 to 450° C, the lower limit is more preferably 250° C or more, and the upper limit is more preferably 400° C or less.

[0039]

[Method for Producing Unsaturated Carboxylic Acid Ester]

A method for producing an unsaturated carboxylic acid ester according to the present invention esterifies an unsaturated carboxylic acid produced by the method according to the present invention. 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 gas phase catalytic oxidation of propylene, isobutylene, primary butyl alcohol, tertiary butyl alcohol or methyl tertiary butyl ether, or gas phase catalytic oxidation of (meth)acrolein.

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

[0040]

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".

[0041]

(Powdering Rate at Dropping)

The powdering rate at dropping, which is an index of the mechanical strength of the catalyst molded body, was measured by the following method. The catalyst molded body was filled by dropping 100 g of the catalyst molded body from the upper opening of a stainless-steel cylinder so as to be placed the longitudinal direction of the stainless-steel cylinder vertically, wherein the cylinder had an inner diameter of 27.5mm and a length of 6 meters, and its lower opening was closed with a sheet made of stainless steel. Among the catalyst molded body collected by opening the lower opening, the mass of the catalyst molded body that did not pass through the sieve with a 1-mm aperture was set to α g, and the powdering rate at dropping was calculated by the following equation. The smaller the powdering rate at dropping, the higher the mechanical strength, and the larger the powdering rate, the lower the mechanical strength. In addition, the powdering rate at dropping in Table 1 is an average value of the powdering rates at dropping measured for each catalyst molded body after the catalyst molded body was manufactured 10 times under the same conditions.

$$\text{Powdering rate at dropping (\%)} = \{(100-\alpha)/100\} \times 100$$

[0042]

(Analysis of Source Gas and Products)

The analysis of the source gas and the product was carried out using gas chromatography. In Examples 1 to 3 and Comparative Examples 1 to 3, the total yield of methacrolein and methacrylic acid was calculated by the following formula.

$$\text{Total yield of methacrolein and methacrylic acid (\%)} = (B+C)/A \times 100$$

Here, A is the number of moles of isobutylene supplied, B is the number of moles of methacrolein produced, and C is the number of moles of methacrylic acid produced.

Examples 1 to 3 and Comparative Examples 1 to 3 show only the case where the raw material is isobutylene, but also in the case where tertiary butyl alcohol is used as the

raw material, the isobutylene is dehydrated quickly 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.

In addition, in Examples 4 and Comparative Examples 4 to 6, the yield of methacrylic acid produced is defined as follows:

$$\text{Yield of methacrylic acid (\%)} = (E/D) \times 100$$

Where D is the number of moles of methacrolein supplied and E is the number of moles of methacrylic acid produced.

[0043]

(Average Fiber Diameter)

The average fiber diameter of the cellulose nanofibers was calculated from the analysis results by scanning electron microscopy. Specifically, a dispersion liquid dispersed in pure water so that the content of cellulose nanofibers was 0.05% by mass was cast on a wafer and dried, and then observed by scanning electron microscopy. Assuming an axis of an image width arbitrarily in vertical and horizontal directions in the observation field, an image is obtained by adjusting the sample, magnification, and the like so that 20 to 100 fibers intersect the axis. After the image was obtained, two random axes at vertical and horizontal directions were drawn per image, and the values of the fiber diameter and the fiber length were read for arbitrary 20 pieces from the fibers crossing each axis. In this manner, three non-overlapping surface images were photographed by scanning electron microscopy, and the values of the fiber diameter and the fiber length of 20 fibers crossing each other in the two axes were read to obtain information on the fiber diameters of 120 fibers. The average fiber diameter was calculated by two significant digits from the arithmetic average of the fiber diameters obtained.

[0044]

(Composition Ratio of Catalyst Component)

The molar ratio of each element was determined by analyzing the component in which the catalyst was dissolved in aqueous ammonia by ICP atomic emission spectrometry. The molar ratio of ammonium species was also determined by analyzing the catalytic components with the Kjeldahl method.

[0045]

(Content of Cellulose Nanofibers)

The content of cellulose nanofibers in the catalyst molded body was calculated by the following formula (III):

$$\text{Cellulose nanofiber content [mass \%]} = (M2/M1) \times 100 \qquad \text{(III)}$$

In the above formula (III), the mass M1 of the catalyst molded body was the sum of the charge amounts of the catalyst dried body, hydroxypropyl methylcellulose and cellulose nanofibers. In addition, the mass M2 of cellulose nanofibers was set as the charged amounts of cellulose nanofibers.

[0046]

[Example 1]

To 1,000 parts of pure water, 500 parts of ammonium paramolybdate, 12.4 parts of ammonium paratungstate, 2.3 parts of potassium nitrate, 27.5 parts of antimony trioxide and 66.0 parts of bismuth trioxide were added and the mixture was heated and stirred (Liquid A). Separately, 114.4 parts of ferric nitrate, 274.7 parts of cobalt nitrate and 35.1 parts of zinc nitrate were sequentially added to 1,000 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 13,000 rpm to obtain a catalyst dried body having an average particle diameter of 46 μm. The composition of the catalyst excluding oxygen of the catalyst dried product was $Mo_{12}W_{0.2}Bi_{1.2}Fe_{1.2}Sb_{0.8}Co_{4.0}Zn_{0.5}K_{0.1}(NH_4)_{12.3}$.

With respect to 100 parts of the catalyst dried body, 4 parts of hydroxypropyl methylcellulose and a dispersion liquid obtained by dispersing 1 part of cellulose nanofibers having an average fiber diameter of 40 nm in 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, thereby obtaining a mixture.

The resulting mixture was extruded using a plunger type extruder, and molded into a ring shape having an outer diameter of 5 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 12 hours to obtain a catalyst molded body. Table 1 shows the measurement results of the powdering rate at dropping of the catalyst molded body.

Subsequently, the catalyst molded body was filled in a reaction tube and calcined under air flow at 450° C for 3 hours. Then, a gas phase catalytic oxidation

reaction of isobutylene was carried out using a source gas of 5% by volume of isobutylene, 12% by volume of oxygen, 10% by volume of water vapor and 73% by volume of nitrogen under normal pressure at a reaction temperature of 340° C, and a contact time of 3.6 seconds. The total yields of methacrolein and methacrylic acid were determined by collecting the products and analyzing them by gas chromatography. The results are shown in Table 1.

[0047]

[Example 2]

A catalyst molded body was produced in the same manner as in Example 1, except that the content of cellulose nanofibers dispersed in pure water was 0.5 parts, and the powdering rate at dropping was measured as in Example 1, followed by calcining and reaction evaluation of the catalyst molded body. The results are shown in Table 1.

[0048]

[Example 3]

A catalyst molded body was produced in the same manner as in Example 1, except that the content of cellulose nanofibers dispersed in pure water was changed to 0.25 parts, and powdering rate at dropping was measured as in Example 1, followed by calcining and reaction evaluation of the catalyst molded body. The results are shown in Table 1.

[0049]

[Comparative Example 1]

A catalyst molded body was produced in the same manner as in Example 1, except that the cellulose nanofiber dispersion was not mixed with the catalyst dried body, and instead, 45 parts of pure water was mixed, and the powdering rate at dropping was measured as in Example 1, followed by calcining and reaction evaluation of the catalyst molded body. The results are shown in Table 1.

[0050]

[Comparative Example 2]

A catalyst molded body was produced in the same manner as in Example 1, except that the cellulose nanofiber dispersion was not mixed with the catalyst molded body, and instead, 45 parts of pure water and 1 parts of crystalline cellulose having an average particle diameter of 50 μm were mixed, and the powdering rate at dropping was

measured as in Example 1, followed by calcining and reaction evaluation of the catalyst molded body. The results are shown in Table 1.

[0051]

[Comparative Example 3]

A catalyst molded body was produced in the same manner as in Example 1, except that the cellulose nanofiber dispersion was not mixed with the catalyst molded body, and instead, 45 parts of pure water and 5.0 parts of crystalline cellulose having an average particle diameter of 50 μm were mixed, and the powdering rate at dropping was measured as in Example 1, followed by calcining and reaction evaluation of the catalyst molded body. The results are shown in Table 1.

[0052]

[Example 4]

To 4,000 parts of pure water, 1,000 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 dissolved, and the temperature was increased to 95° C while stirring, and the resultant liquid was stirred for 3 hours while keeping the temperature at 95° C. After cooling to 90° C, while stirring using a rotary blade stirrer, a solution in which 124 parts of cesium bicarbonate was dissolved in 200 parts of pure water was added and stirred for 15 minutes. Then, a solution obtained by dissolving 92 parts of ammonium carbonate in 200 parts of pure water was added and stirred for another 20 minutes. The catalyst raw material liquid obtained as described above was dried using a co-current spray dryer under 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 product are $P_{1.2}Mo_{12}V_{0.5}Cu_{0.05}Cs_{1.1}(NH_4)_{3.8}$.

With respect to 100 parts of the catalyst dried body, 4 parts of hydroxypropyl methylcellulose and a dispersion obtained by dispersing 0.5 parts of cellulose nanofibers having an average fiber diameter of 20 nm in 30 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, thereby obtaining a mixture.

The resulting mixture was extruded using a plunger type extruder and molded into a cylindrical shape having an outer diameter of 6 mm and a length of 5 mm, and then

calcined in a hot air dryer at 90° C for 12 hours to obtain a catalyst molded body. Table 2 shows the measurement results of the powdering rate at dropping of the catalyst molded body.

Subsequently, the catalyst molded body was filled in a reaction tube and calcined under air flow at 380° C for 10 hours. Then, a gas phase catalytic oxidation reaction of methacrolein was carried out using a source gas of 5% by volume of methacrolein, 10% by volume of oxygen, 30% by volume of water vapor, and 55% by volume of nitrogen under normal pressure at a reaction temperature of 305° C, and a contact time of 7.1 seconds. The product was collected and analyzed by gas chromatography to determine the yield of methacrylic acid. The results are shown in Table 2.

[0053]

[Comparative Example 4]

A catalyst molded body was produced in the same manner as in Example 4, except that the cellulose nanofiber dispersion was not mixed with the catalyst dried body and 30 parts of pure water was mixed instead, and the powdering rate at dropping was measured, followed by calcining and reaction evaluation of the catalyst molded body. The results are shown in Table 2.

[0054]

[Comparative Example 5]

A catalyst molded body was produced in the same manner as in Example 4, except that the cellulose nanofiber dispersion was not mixed with the catalyst dried body, and instead, 45 parts of pure water and 1 parts of crystalline cellulose having an average particle diameter of 50 μm were mixed, and the powdering rate at dropping was measured, followed by calcining and reaction evaluation of the catalyst molded body. The results are shown in Table 2.

[0055]

[Comparative Example 6]

A catalyst molded body was produced in the same manner as in Example 1, except that the cellulose nanofiber dispersion was not mixed with the catalyst molded body, and instead, 45 parts of pure water and 8 parts of crystalline cellulose having an average particle diameter of 50μm were mixed, and the powdering rate at dropping was measured, followed by calcining and reaction evaluation of the catalyst molded body.

The results are shown in Table 2.

[0056]

Table 1

	Content (mass%)			Average fiber diameter of cellulose nanofiber (nm)	Powdering rate at dropping (%)	Total yield of methacrolein and methacrylic acid (%)
	Cellulose nanofiber	Hydroxypropyl methylcellulose	Crystalline cellulose			
Exmple 1	0.95	3.81	-	40	0.5	87.5
Exmple 2	0.48	3.83	-	40	0.7	86.8
Exmple 3	0.24	3.84	-	40	0.8	87.0
Comp. Ex. 1	-	3.85	-	-	1.5	86.5
Comp. Ex. 2	-	3.81	0.95	-	1.2	87.0
Comp. Ex. 3	-	3.67	4.59	-	0.5	68.1

[0057]

Table 2

	Content (mass%)			Average fiber diameter of cellulose nanofiber (nm)	Powdering rate at dropping (%)	Yield of methacrylic acid (%)
	Cellulose nanofiber	Hydroxypropyl methylcellulose	Crystalline cellulose			
Example 4	0.48	3.83	-	20	5.8	65.5
Comp. Ex. 4	-	3.85	-	-	8.1	64.8
Comp. Ex. 5	-	3.81	0.95	-	7.6	65.3
Comp. Ex. 6	-	3.57	7.14	-	6.0	64.5

[0058]

As shown in Table 1, when a catalytic component having a composition ratio of $Mo_{12}W_{0.2}Bi_{1.2}Fe_{1.2}Sb_{0.8}Co_{4.0}Zn_{0.5}K_{0.1}(NH_4)_{12.3}$ included in Formula (I) is used, Examples 1 to 3, which contain cellulose nanofibers having an average fiber diameter of 1 to 300 nm, can provide a catalyst molded body having a low powdering ratio at dropping and high mechanical strength, and high total yield of methacrolein and methacrylic acid. On the other hand, Comparative Examples 1 and 2 in which the catalyst molded body did not contain cellulose nanofibers had the same total yield of methacrolein and methacrylic acid as in Examples 1 to 3, but had a high powdering ratio at dropping and a low mechanical strength. Therefore, as shown in Comparative Example 3, when the mechanical strength was set to be similar to that of Example 1 by

a binder other than cellulose nanofibers, the total yield of methacrolein and methacrylic acid was remarkably reduced.

Since the catalyst molded bodies of Examples 1 to 3 have a high yield of methacrolein and methacrylic acid and a high mechanical strength, the increase in differential pressure can be suppressed and a high yield can be maintained for a long period of time because the catalyst is less powdered or cracked in continuous operation. Therefore, the catalyst life is long, and the frequency of replacement of the catalyst can be reduced.

[0059]

Similarly, when a catalyst component having a composition ratio of $P_{1.2}Mo_{12}V_{0.5}Cu_{0.05}Cs_{1.1}(NH_4)_{3.81}$ included in Formula (II) is used, Example 4 containing a cellulose nanofiber having an average fiber diameter of 1 to 300 nm can provide a catalytic molded body having a low powdering rate at dropping and high mechanical strength, and also has a high yield of methacrylic acid. On the other hand, in Comparative Example 4 in which the catalyst molded body did not contain cellulose nanofibers, the powdering rate at dropping was high, the mechanical strength was low, and the yield of methacrylic acid was slightly lower. In Comparative Example 5, although the yield of methacrylic acid was similar to that of Example 4, the powdering rate at dropping was high and the mechanical strength was low. Therefore, as shown in Comparative Example 6, when the mechanical strength was set to be similar to that of Example 4 by a binder other than cellulose nanofibers, the yield of methacrylic acid decreased.

Since the catalyst molded body of Example 4 has a high yield of methacrylic acid and high mechanical strength, the increase in differential pressure can be suppressed and a high yield can be maintained for a long period of time because the catalyst is less powdered or cracked in continuous operation. Therefore, the catalyst life is long, and the frequency of replacement of the catalyst can be reduced.

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

INDUSTRIAL APPLICABILITY

[0060]

According to the present invention, it is possible to provide a catalyst molded body having high yield and high mechanical strength. By using such a catalyst molded body, it is possible to provide a method for producing an unsaturated aldehyde and an unsaturated carboxylic acid capable of maintaining a high yield in a long period of time.

[0061]

While the present invention has been specifically described by way of embodiments and examples, the present invention is not limited thereto, and various changes that can be understood by those skilled in the art within the scope of the present invention can be made in the configuration and details of the present invention.

This application claims priority to Japanese Patent Application No. 2018-046637, filed March 14, 2018, the entire disclosure of which is incorporated herein by reference.

CLAIMS

1. A catalyst molded body comprising a catalyst component capable of producing an unsaturated aldehyde and/or an unsaturated carboxylic acid by gas phase catalytic oxidation with molecular oxygen, and a cellulose nanofiber having an average fiber diameter of 1 to 300 nm.

2. The catalyst molded body as claimed in claim 1, wherein, when the mass of the catalyst molded body is M1 [g] and the mass of the cellulose nanofiber is M2 [g], the cellulose nanofiber content calculated by the following formula (III) is 0.1 to 5% by mass:

Cellulose nanofiber content [% by mass] = (M2/M1) × 100 (III).

3. The catalyst molded body as claimed in claim 1 or 2, further comprising a binder.

4. The catalyst molded body as claimed in claim 3, wherein the binder is water-soluble.

5. The catalyst molded body as claimed in claim 3, wherein the binder is a water-soluble organic binder.

6. A catalyst molded body obtained by calcining the catalyst molded body as claimed in any one of claims 1 to 5.

7. The catalyst molded body as claimed in any one of claims 1 to 6, which is produced by a process comprising extrusion molding.

8. The catalyst molded body as claimed in any one of claims 1 to 7, wherein the catalyst component has a composition represented by the following formula (I), and is a catalyst for producing an unsaturated aldehyde and an unsaturated carboxylic acid by which propylene, isobutylene, primary butyl alcohol, tertiary butyl alcohol or methyl tertiary butyl ether is subjected to a gas-phase catalytic oxidation with molecular oxygen:

$$Mo_{a1}Bi_{b1}Fe_{c1}A_{d1}E1_{e1}G1_{f1}J1_{g1}Si_{h1}(NH_4)_{i1}O_{j1} \quad (I)$$

(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 a1, b1, c1, d1, e1, f1, g1, h1, i1, and j1 represent the molar ratio of each component, and when a1 = 12, b1 = 0.01-3, c1 = 0.01-5, d1 = 0.01-12, e1 = 0-8, f1 = 0-5, g1 = 0.001-2, h1 = 0-20, i1 = 0-30, and j1 is the molar ratio of oxygen necessary to satisfy the valence of each above component.)

9. The catalyst molded body as claimed in any one of claims 1 to 7, wherein the catalyst component has a composition represented by the following formula (II), and is a catalyst for producing an unsaturated carboxylic acid by a gas-phase catalytic oxidation of (meth)acrolein with molecular oxygen:

$$P_{a2}Mo_{b2}V_{c2}Cu_{d2}E2_{e2}G2_{f2}J2_{g2}(NH_4)_{h2}O_{i2} \qquad (II)$$

(In Formula (II), P, Mo, V, Cu, NH_4 and O represent phosphorus, 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 the molar ratio of each component, when b2 = 12, a2 = 0.1-3, c2 = 0.01-3, d2 = 0.01-2, e2 = 0-3, f2 = 0-3, g2 = 0.01-3, h2 = 0-30, and i2 is the molar ratio of oxygen necessary to satisfy the valence of each above component.)

10. A method for producing unsaturated aldehydes and unsaturated carboxylic acids, 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 as claimed in claim 8.

11. 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 a catalyst molded body as claimed in claim 9.

12. A process for producing an unsaturated carboxylic ester, in which the unsaturated carboxylic acid produced by the method as claimed in claim 10 or 11.

13. A method for producing an unsaturated carboxylic acid ester comprising a step of producing an unsaturated carboxylic acid by the method as claimed in claim 10 or 11 and a step of esterifying the unsaturated carboxylic acid.

ABSTRACT

The present invention provides a catalyst molded body having high yield and mechanical strength, wherein the catalyst molded body includes a catalyst for producing an unsaturated aldehyde and an unsaturated carboxylic acid, or a catalyst for producing an unsaturated carboxylic acid, and a cellulose nanofiber having an average fiber diameter of 1 to 300 nm.