

PROCESS FOR PRODUCING METHACRYLIC ACID

Background of the Invention

Field of the Invention

[0001]

The present application claims the Paris Convention priority based on Japanese Patent Application No. 2013-56072 filed on March 19, 2013, the entire content of which is incorporated herein by reference.

The present invention relates to a process for producing methacrylic acid.

Description of the Related Art

[0002]

As one of processes for producing methacrylic acid, there is known a process of subjecting methacrolein to vapor phase catalytic oxidation with molecular oxygen in the presence of a catalyst. For example, Patent Document 1 (JP-A-2005-272313) describes a process of performing initial operation at the lowest temperature of a catalyst layer of 290°C or higher and 310°C or lower, when methacrylic acid is produced by supplying methacrolein and oxygen into a reactor provided with a catalyst layer of a catalyst for producing methacrylic acid, and oxidizing methacrolein in a continuous manner.

[0001]

Patent Document 1: JP-A-2005-272313

Summary of the Invention

[0004]

However, the aforementioned process is not necessarily satisfactory in respect of durability of the catalyst activity, and a process capable of producing methacrylic acid with good productivity over a further longer period of time has been desired.

[0005]

Then, an object of the present invention is to provide a process for producing methacrylic acid with good productivity over a long period of time.

[0006]

In order to solve the aforementioned problem, the present inventors intensively studied and, as a result, completed the present invention.

[0007]

That is, the present invention includes the following embodiments.

[1] A process for producing methacrylic acid comprising supplying methacrolein, isobutylene and oxygen into a reactor for producing methacrylic acid provided with a catalyst layer containing a catalyst for producing methacrylic acid, and oxidizing the methacrolein in a continuous manner to obtain methacrylic acid, wherein the maximum temperature in the catalyst layer is 330°C or lower.

[2] The process according to [1], wherein the maximum temperature in the catalyst layer is set to 330°C or lower by adjusting a supply amount of the isobutylene.

[3] The process according to [1] or [2], wherein at least a part of the methacrolein is contained in a reaction mixture obtained by oxidizing

isobutylene with oxygen in the presence of a catalyst for producing methacrolein, and at least a part of isobutylene to be supplied into the reactor for producing methacrylic acid is isobutylene different from unreacted isobutylene contained in the reaction mixture.

[4] The process according to claim [1] or [2], wherein at least a part of the methacrolein is contained in a reaction mixture obtained by oxidizing isobutylene with oxygen in the presence of a catalyst for producing methacrolein in a reactor for producing methacrolein with a catalyst for producing methacrolein contained therein, an extraction port of the reactor for producing methacrolein is connected to a supply port of the reactor for producing methacrylic acid with a connecting line, an isobutylene supplying line is connected to the connecting line, and oxidation of methacrolein in the reactor for producing methacrylic acid is performed while isobutylene is supplied to the isobutylene supplying line.

[5] The process according to any one of [1] to [4], wherein oxidation of methacrolein in the reactor for producing methacrylic acid is performed by supplying a mixed gas, the mixed gas containing methacrolein, isobutylene and oxygen and having a content of isobutylene of 50 to 3000 volume ppm, into the reactor for producing methacrylic acid.

[6] The process according to any one of [1] to [5], wherein the reactor is a fixed bed reactor.

[7] The process according to any one of [1] to [6], wherein the catalyst for producing methacrylic acid is made of a heteropolyacid compound comprising phosphorus and molybdenum.

[8] The process according to [7], wherein the heteropolyacid

compound further comprises vanadium, at least one element selected from the group consisting of potassium, rubidium, cesium and thallium, and at least one element selected from the group consisting of copper, arsenic, antimony, boron, silver, bismuth, iron, cobalt, lanthanum and cerium.

[9] The process according to any one of [3] to [8], wherein the catalyst for producing methacrolein is made of a complex oxide containing molybdenum, bismuth and iron.

[10] A process for producing a methacrylic acid ester comprising esterification reacting the methacrylic acid produced by the production process according to any one of [1] to [9], and alcohol in the presence of an esterification catalyst.

[0008]

According to the present invention, methacrylic acid can be obtained with good productivity over a long period of time.

Detailed Description of the Invention

[0009]

The present invention will be explained in detail below.

[0010]

The catalyst for producing methacrylic acid used in the present invention is not particularly limited, but a catalyst made of a heteropolyacid compound comprising phosphorus and molybdenum is preferable. The heteropolyacid compound constituting the catalyst may be free heteropolyacid or a salt of heteropolyacid. Among them, an acidic salt (partially neutralized salt) of heteropolyacid is preferable, and an acidic salt

of Keggin type heteropolyacid is further preferable.

[0011]

It is desirable that the catalyst for producing methacrylic acid contains vanadium as an element other than phosphorus and molybdenum, and it is desirable that the catalyst contains at least one element (hereinafter, sometimes referred to as element X) selected from the group consisting of potassium, rubidium, cesium and thallium, and at least one element (hereinafter, sometimes referred to as element Y) selected from the group consisting of copper, arsenic, antimony, boron, silver, bismuth, iron, cobalt, lanthanum and cerium. Usually, a catalyst containing phosphorus, vanadium, the element X and the element Y respectively at a ratio of 3 atoms or less relative to 12 atoms of molybdenum is suitably used.

[0012]

The preferable composition of the heteropolyacid compound constituting the catalyst for producing methacrylic acid obtained in the present invention is as in the following formula (i).

[0013]



(In the formula (i), P, Mo and V each represent phosphorus, molybdenum and vanadium, X represents at least one element X selected from the group consisting of potassium, rubidium, cesium and thallium, Y represents at least one element Y selected from the group consisting of copper, arsenic, antimony, boron, silver, bismuth, iron, cobalt, lanthanum and cerium, O represents oxygen, when $b = 12$, $0 < a \leq 3$, $0 \leq c \leq 3$, $0 \leq d \leq 3$, and $0 \leq e \leq 3$ are satisfied, and x is a value determined by the oxidation state

of each element. In addition, when each of X and Y is two or more elements, the total ratio of the two or more elements should satisfy $0 < d \leq 3$ and $0 < e \leq 3$ when $b = 12$.)

[0014]

As a raw material for obtaining the catalyst for producing methacrylic acid, usually, compounds containing elements contained in the heteropolyacid compound, for example, an oxo acid, an oxo acid salt, an oxide, a nitrate, a carbonate, a bicarbonate, a hydroxide, a halide, and an ammine complex of the elements are used at a ratio satisfying a desired atomic ratio. As the compound containing phosphorus, phosphoric acid, a phosphate and the like are used, as the compound containing molybdenum, molybdic acid, a molybdate such as ammonium molybdate, molybdenum oxide, molybdenum chloride and the like are used, and as the compound containing vanadium, vanadic acid, a vanadate (metavanadate) such as ammonium vanadate (ammonium metavanadate), vanadium oxide, vanadium chloride and the like are used. As the compound containing the element X, oxides such as potassium oxide, rubidium oxide, and cesium oxide; nitrates such as potassium nitrate, rubidium nitrate, cesium nitrate, and thallium nitrate; carbonates such as potassium carbonate, rubidium carbonate, and cesium carbonate; bicarbonates such as potassium bicarbonate and cesium bicarbonate; hydroxides such as potassium hydroxide, rubidium hydroxide, and cesium hydroxide; and halides such as potassium chloride, rubidium chloride, cesium fluoride, cesium chloride, cesium bromide, and cesium iodide, and the like are used. As the compound containing the element Y, an oxo acid, an oxo acid salt, a nitrate, a carbonate, a hydroxide, a halide and

the like are used.

[0015]

The process for producing the catalyst for producing methacrylic acid is not particularly limited, and examples thereof include a process of subjecting a catalyst precursor prepared from the catalyst raw materials to calcination. This catalyst precursor can be usually prepared by mixing the catalyst raw materials in water to obtain an aqueous solution or an aqueous slurry and, then, drying this aqueous mixed liquid. The precursor may be, for example, a precursor obtained by molding the dried material, a precursor obtained by heat-treating the dried material (pre-calcination) and molding the material, or a precursor obtained by molding the dried material and heat-treating the material. Herein, the method of drying the aqueous mixed liquid is not particularly limited, and a method usually used in this field, such as evaporation to dryness, a spray drying method, a drum drying method, or an air flow drying method can be adopted. Among them, the drying is preferably performed by a spray drying method using a spray drier or the like. The molding may be performed by a method usually used in this field, such as compression molding or extrusion molding, and examples of the shape after molding include a ring shape, a pellet shape, a spherical shape, and a cylindrical shape. A catalyst in which a catalytic component is supported by a carrier such as silica, alumina, silicon carbide, or silicon nitride may be used. Upon molding, if necessary, water, a molding aid, a pore forming agent or the like may be added to the dried material. Examples of the molding aid include ammonium nitrate, in addition to a ceramic fiber and a glass fiber. Particularly, ammonium nitrate has not

only the function as the molding aid, but also the function as the pore forming agent. As the diameter of a molded product, 3 to 10 mm is preferable. As used herein, the diameter of a molded product means the diameter of a sphere in the case of a spherical particulate shape, the diameter of a circular cross section in the case of a cylindrical shape, or the maximum diameter of a cross section in the case of other shapes. As the molded body, a molded body having falling strength defined below of 97% or more is preferable.

Falling strength: Ratio (wt%) of a catalyst remaining on a sieve relative to a fallen catalyst, when a pipe having an internal diameter of 30 mm and a length of 5000 mm is stood upright on a JIS standard gauze sieve having an aperture of 2.36 mm, and about 30 g of a catalyst is fallen from above the pipe.

By using a catalyst having such falling strength, powdering and disintegration at transportation of the catalyst or filling into a reactor can be suppressed.

[0016]

As the method of preparing the catalyst precursor, it is desirable that an ammonium compound is used as a catalyst raw material, or ammonia or an ammonium salt is added to obtain an aqueous mixed liquid containing an ammonium radical, the liquid is dried and, thereafter, heat-treated and molded, or molded and then heat-treated. According to these formulations, at heat treatment, a structure of Keggin type heteropolyacid salt can be formed, and a catalyst precursor made of the thus obtained Keggin type heteropolyacid salt is particularly suitable for calcination described later.

[0017]

It is preferable that a molded product obtained by the molding is subsequently subjected to temperature and humidity control treatment. Specifically, the temperature and humidity control treatment is performed by exposing the molded product to an atmosphere of 40 to 100°C and a relative humidity of 10 to 60% for around 0.5 to 10 hours. The treatment may be performed in a tank which has been temperature-and-humidity-controlled, or may be performed by blowing a temperature-and-humidity-controlled gas to the molded product, for example. As an atmosphere gas when the treatment is performed, usually the air is used, but an inert gas such as nitrogen may also be used.

[0018]

It is desirable that heat treatment after the drying or molding is performed at a temperature around 180 to 300°C under an atmosphere of an oxidizing gas or a non-oxidizing gas.

[0019]

The thus obtained catalyst precursor is subjected to calcination. The calcination method is not particularly limited and calcination can be performed by a method usually used in this field. For example, calcination may be performed under an atmosphere of an oxidizing gas such as oxygen, or may be performed under an atmosphere of a non-oxidizing gas such as nitrogen, and the calcination temperature is preferably 300°C or higher. Among them, in respect that a catalyst for producing methacrylic acid having a good catalyst life is obtained, it is preferable to perform multi-stage calcination under an atmosphere of an oxidizing gas or a non-oxidizing gas,

and it is more preferable to adopt a two-stage calcination method, in which first stage calcination is performed under an atmosphere of an oxidizing gas and, then, second stage calcination is performed under an atmosphere of a non-oxidizing gas.

[0020]

The oxidizing gas used in calcination is a gas containing an oxidizing substance, and examples thereof include an oxygen-containing gas. When an oxygen-containing gas is used, the oxygen concentration thereof should be usually around 1 to 30 volume%, and as an oxygen source, usually, the air or pure oxygen is used and, if necessary, the gas is diluted with an inert gas. In addition, in the oxidizing gas, moisture may be present as necessary, and the concentration thereof is usually 10 volume% or lower. Among them, as the oxidizing gas, the air is preferable. Calcination performed under the oxidizing gas atmosphere is usually conducted under a stream of such an oxidizing gas. The temperature for calcination performed under the oxidizing gas atmosphere is preferably 360 to 410°C, and more preferably 380 to 400°C.

[0021]

The non-oxidizing gas used in calcination is a gas containing substantially no oxidizing substance such as oxygen, and examples thereof include inert gases such as nitrogen, carbon dioxide, helium, and argon. In addition, moisture may be present in the non-oxidizing gas as necessary, and the concentration thereof is usually 10 volume% or lower. As the non-oxidizing gas, inter alia, nitrogen is preferable. Calcination performed under the non-oxidizing gas atmosphere is usually conducted under a stream

of such a non-oxidizing gas. The temperature for calcination performed under the non-oxidizing gas atmosphere is preferably 420 to 500°C, and more preferably 420 to 450°C.

[0022]

When these calcination temperatures are lower than predetermined values, the activity of the resulting catalyst may become insufficient or the catalyst life may be insufficient. On the other hand, when these calcination temperatures exceed predetermined values, since the catalyst tends to be degraded and sintered, the activity of the resulting catalyst may become insufficient. The time for each calcination is each appropriately adjusted, and is usually around 1 to 20 hours. It is desirable that each calcination is performed while flowing a gas used as an atmosphere gas.

[0023]

The process for producing methacrylic acid of the present invention is to supply methacrolein, isobutylene and oxygen into a reactor for producing methacrylic acid provided with a catalyst layer containing a catalyst for producing methacrylic acid, and to oxidize methacrolein in a continuous manner, and the process is carried out so that the maximum temperature in the catalyst layer becomes 330°C or lower.

[0024]

In the oxidation, the molar ratio of oxygen relative to methacrolein is preferably 1 to 5. The reaction temperature is preferably 250 to 320°C, and the reaction pressure is preferably 0.1 to 0.3 MPa. The reaction temperature indicates the lowest temperature in the catalyst layer, that is, the temperature of a portion having the lowest temperature in the catalyst

layer.

[0025]

The oxidation can be performed in a continuous manner by extracting a reaction mixture from the reactor for producing methacrylic acid, while methacrolein, isobutylene and oxygen are supplied into the reactor. The oxidation is performed by contacting methacrolein, isobutylene and oxygen with a catalyst for producing methacrylic acid. As a reaction system, reaction systems such as a fluidized bed, a fixed bed, and a moving bed can be adopted, and it is desirable from the viewpoint of productivity and operability to perform the oxidation by a fixed bed flowing system in which methacrolein, isobutylene and oxygen are flowed through a fixed bed reactor filled with the catalyst for producing methacrylic acid. In oxidation by the fixed bed flowing system, a reaction can be performed by, for example, flowing a mixed gas containing methacrolein, isobutylene and oxygen through the fixed bed reactor provided with a catalyst layer filled with the catalyst for producing methacrylic acid by upflow or downflow. As the fixed bed reactor, various fixed bed reactors of flow system in which a reactor is provided with a raw material supply port and a reaction gas outlet port can be used. The number of reaction tubes is not particularly limited, and either of a monotubular fixed bed reactor and a multitubular fixed bed reactor can be used. A multitubular fixed bed reactor is preferably used. The internal diameter of this reaction tube is usually 10 to 40 mm, and preferably 15 to 35 mm. In addition, a fixed bed reactor of heat-insulating system or heat-exchanging system can be used. The supply of methacrolein, isobutylene and oxygen may be performed by preparing a mixed gas

containing methacrolein, isobutylene and oxygen, and supplying the mixed gas through a supply port of the reactor for producing methacrylic acid, or by supplying methacrolein, isobutylene and oxygen, respectively, through separate supply ports, or by supplying two selected from the group consisting of methacrolein, isobutylene and oxygen, and remaining one through separate supply ports. It is preferable to supply a mixed gas containing methacrolein isobutylene and oxygen into the reactor for producing methacrylic acid.

In addition, methacrolein, isobutylene and oxygen may be supplied, respectively, through separate supply ports by division.

[0026]

In the oxidation of methacrolein, as the oxygen source, usually, the air is used. The mixed gas may contain an inert gas such as nitrogen, carbon dioxide, carbon monoxide, water vapor, or argon as a component other than methacrolein, isobutylene and oxygen [hereinafter, sometimes referred to as a different component]. Two or more of these inert gases may be contained.

In addition, acetaldehyde, acetone, acrolein, acetic acid, acrylic acid, methacrylic acid, maleic acid, terephthalic acid and the like, which can be contained as impurities in raw materials to be used, may be contained in the mixed gas as long as the effect of the present invention is not impaired.

[0027]

It is not necessarily required that methacrolein is a purified product of high purity. For example, a reaction mixture containing methacrolein obtained by the reaction of oxidizing isobutylene may be used without

purification to high-purity methacrolein, the methacrolein may be unreacted methacrolein which is recovered from the reaction mixture obtained after the reaction of oxidizing methacrolein, or may be a mixture of methacrolein obtained by the reaction of oxidizing isobutylene and unreacted methacrolein recovered from the reaction mixture obtained after the reaction of oxidizing methacrolein. As the methacrolein which is used in the process for producing methacrylic acid of the present invention, methacrolein, at least a part of which is contained in the reaction mixture obtained by oxidizing isobutylene with oxygen in the presence of the catalyst for producing methacrolein, is preferable.

[0028]

As the isobutylene which is used in the process for producing methacrylic acid of the present invention, isobutylene, at least a part of which is different from unreacted isobutylene contained in the reaction mixture obtained by oxidizing isobutylene with oxygen in the presence of the catalyst for producing methacrolein, is preferable. That is, as isobutylene to be supplied into the reactor for producing methacrylic acid, it is preferable not to use only unreacted isobutylene which is contained in the reaction mixture obtained by oxidizing isobutylene in the presence of the catalyst for producing methacrolein, but to use, as at least a part thereof, isobutylene different from such unreacted isobutylene (isobutylene which is a newly prepared product, isobutylene recovered from other reaction systems, etc.).

[0029]

When the oxidation of methacrolein is performed by supplying a mixed gas containing methacrolein, isobutylene and oxygen into the reactor

for producing methacrylic acid, examples of the mixed gas include (a) a mixed gas of methacrolein, isobutylene, oxygen and an optionally contained different component, (b) a mixed gas of a reaction mixture containing methacrolein, unreacted isobutylene and unreacted oxygen obtained by the reaction of oxidizing isobutylene, and an optionally contained different component, (c) a mixed gas of a reaction mixture containing methacrolein and unreacted isobutylene obtained by the reaction of oxidizing isobutylene; oxygen; and an optionally contained different component, (d) a mixed gas of a reaction mixture containing methacrolein and unreacted isobutylene obtained by the reaction of oxidizing isobutylene; isobutylene; oxygen; and an optionally contained different component, (e) a mixed gas of a reaction mixture containing methacrolein obtained by the reaction of oxidizing isobutylene, but not containing unreacted isobutylene; isobutylene; oxygen; and an optionally contained different component, and (f) a mixed gas of methacrolein obtained by purifying a reaction mixture containing methacrolein obtained by the reaction of oxidizing isobutylene; isobutylene; oxygen; and an optionally contained different component. In the mixed gases (c), (d) and (e), unreacted oxygen may be contained in the reaction mixture. In the mixed gas (f), at least one selected from the group consisting of unreacted isobutylene and unreacted oxygen may be contained in the reaction mixture.

[0030]

The catalyst layer refers to a portion in which a catalyst for producing methacrylic acid is contained in the reactor for producing methacrylic acid, and examples thereof include a catalyst layer made of a

catalyst for producing methacrylic acid, a catalyst layer made of a mixture of a catalyst for producing methacrylic acid and a diluent, and a catalyst layer in which a layer made of at least one layer of a catalyst for producing methacrylic acid and a layer made of a mixed catalyst of at least one layer of a catalyst for producing methacrylic acid and a diluent are laminated (hereinafter, sometimes referred to as laminated catalyst layer). As the diluent, a diluent which is inert to the oxidation of methacrolein is used, and examples thereof include silica, alumina, silicon carbide, and silicon nitride, and two or more thereof may be used if necessary. The catalysts for producing methacrylic acid used in the catalyst layer are not limited to the same composition, but catalysts each having different composition can be used. For example, when the catalyst layer is a catalyst layer made of a catalyst for producing methacrylic acid, the catalyst layer may be a catalyst layer made of catalysts having the same composition, a catalyst layer made of a mixture of a plurality of catalysts having different compositions, or a catalyst layer in which a plurality of layers of catalysts having different compositions are laminated. When the catalyst layer is a catalyst layer made of a mixture of a catalyst for producing methacrylic acid and a diluent, catalysts and diluents constituting the catalyst layer may have the same composition, respectively; or may be a mixture of a plurality of catalysts having different compositions or a mixture of a plurality of diluents having different compositions. When the catalyst layer is a laminated catalyst layer, catalysts constituting a layer made of a catalyst for producing methacrylic acid may have the same composition, or may be a mixture of catalysts having different compositions. In addition, when there are a

plurality of layers made of a catalyst for producing methacrylic acid, the compositions of the mutual catalysts of respective layers may be the same or different from each other. When the catalyst layer is a laminated catalyst layer, catalysts constituting a layer made of a mixed catalyst of a catalyst for producing methacrylic acid and a diluent may have the same composition, or may be a mixture of catalysts having different compositions. In addition, when there are a plurality of layers made of a mixed catalyst of a catalyst for producing methacrylic acid and a diluent, the compositions of the mutual catalysts of respective layers, the compositions of the diluents, and the content ratios of the diluents may be the same or different from each other respectively. When the oxidation is performed by a fixed bed flowing system, a layer made of a diluent may be formed at an inlet portion or outlet portion of a catalyst layer and/or between layers.

[0031]

In the production of methacrylic acid, since the reaction of oxidizing methacrolein is an exothermic reaction, usually, the catalyst layer has a temperature distribution. The maximum temperature in the catalyst layer represents the highest temperature which is reached in the catalyst layer. Such maximum temperature can be obtained as the highest temperature which is detected by, for example, measuring the temperature of the catalyst layer with a temperature measuring device such as a thermocouple, and recording the temperature distribution of the catalyst layer. When the oxidation is performed by a fixed bed flowing system, the maximum temperature in the catalyst layer may be obtained by recording the temperature distribution of the tube axis direction of the reactor in the

catalyst layer. Examples of the method of measuring temperature include a method of measuring the temperature of each portion in the catalyst layer using a multipoint thermocouple, and a method of inserting a protecting tube in the catalyst layer, and moving the thermocouple in the protecting tube to thereby measure the temperature of each portion in the catalyst layer.

[0032]

In the production of methacrylic acid, since the reaction of oxidizing methacrolein is an exothermal reaction, there is a possibility that deterioration of the catalyst is caused due to heat generation. Particularly, when the reaction is performed by a fixed bed flowing system, since an excessive oxidation reaction occurs in a hot spot (abnormal local rise in temperature) generated in the catalyst layer, the yield may be reduced in many cases and, further, since an excessive heat load is applied to the catalyst, the catalyst is deteriorated and the catalyst life may be reduced. Hence, in the process for producing methacrylic acid of the present invention, the oxidation is performed so that the maximum temperature in the catalyst layer becomes 330°C or lower. The lower limit of the maximum temperature in the catalyst layer becomes temperature exceeding the reaction temperature, and it is preferable that $T+5 \leq T_{\max}$ is satisfied when the maximum temperature is defined as $T_{\max}$ (°C) and the reaction temperature is defined as T (°C).

[0033]

The maximum temperature in the catalyst layer can be adjusted by the reaction temperature, the supply amount of methacrolein to be supplied into the reactor for producing methacrylic acid, the supply amount of

isobutylene or the like, and among them, it is preferable to adjust the maximum temperature by the supply amount of isobutylene. The reaction temperature in oxidation of methacrolein can be adjusted by adjusting the temperature of a temperature regulating means such as a heater, a jacket, or a heat medium bath included in the reactor. When the oxidation is performed using a fixed bed reactor, the fixed bed reactor is usually provided with a heat medium bath for temperature adjustment composed of a nitrate of an alkali metal or the like. Since this heat medium temperature indicates the lowest temperature of the catalyst layer, adjustment of the reaction temperature may be performed by adjusting this heat medium temperature. The temperature of the temperature regulating means is usually adjusted in the range of 250 to 320°C. When the oxidation is performed by supplying a mixed gas containing methacrolein, isobutylene and oxygen into the reactor for producing methacrylic acid, it is preferable to adjust the maximum temperature in the catalyst layer by adjusting the content of isobutylene in the mixed gas. The content of isobutylene in the mixed gas may be adjusted in the range of 50 to 3,000 volume ppm, preferably in the range of 150 to 2,000 volume ppm, and more preferably in the range of 300 to 1,500 volume ppm. When the content of isobutylene in the mixed gas is too small, it becomes difficult to obtain the effect of suppressing a rise in the maximum temperature in the catalyst layer, and when the content of isobutylene in the mixed gas is too large, the amount of heat generated by oxidation of isobutylene is increased, and it becomes difficult to obtain the effect of suppressing a rise in the maximum temperature in the catalyst layer.

[0034]

Examples of the method of making the content of isobutylene in the mixed gas to 50 to 3,000 volume ppm include (A) a method of preparing the mixed gas by adjusting the mixing ratio among methacrolein, isobutylene, oxygen and an optionally contained different component so that the content of isobutylene becomes 50 to 3,000 volume ppm; (B) a method of obtaining a mixed gas containing methacrolein, isobutylene and oxygen by adjusting the content of isobutylene in a reaction gas to be obtained containing methacrolein, unreacted isobutylene and unreacted oxygen at 50 to 3,000 volume ppm, by adjusting the conversion of isobutylene in the reaction of oxidizing isobutylene; and (C) a method of mixing a reaction gas containing methacrolein and unreacted isobutylene obtained by the reaction of oxidizing isobutylene with at least one component selected from the group consisting of methacrolein, isobutylene, oxygen and an optionally contained different component, so that the content of isobutylene becomes 50 to 3,000 volume ppm, to obtain a mixed gas containing methacrolein, isobutylene, and oxygen. From the viewpoint of productivity, the method (B) or (C) is preferable, and the method (C) is more preferable. In the method (C), the content of isobutylene in the reaction gas containing methacrolein and unreacted isobutylene obtained by the reaction of oxidizing isobutylene can be adjusted by adjusting the conversion of isobutylene in the reaction of oxidizing isobutylene, and unreacted oxygen may be contained in the reaction gas. In the method (A) or (C), it is preferable to use an inert gas such as nitrogen, carbon dioxide, carbon monoxide, water vapor, or argon as an optionally contained different component.

[0035]

The content of methacrolein in the mixed gas is preferably 2.0 to 5.0 volume%. When water vapor is contained, the content of water vapor is preferably 1 to 30 volume%. The flow velocity of the mixed gas is, as the space velocity of the mixed gas in the catalyst for producing methacrylic acid, preferably 500 to 5,000 h^{-1} based on the standard state (in terms of 0°C, 0.1 MPa). The space velocity can be obtained by dividing the amount of the mixed gas passing through the reactor for producing methacrylic acid per hour (L/h) by the volume (L) of the catalyst for producing methacrylic acid in the reactor for producing methacrylic acid.

[0036]

The reaction of oxidizing isobutylene is performed by oxidizing isobutylene with oxygen, in the presence of the catalyst for producing methacrolein.

[0037]

As the catalyst for producing methacrolein, a catalyst made of a complex oxide containing molybdenum, bismuth and iron is preferable. This catalyst can be produced by, for example, the methods disclosed in JP-A-59-46132, JP-A-60-163830, JP-A-2000-288396, and JP-A-2009-274034.

[0038]

In the reaction of oxidizing isobutylene, methacrylic acid can be generated together with methacrolein, and generated methacrylic acid may be contained in the mixed gas containing methacrolein, isobutylene and oxygen.

[0039]

The reaction of oxidizing isobutylene is performed by, for example, oxidizing isobutylene in a mixed gas containing isobutylene and oxygen, with oxygen, in a continuous manner, by extracting a reaction mixture from a reactor for producing methacrolein with a catalyst for producing methacrolein, while supplying the mixed gas into the reactor for producing methacrolein.

[0040]

As a reaction system in the reaction of oxidizing isobutylene, reaction systems such as a fluidized bed, a fixed bed, and a moving bed can be adopted, and it is desirable from the viewpoint of productivity and operability to perform the reaction by a fixed bed flowing system in which a mixed gas containing isobutylene and oxygen is flowed through the fixed bed reactor filled with the catalyst for producing methacrolein. A reaction by the fixed bed flowing system can be performed by, for example, passing the mixed gas containing isobutylene and oxygen through the fixed bed reactor filled with the catalyst for producing methacrolein by upflow or downflow. In addition, as the fixed bed reactor, various fixed bed reactors of flowing system in which a reactor is provided with a raw material supply port and a reaction gas outlet port can be used. The number of reaction tubes is not particularly limited, and either of a monotubular fixed bed reactor and a multitubular fixed bed reactor can be used, but a multitubular fixed bed reactor is preferably used. The internal diameter of this reaction tube is preferably 10 to 40 mm, and more preferably 15 to 35 mm. In addition, a fixed bed reactor of heat-insulating system or heat-exchanging system can be used.

[0041]

As an oxygen source in the reaction of oxidizing isobutylene, usually, the air is used. A mixed gas containing isobutylene and oxygen may contain an inert gas such as nitrogen, carbon dioxide, carbon monoxide, water vapor, or argon as a component other than isobutylene and oxygen. In addition, two or more of these inert gases may be contained.

[0042]

The content of isobutylene in the mixed gas containing isobutylene and oxygen is preferably 1 to 10 volume%, and the molar ratio of oxygen relative to isobutylene is preferably 1 to 3. When water vapor is contained, the content of water vapor is preferably 1 to 35 volume%. The flow velocity of the mixed gas is, as the space velocity of the mixed gas in the catalyst for producing methacrolein, preferably 500 to 5,000 h⁻¹ based on the standard state (in terms of 0°C, 0.1 MPa). The space velocity can be obtained by dividing the amount of mixed gas passing through the reactor for producing methacrolein per hour (L/h) by the volume (L) of the catalyst for producing methacrolein in the reactor for producing methacrolein. The reaction temperature is usually 250 to 450°C, and the reaction pressure can be reduced pressure, but is usually 0.1 to 0.5 MPa.

[0043]

The content of isobutylene in a reaction gas obtained after the reaction of oxidizing isobutylene can be adjusted by the conversion of isobutylene, and as the conversion of isobutylene is higher, a reaction gas having a smaller content of isobutylene is obtained. By setting the conversion of isobutylene to 100%, a reaction mixture not containing

isobutylene (isobutylene content: 0 volume ppm) is obtained. The conversion of isobutylene can be regulated by, for example, adjusting the reaction temperature, and as the reaction temperature is higher, the conversion of isobutylene can be increased more.

[0044]

As methacrolein to be supplied into the reactor for producing methacrylic acid, when methacrolein contained in a reaction mixture obtained by oxidizing isobutylene with oxygen in the presence of a catalyst for producing methacrolein is used as at least a part thereof, examples of the method of supplying methacrolein into the reactor for producing methacrylic acid include a method of connecting an extraction port of the reactor for producing methacrolein and a supply port of the reactor for producing methacrylic acid with a connecting line; extracting a reaction mixture obtained by oxidizing isobutylene with oxygen in the presence of a catalyst for producing methacrolein from an extraction port of the reactor for producing methacrolein; and supplying methacrolein contained in the reaction mixture through the supply port of the reactor for producing methacrylic acid via the connecting line. A device for purifying the reaction mixture obtained by oxidizing isobutylene with oxygen may be appropriately provided on the connecting line.

[0045]

Examples of the method of supplying isobutylene into the reactor for producing methacrylic acid include a method of connecting the connecting line with an isobutylene supplying line; supplying isobutylene from the isobutylene supplying line; thereby, mixing methacrolein contained in the

reaction mixture extracted from the reactor for producing methacrolein with isobutylene by joining them together; and thereafter, supplying the mixture through the supply port of the reactor for producing methacrylic acid via the connecting line, and a method of mixing the reaction mixture containing methacrolein, which is extracted from the reactor for producing methacrolein, with isobutylene which is supplied through the isobutylene supplying line in the connecting line; and supplying the mixture through the supply port of the reactor for producing methacrylic acid via the connecting line is suitably adopted. The isobutylene supplied through the isobutylene supplying line may be supplied with an inert gas such as nitrogen.

[0046]

The supply of oxygen into the reactor for producing methacrylic acid may be performed by connecting the connecting line with an oxygen supplying line, and supplying oxygen through the oxygen supplying line, or by supplying oxygen with isobutylene through the isobutylene supplying line, or by connecting a supply port different from the supply port which is connected with the connecting line of the reactor for producing methacrylic acid, with an oxygen supplying line, and supplying oxygen through the oxygen supplying line. The oxygen supplied through the oxygen supplying line may be supplied with an inert gas such as nitrogen.

[0047]

When the oxidation of methacrolein is performed by supplying a mixed gas containing methacrolein, isobutylene and oxygen into the reactor for producing methacrylic acid, the methacrolein conversion at an outlet of the reactor for producing methacrylic acid is preferably 70 to 100%, and more

preferably 80 to 100%. Since there is a tendency that the methacrolein conversion at the outlet of the reactor is increased as the reaction temperature is higher, the content of isobutylene in a mixed gas containing methacrolein, isobutylene and oxygen is smaller, the space velocity of methacrolein in the catalyst for producing methacrolein is smaller, or the supply amount of oxygen to methacrolein is larger, the methacrolein conversion can be adjusted by adjusting at least one condition among them. The reaction temperature, as well as the content of isobutylene in a mixed gas containing methacrolein, isobutylene and oxygen can be adjusted by the aforementioned method. The space velocity of methacrolein in the catalyst for producing methacrolein may be adjusted by regulating the content of methacrolein in the mixed gas used in oxidation of methacrolein, the supply amount of the mixed gas used in oxidation of methacrolein, or the like. The supply amount of oxygen relative to methacrolein may be adjusted by regulating the content of methacrolein and the content of oxygen in the mixed gas used in oxidation of methacrolein. At the time point when oxidation of methacrolein is initiated by supplying the mixed gas into the reactor for producing methacrylic acid, the methacrolein conversion at the outlet of the reactor for producing methacrylic acid is preferably at least 75%, more preferably at least 85%, and further preferably at least 90%.

[0048]

In the production of methacrylic acid, particularly upon initiation of production of methacrylic acid, if the supply amount of methacrolein is rapidly increased, there is a possibility that deterioration of the catalyst is caused due to heat generation, and when the reaction is performed by a fixed

bed flowing system, the yield may be reduced and the catalyst life may be reduced at a hot spot generated in the catalyst layer. For this reason, in the process for producing methacrylic acid of the present invention, particularly, upon initiation of production of methacrylic acid, that is, upon startup, it is effective in suppression of a reduction in a catalyst life to perform the process so that the maximum temperature in the catalyst layer becomes 330°C or lower. The maximum temperature in the catalyst layer can be adjusted by, as described above, the reaction temperature, the supply amount of methacrolein to be supplied into the reactor for producing methacrylic acid, the supply amount of isobutylene, and the like, and upon startup, a method of adjusting the maximum temperature in the catalyst layer by supplying a mixed gas containing methacrolein, isobutylene and oxygen into a reactor for producing methacrylic acid, and adjusting the content of isobutylene in the mixed gas is preferably adopted. The content of isobutylene in the mixed gas may be adjusted in the range of 50 to 3,000 volume ppm, preferably in the range of 150 to 2,000 volume ppm, and more preferably in the range of 300 to 1,500 volume ppm.

[0049]

It is preferable to perform the startup so that the supply amount of methacrolein is increased gradually or stepwisely instead of rapidly increasing the supply amount to the predetermined supply amount of methacrolein, and examples of the method of the startup include (D) a method of performing startup by supplying a mixed gas containing methacrolein, isobutylene and oxygen into a reactor for producing methacrylic acid so that the maximum temperature in the catalyst layer

becomes 330°C or lower, to thereby initiate production of methacrylic acid; and increasing the supply amount of methacrolein to the predetermined supply amount of methacrolein gradually or stepwisely, while the maximum temperature in the catalyst layer is regulated at 330°C or lower, (E) a method of performing startup by first supplying a mixed gas containing methacrolein and oxygen into a reactor for producing methacrylic acid so that the maximum temperature in the catalyst layer becomes 330°C or lower, to thereby initiate production of methacrylic acid; and supplying a mixed gas containing methacrolein, isobutylene and oxygen into the reactor for producing methacrylic acid during increasing the supply amount of methacrolein to the predetermined supply amount of methacrolein gradually or stepwisely, while the maximum temperature in the catalyst layer is regulated at 330°C or lower, and (F) a method of performing startup by first supplying a mixed gas containing methacrolein and oxygen into a reactor for producing methacrylic acid so that the maximum temperature in the catalyst layer becomes 330°C or lower, to thereby initiate production of methacrylic acid; increasing the supply amount of methacrolein to the predetermined supply amount of methacrolein gradually or stepwisely, while the maximum temperature in the catalyst layer is regulated at 330°C or lower; and after the supply amount of methacrolein has reached the predetermined supply amount of methacrolein, that is, after the steady state has been realized, supplying a mixed gas containing methacrolein, isobutylene and oxygen into the reactor for producing methacrylic acid, while the predetermined supply amount of methacrolein is maintained and the maximum temperature in the catalyst layer is regulated at 330°C or lower. In the methods (E) and (F), if

the condition that the maximum temperature in the catalyst layer becomes 330°C or lower is satisfied, isobutylene may be contained in the mixed gas containing methacrolein and oxygen used at initial supply and at the stage of increasing the supply amount of methacrolein to the predetermined supply amount of methacrolein, and the content of the isobutylene is, for example, in the range of less than 50 volume ppm. The period until the amount reaches the predetermined supply amount of methacrolein, that is, the time of startup, is preferably within 300 hours from the initiation of supply of methacrolein, although it depends on the nature of the catalyst and other conditions.

[0050]

In the steady state after the startup, the oxidation of methacrolein is continued, and examples of the method of operating the continuation include (G) a method of continuing oxidation at a constant reaction temperature for a period in which the predetermined methacrolein conversion can be maintained, (H) a method of continuing oxidation until the temperature reaches a set upper limit temperature while gradually or stepwisely raising the reaction temperature, so that the predetermined methacrolein conversion can be maintained, (I) a method of continuing oxidation at a constant reaction temperature for a period in which the predetermined methacrolein conversion can be maintained, and then continuing oxidation until the temperature reaches a set upper limit temperature while gradually or stepwisely raising the reaction temperature, so that this predetermined methacrolein conversion can be maintained, and (J) a method of continuing oxidation until a set reaction condition is achieved by making a change in the

reaction condition such as reduction in the space velocity of methacrolein in a catalyst for producing methacrolein or increase in the supply amount of oxygen relative to methacrolein, so that the predetermined methacrolein conversion can be maintained. The method (G) or (I) is preferable in respect of productivity. Herein, continuation of oxidation of methacrolein at a constant reaction temperature refers to continuation of oxidation of methacrolein so that the temperature is in the range of $\pm 5^{\circ}\text{C}$ relative to the reaction temperature at the time of initiation of oxidation of methacrolein. In order to make the temperature in the range of $\pm 5^{\circ}\text{C}$ relative to the reaction temperature at the time of the initiation of oxidation, adjustment should be performed as in the aforementioned adjustment of the reaction temperature in the oxidation of methacrolein. It is preferable that continuation of the oxidation at a constant reaction temperature is performed so that the temperature comes into the range of $\pm 3^{\circ}\text{C}$ relative to the reaction temperature at the time of the initiation of oxidation. When oxidation of methacrolein is continued at a constant reaction temperature, it is preferable that the reaction temperature therefor is in the range of 260 to 290°C . In the method (G) or (I), the predetermined methacrolein conversion is appropriately set, and for example, the predetermined conversion may be set in the range of 50 to 80%, and preferably set in the range of 65 to 75%. In the method (H) or (J), the predetermined methacrolein conversion is appropriately set, and for example, the predetermined conversion may be set in the range of 60 to 90%.

[0051]

The catalyst for producing methacrylic acid used in the oxidation of

methacrolein can be used again by reproducing the catalyst by the reproduction treatment method described in, for example, JP-A-58-156351, JP-A-6-7685, JP-A-2000-191582, JP-A-2003-306464 and the like. As the method of reproduction treatment, a method which can be performed while a catalyst is filled in a reactor for producing methacrylic acid is preferable, and particularly, a method of performing heat treatment at 290 to 400°C under the flow of a gas containing at least 3 volume% of oxygen and at least 3 volume% of water vapor is preferable, as described in JP-A-2003-306464.

[0052]

Thus, durability of catalyst performance can be enhanced, and methacrylic acid can be produced with good productivity over a long period of time. Post-treatment operation of a gas generated in the reaction and containing the resulting methacrylic acid is appropriately selected, and examples thereof include a method of subjecting the gas to separation and purification operation after condensation or absorption of water. Recovered unreacted methacrolein can be recycled as a raw material, and an exhaust gas can be recycled as the inert gas source, optionally after being subjected to treatment such as burning.

[0053]

The resulting methacrylic acid is suitably used as a raw material for producing a methacrylic ester by, for example, subjecting the resulting methacrylic acid to an esterification reaction in the presence of an esterification catalyst.

[0054]

Examples of alcohol to be used in the esterification reaction include

methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, isobutyl alcohol, sec-butyl alcohol, tert-butyl alcohol, and ethylene glycol. Examples of a preferable embodiment include an embodiment of producing methyl methacrylate by using methanol. Examples of the esterification catalyst include acid catalysts such as sulfuric acid and a strongly acidic ion exchange resin. The esterification reaction can be performed according to, for example, the method described in JP-B-48-1369, JP-B-61-4378, JP-A-6-298702, JP-A-2003-26633 or the like.

Examples

[0055]

The present invention will be specifically explained below by way of examples, but the present invention is not limited thereto.

[0056]

In addition, the air and nitrogen used below contain substantially no moisture.

[0057]

In each example, a mixed gas to be supplied to a reactor for producing methacrylic acid was analyzed by gas chromatography to obtain the content of isobutylene, the content of methacrolein, the content of oxygen and the content of water vapor in the mixed gas. In addition, the reaction mixture at the outlet of the reactor for producing methacrylic acid was analyzed by gas chromatography and the methacrolein conversion at the outlet of the reactor for producing methacrylic acid was calculated by the following equation.

[0058]

Methacrolein conversion (%) = [(content of methacrolein in mixed gas to be supplied to reactor for producing methacrylic acid (mol)) - (content of methacrolein in reaction mixture at outlet of reactor for producing methacrylic acid (mol))]/[content of methacrolein in mixed gas to be supplied to reactor for producing methacrylic acid (mol)] × 100

[0059]

Reference Example 1

[Preparation of catalyst for producing methacrolein]

In 15,000 g of warm water, 13,241 g of ammonium molybdate $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}]$ was dissolved, and this was named as A liquid. In 6,000 g of warm water, 6,060 g of iron (III) nitrate $[\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$, 13,096 g of cobalt nitrate $[\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ and 585 g of cesium nitrate (CsNO_3), then, 2,910 g of bismuth nitrate $[\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}]$ was dissolved, and this was named as B liquid. To the A liquid was added the B liquid while stirring the A liquid to obtain a slurry, which was subsequently spray-dried to obtain a dried material. To the resulting dried material was added 2.54 parts by mass of antimony trioxide $[\text{Sb}_2\text{O}_3]$ based on 100 parts by mass of the dried material, which was molded into a ring shape having an external diameter of 6.0 mm, an internal diameter of 2.0 mm and a length of 6 mm together with 6 parts by mass of a silica alumina fiber (RFC400-SL manufactured by ITM Co., Ltd.), and the ring was calcined at 543°C for 6 hours under an air atmosphere to obtain a catalyst for producing methacrolein. The catalyst composition except for oxygen was $\text{Mo}_{12}\text{Bi}_{0.96}\text{Sb}_{0.48}\text{Fe}_{2.4}\text{Co}_{7.2}\text{Cs}_{0.48}\text{Si}_{1.43}\text{Al}_{1.55}$.

[0060]

Reference Example 2

[Preparation of catalyst for producing methacrylic acid]

In 224 kg of ion-exchanged water heated to 40°C were dissolved 38.2 kg of cesium nitrate $[\text{CsNO}_3]$, 24.2 kg of 85 wt% orthophosphoric acid, and 25.2 kg of 70 wt% nitric acid, and this was named as C liquid. On the other hand, in 330 kg of ion-exchanged water heated to 40°C was dissolved 297 kg of ammonium molybdate tetrahydrate $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}]$, 8.19 kg of ammonium metavanadate $[\text{NH}_4\text{VO}_3]$ was suspended therein, and this was named as D liquid. The C liquid and the D liquid were adjusted to 40°C, the C liquid was added dropwise to the D liquid under stirring, and the mixture was stirred at 120°C for 5.8 hours in a sealed vessel. Then, 10.2 kg of antimony trioxide $[\text{Sb}_2\text{O}_3]$ and 10.2 kg of copper nitrate trihydrate $[\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}]$ were suspended in 23 kg of ion-exchanged water and added to the mixture, and this was stirred at 120°C for 5 hours in a sealed vessel. The thus obtained slurry was dried with a spray drier. To 100 parts by weight of this dried powder were added 4 parts by weight of a silica alumina fiber [RFC400-SL, manufactured by ITM Co., Ltd.], 13 parts by weight of ammonium nitrate, and 9.7 parts by weight of ion-exchanged water, and the mixture was kneaded and extrusion-molded into a cylindrical shape having a diameter of 5 mm and a height of 6 mm. This molded product was dried at a temperature of 90°C and a humidity of 30% RH for 3 hours, and held in the air stream at 220°C for 22 hours, subsequently, at 250°C for 1 hour to heat-treat the molded product, thereby, a catalyst precursor made of Keggin type heteropolyacid salt was obtained.

[0061]

The temperature of the resulting catalyst precursor was raised to 390°C in a stream of a mixed gas of the air and steam (moisture content: 1.4 volume%), and the precursor was held at the same temperature for 3 hours. Then, the air was switched with nitrogen, the temperature of the precursor was raised to 435°C in a nitrogen stream, the precursor was calcined by being held at the same temperature for 3 hours, and cooled to 70°C in a nitrogen stream to obtain a catalyst for producing methacrylic acid. This catalyst for producing methacrylic acid was made of an acidic salt of Keggin type heteropolyacid containing phosphorus, molybdenum, vanadium, antimony, copper and cesium at an atomic ratio of 1.5 : 12 : 0.5 : 0.5 : 0.3 : 1.4.

[0062]

Example 1 [Preparation of methacrylic acid]

Into a reaction tube for producing methacrolein made of steel having an internal diameter of 25.4 mm provided with a heat medium bath was filled 1,300 ml of the catalyst for producing methacrolein obtained in Reference Example 1, a raw material gas (A) prepared by mixing isobutylene, the air, steam and nitrogen was supplied to the reaction tube for producing methacrolein at a space velocity of 650 h⁻¹ (based on the standard state), and a reaction of oxidizing isobutylene was initiated at a reaction temperature of 350°C.

[0063]

Into a reaction tube for producing methacrylic acid made of steel having an internal diameter of 30 mm provided with a heat medium bath was filled 2,000 ml of the catalyst for producing methacrylic acid obtained in Reference Example 2. A protecting tube (external diameter 4 mm, internal

diameter 3 mm) was inserted into the reaction tube for producing methacrylic acid, a multipoint sheathed thermocouple (diameter 1.8 mm) was placed into the protecting tube, and the temperature of a catalyst layer of the catalyst for producing methacrylic acid was measured. The supply of a mixed gas (B) prepared by mixing a reaction gas extracted from the outlet of the reaction tube for producing methacrolein by the reaction of oxidizing isobutylene, the air and nitrogen to the reaction tube for producing methacrylic acid filled with the catalyst for producing methacrylic acid was initiated at a space velocity of 550 h^{-1} (based on the standard state) at a temperature of a heat medium for heating the reaction tube of 280°C . Then, the supply amount of the mixed gas (B) was increased stepwisely over 23 hours from initiation of supply of the mixed gas (B) until the space velocity became 750 h^{-1} (based on the standard state). The composition of the mixed gas (B) during the period of less than 23 hours from initiation of supply of the mixed gas (B) was methacrolein content: 0.7 to 2.0 volume%, oxygen content: 4.9 to 12.7 volume%, isobutylene content: 0 volume ppm, and water vapor content: 11.1 to 14.8 volume%, the maximum temperature of the catalyst layer of the catalyst for producing methacrylic acid was 290 to 318°C , and the methacrolein conversion was fluctuated in the range of 99 to 100%. In addition, during the period of 23 hours from initiation of supply of the mixed gas (B), the supply amount of the raw material gas (A) to be supplied to the reaction of oxidizing isobutylene was also increased stepwisely to a space velocity of 850 h^{-1} (based on the standard state). During the period of less than 23 hours from initiation of supply of the mixed gas (B), the composition of the raw material gas (A) was such that the isobutylene content was 0.8 to

2.8 volume%, the molecular oxygen content was 5 to 13 volume%, the water vapor content was 7 to 35 volume%, and the isobutylene conversion was fluctuated 100%, and the reaction temperature in the reaction of oxidizing isobutylene was 345 to 350°C. The composition of the raw material gas (A) before initiation of supply of a mixed gas (C) after 23 hours have passed from initiation of supply of the mixed gas (B) was such that the isobutylene content was 2.8 volume%, the molecular oxygen content was 8.0 volume%, and the water vapor content was 9.8 volume%, and the isobutylene conversion was 100%.

[0064]

After 23 hours have passed from initiation of supply of the mixed gas (B), a mixed gas (C) (methacrolein content: 1.9 volume%, molecular oxygen content: 7.8 volume%, isobutylene content: 600 volume ppm, water vapor content: 11.0 volume%) prepared by mixing a reaction gas (isobutylene content: 0 volume ppm) extracted from the outlet of the reaction tube for producing methacrolein by the reaction of oxidizing isobutylene, isobutylene, the air, and nitrogen was supplied to the reaction tube for producing methacrylic acid in place of a mixed gas (B). In addition, isobutylene was supplied through an isobutylene supplying line connected on a connecting line which connects the outlet of the reaction tube for producing methacrolein and the inlet of the reaction tube for producing methacrylic acid, the air was supplied through an air supplying line connected on the connecting line, and nitrogen was supplied through a nitrogen supplying line connected on the connecting line. The maximum temperature of the catalyst layer of the catalyst for producing methacrylic acid immediately

after switching with the mixed gas (C) was 320°C. The supply amount of the mixed gas (C) was increased stepwisely over 180 hours from initiation of supply of the mixed gas (C) until the space velocity became 910 h⁻¹ (based on the standard state). The composition of the mixed gas (C) during the period of less than 180 hours from initiation of supply of the mixed gas (C) was methacrolein content: 1.9 to 2.5 volume%, oxygen content: 6.7 to 8.3 volume%, isobutylene content: 550 to 600 volume ppm, and water vapor content: 11.0 to 11.7 volume%, the maximum temperature of the catalyst layer of the catalyst for producing methacrylic acid was 320 to 322°C, and the methacrolein conversion was fluctuated in the range of 98.0 to 98.3%. The maximum temperature of the catalyst layer of the catalyst for producing methacrylic acid at the time point of 180 hours from initiation of supply of the mixed gas (C) was 322°C, and when the methacrolein conversion was obtained by the aforementioned equation, the conversion was found to be 98%. In addition, during the period of 180 hours from initiation of supply of the mixed gas (C), the supply amount of the raw material gas (A) to be supplied to the reaction of oxidizing isobutylene was also increased stepwisely to a space velocity of 1,100 h⁻¹ (based on the standard state). During the period of less than 180 hours from initiation of supply of the mixed gas (C), the composition of the raw material gas (A) was such that the isobutylene content was 2.8 to 3.9 volume%, the molecular oxygen content was 8.0 to 11.0 volume%, the water vapor content was 9.8 to 9.9 volume%, and the isobutylene conversion was fluctuated 99.9 to 100%, and the reaction temperature in the reaction of oxidizing isobutylene was 345°C.

[0065]

Production of methacrylic acid was performed by regulating the content of isobutylene in a mixed gas to be supplied to the reaction tube for producing methacrylic acid by adjusting the isobutylene conversion of the reaction of oxidizing isobutylene and the supply amount of isobutylene to be supplied through the isobutylene supplying line during the period of 2,200 hours after initiation of supply of the mixed gas (C) from 180 hours after initiation of supply of the mixed gas (C) (2,020 hours from the time point when the space velocity of the mixed gas (C) became 910 h^{-1} (based on the standard state)); supplying the mixed gas to the reaction tube for producing methacrylic acid under the condition of a temperature of a heat medium for heating the reaction tube for producing methacrylic acid of 279°C and a space velocity of 910 h^{-1} (based on the standard state) while the content of isobutylene in the mixed gas was made to be in the range of 302 to 1,000 volume ppm. In addition, in the mixed gas which was supplied to the reaction tube for producing methacrylic acid during the period of 2,200 hours after initiation of supply of the mixed gas (C) from 180 hours after initiation of supply of the mixed gas (C), the content of methacrolein was 2.8 to 3.2 volume%, the content of molecular oxygen was 7.8 volume%, and the content of water vapor was 11.4 volume%, and the maximum temperature of the catalyst layer of the catalyst for producing methacrylic acid was in the range of 302 to 322°C . During the period of 2,200 hours after initiation of supply of the mixed gas (C) from 180 hours after initiation of supply of the mixed gas (C), the composition of the raw material gas (A) was such that the content of isobutylene was 4.2 to 4.7 volume%, the content of molecular oxygen was 11 to 12 volume%, and the content of water vapor was 8.4 to 8.9

volume%, and the isobutylene conversion was fluctuated in the range of 98.5 to 99.5%, the adjustment of the isobutylene conversion was performed by regulating the reaction temperature of the reaction of oxidizing isobutylene, and the reaction temperature was between 323 to 334°C. When the methacrolein conversion at the time point when 2,200 hours have passed from initiation of supply of the mixed gas (C) was obtained by the aforementioned equation, the conversion was found to be 93%.

[0066]

Comparative Example 1

A reaction of oxidizing isobutylene was initiated by the same operation as that of Example 1. Into a reaction tube for producing methacrylic acid made of steel having an internal diameter of 30 mm provided with a heat medium bath was filled 2000 ml of the catalyst for producing methacrylic acid obtained in Reference Example 2. A protecting tube (external diameter 4 mm, internal diameter 3 mm) was inserted into the reaction tube for producing methacrylic acid, a multipoint sheathed thermocouple (diameter 1.8 mm) was placed into the protecting tube, and the temperature of a catalyst layer of the catalyst for producing methacrylic acid was measured. The supply of a mixed gas (D) prepared by mixing a reaction gas extracted from the outlet of the reaction tube for producing methacrolein by the reaction of oxidizing isobutylene, the air and nitrogen to the reaction tube for producing methacrylic acid filled with the catalyst for producing methacrylic acid was initiated at a space velocity of 550 h^{-1} (based on the standard state) at a temperature of a heat medium for heating the reaction tube of 280°C. Then, the supply amount of the mixed gas (D) was

increased stepwisely over 5 hours from initiation of supply of the mixed gas (D) until the space velocity became 910 h^{-1} (based on the standard state). The composition of the mixed gas (D) at the time point of 5 hours from initiation of supply of the mixed gas (D) was methacrolein content: 2.5 volume%, oxygen content: 7.8 volume%, isobutylene content: 41 volume ppm, and water vapor content: 11.0 volume%, the maximum temperature of the catalyst layer of the catalyst for producing methacrylic acid was 333°C , and when the methacrolein conversion was obtained by the aforementioned equation, the conversion was found to be 98%. In addition, during the period of 5 hours from initiation of supply of the mixed gas (D), the supply amount of the raw material gas (A) to be supplied to the reaction of oxidizing isobutylene was also increased stepwisely to a space velocity of $1,100 \text{ h}^{-1}$ (based on the standard state). The composition of the raw material gas (A) at the time point of 5 hours from initiation of supply of the mixed gas (D) was such that the isobutylene content was 4.2 volume%, the molecular oxygen content was 11 volume%, the water vapor content was 8.9 volume%, and the isobutylene conversion was 99.9%.

[0067]

Production of methacrylic acid was performed by regulating the content of isobutylene in the resulting reaction gas by adjusting the isobutylene conversion of the reaction of oxidizing isobutylene during the period of 2,200 hours after initiation of supply of the mixed gas (D) from 5 hours after initiation of supply of the mixed gas (D) (2,195 hours from the time point when the space velocity of the mixed gas (D) became 910 h^{-1} (based on the standard state)); supplying a mixed gas prepared by mixing the

reaction gas, the air and nitrogen to the reaction tube for producing methacrylic acid under the condition of a temperature of a heat medium for heating the reaction tube for producing methacrylic acid of 280°C and a space velocity of 910 h⁻¹ (based on the standard state) while the content of isobutylene in the mixed gas was made to be in the range of 41 to 279 volume ppm. In addition, in the mixed gas which was supplied to the reaction tube for producing methacrylic acid during the period of 2,200 hours after initiation of supply of the mixed gas (D) from 5 hours after initiation of supply of the mixed gas (D), the content of methacrolein was 2.8 to 3.6 volume%, the content of molecular oxygen was 7.8 volume%, and the content of water vapor was 11.4 volume%. During the period of 2,200 hours after initiation of supply of the mixed gas (D) from 5 hours after initiation of supply of the mixed gas (D), the composition of the raw material gas (A) was such that the content of isobutylene was 4.2 to 5.4 volume%, the content of molecular oxygen was 11.0 to 12.8 volume%, and the content of water vapor was 7.0 to 8.9 volume%, and the isobutylene conversion was fluctuated in the range of 99.4 to 99.9%, the adjustment of the isobutylene conversion was performed by regulating the reaction temperature of the reaction of oxidizing isobutylene, and the reaction temperature was between 345 to 355°C. When the methacrolein conversion was obtained by the aforementioned equation after 1,973 hours have passed from initiation of supply of the mixed gas (D) (after 1,968 hours have passed from the time point when the space velocity of the mixed gas (D) became 910 h⁻¹ (based on the standard state)), the conversion was found to be 87%. When the methacrolein conversion was obtained by the aforementioned equation after 2,200 hours have passed

from initiation of supply of the mixed gas (D), the conversion was found to be 84%.

What is claimed is:

1. A process for producing methacrylic acid comprising supplying methacrolein, isobutylene and oxygen into a reactor for producing methacrylic acid provided with a catalyst layer containing a catalyst for producing methacrylic acid, and oxidizing the methacrolein in a continuous manner to obtain methacrylic acid, wherein the maximum temperature in the catalyst layer is 330°C or lower, and

wherein at least a part of the methacrolein is contained in a reaction mixture obtained by oxidizing isobutylene with oxygen in the presence of a catalyst for producing methacrolein in a reactor for producing methacrolein containing isobutylene, oxygen, and the catalyst for producing methacrolein, an extraction port of the reactor for producing methacrolein is connected to a supply port of the reactor for producing methacrylic acid with a connecting line, an isobutylene supplying line is connected to the connecting line, and oxidation of methacrolein in the reactor for producing methacrylic acid is performed while isobutylene is supplied to the isobutylene supplying line.

2. The process according to claim 1, wherein the maximum temperature in the catalyst layer is set to 330°C or lower by adjusting a supply amount of the isobutylene.

3. The process according to claim 1 or 2, wherein at least a part of the methacrolein is contained in a reaction mixture obtained by oxidizing isobutylene with oxygen in the presence of a catalyst for producing methacrolein, and at least a part of isobutylene to be supplied into the

reactor for producing methacrylic acid is isobutylene different from unreacted isobutylene contained in the reaction mixture.

4. The process according to any one of claims 1 to 3, wherein oxidation of methacrolein in the reactor for producing methacrylic acid is performed by supplying a mixed gas, the mixed gas containing methacrolein, isobutylene and oxygen and having a content of isobutylene of 50 to 3000 volume ppm, into the reactor for producing methacrylic acid.

5. The process according to any one of claims 1 to 4, wherein the reactor is a fixed bed reactor.

6. The process according to any one of claims 1 to 5, wherein the catalyst for producing methacrylic acid is made of a heteropolyacid compound comprising phosphorus and molybdenum.

7. The process according to claim 6, wherein the heteropolyacid compound further comprises vanadium, at least one element selected from the group consisting of potassium, rubidium, cesium and thallium, and at least one element selected from the group consisting of copper, arsenic, antimony, boron, silver, bismuth, iron, cobalt, lanthanum and cerium.

8. The process according to any one of claims 3 to 7, wherein the catalyst for producing methacrolein is made of a complex oxide containing molybdenum, bismuth and iron.