

DESCRIPTION

METHOD FOR REGENERATING CATALYST FOR PRODUCTION OF
METHACRYLIC ACID AND
5 PROCESS FOR PREPARING METHACRYLIC ACID

Background of the Invention

Technical Field

[0001]

10 The present application claims the Paris Convention priority based on Japanese Patent Application No. 2011-138216 filed on June 22, 2011, the entire content of which is incorporated herein by reference.

The present invention relates to a method for regenerating a catalyst for the production of methacrylic acid by performing a regeneration
15 treatment on a used catalyst (spent catalyst) comprising a heteropolyacid compound containing phosphorus, molybdenum and copper and to a process for preparing methacrylic acid using the regenerated catalyst obtained by the regeneration method.

20 Background Art
[0002]

It is known that catalytic activity of a catalyst for the production of methacrylic acid comprising a heteropolyacid compound containing phosphorus, molybdenum and copper is reduced due to heat load or the like
25 when it is used for a long time in a gas phase catalytic oxidation reaction using methacrolein or the like as a raw material.
[0003]

As a regeneration method of such a used catalyst, there have been proposed methods (see Patent Documents 1-6) for obtaining a regenerated
30 catalyst which comprises a heteropolyacid compound in which the atomic ratio of copper to molybdenum (Cu : Mo) is 0.3 : 12, wherein the methods comprise the steps of mixing the used catalyst, a nitrate ion and an ammonium ion to obtain an aqueous slurry, drying the slurry to obtain a dried catalyst, and then calcining the dried catalyst.

Prior Art Document

Patent Document

[0004]

Patent Document 1: JP-A-2008-80232

5 Patent Document 2: JP-A-2008-86928

Patent Document 3: JP-A-2008-93595

Patent Document 4: JP-A-2009-248034

Patent Document 5: JP-A-2009-248035

Patent Document 6: JP-A-2010-207694

10

Summary of the Invention

Problems to be Solved by the Invention

[0005]

15 However, regenerated catalysts obtained by the conventional
methods are not always satisfactory in the catalytic activity and catalyst life.
[0006]

20 An object of the present invention is to provide a method for
regenerating a catalyst for the production of methacrylic acid, which
satisfactorily restores catalytic activity and catalyst life of a used catalyst
used for the production of methacrylic acid as well as to provide a process for
preparing methacrylic acid at a high yield for a long time by using the
regenerated catalyst obtained by the method.
[0007]

25 The inventors had conducted an intensive research to solve the
above-described problem and accomplished the present invention.
[0008]

More specifically, the present invention has the following
configuration.

30 [1] A method for regenerating a catalyst for the production of
methacrylic acid comprising a heteropolyacid compound containing
phosphorus, molybdenum and copper, wherein the method comprises the
following steps (1) to (3), and wherein the atomic ratio of copper to
molybdenum (Cu : Mo) in the heteropolyacid compound constituting a
regenerated catalyst is from 0.05 : 12 to 0.25 : 12,
35 step (1): mixing a used catalyst used for the production of

methacrylic acid, a nitrate ion, an ammonium ion and water to form an aqueous slurry A in which the atomic ratio of copper to molybdenum (Cu : Mo) has been adjusted to from 0.10 : 12 to 0.50 : 12,

5 step (2): mixing at least a compound containing molybdenum among compounds containing constituent elements of the heteropolyacid compound with water to form an aqueous slurry B in which the atomic ratio of copper to molybdenum (Cu : Mo) has been adjusted to from 0 : 12 to 0.25 : 12, and

10 step (3): mixing the aqueous slurry A obtained in step (1) with the aqueous slurry B obtained in step (2) to form an aqueous slurry C, and then drying and calcining the aqueous slurry C.

 [2] The method according to [1], wherein the heteropolyacid compound further contains at least one element X selected from the group consisting of potassium, rubidium, cesium and thallium, the atomic ratio of the element X to molybdenum (X : Mo) in the heteropolyacid compound
15 constituting the regenerated catalyst is from 0.5 : 12 to 2 : 12, the atomic ratio of the element X to molybdenum (X : Mo) contained in the aqueous slurry A in step (1) is from 2 : 12 to 4 : 12, and the atomic ratio of the element X to molybdenum (X : Mo) contained in the aqueous slurry B in step (2) is from 0 : 12 to 0.5 : 12.

20 [3] The method according to [1] or [2], wherein the aqueous slurry C obtained in step (3) is a slurry obtained by mixing the aqueous slurry A obtained in step (1), the aqueous slurry B obtained in step (2) and a compound containing copper.

25 [4] The method according to [3], wherein the aqueous slurry A, the aqueous slurry B and the compound containing copper are mixed so that the atomic ratio of copper to molybdenum (Cu : Mo) contained in the aqueous slurry C is within the range of from 0.05 : 12 to 0.25 : 12.

30 [5] The method according to any one of [1] to [4], wherein at least one of the aqueous slurry A obtained in step (1) and the aqueous slurry C obtained in step (3) is a slurry subjected to a wet pulverization treatment.

 [6] The method according to any one of [1] to [5], wherein the aqueous slurry C obtained in step (3) is a slurry subjected to a heat treatment at 100°C or more.

35 [7] The method according to any one of [1] to [6], wherein the aqueous slurry A obtained in step (1) contains 0.1 to 3.0 moles of the ammonium ion

per one mole of the nitrate ion.

[8] The method according to any one of [1] to [7], wherein the pH of a liquid phase of the aqueous slurry A obtained in step (1) is 8 or less.

[9] The method according to any one of [1] to [8], wherein the
5 heteropolyacid compound further contains vanadium and at least one
element selected from the group consisting of arsenic, antimony, boron,
silver, bismuth, iron, cobalt, lanthanum and cerium.

[10] A process for preparing methacrylic acid, the process comprising
the steps of:

10 regenerating a catalyst for the production of methacrylic acid by the
regeneration method according to any one of [1] to [9], and

 subjecting a compound selected from the group consisting of
methacrolein, isobutylaldehyde, isobutane and isobutyric acid to a gas phase
catalytic oxidation reaction in the presence of the regenerated catalyst.

15

Effects of the Invention

[0009]

 According to the present invention, catalytic activity and catalyst life
of a used catalyst used for the production of methacrylic acid are
20 satisfactorily restored. Also, methacrylic acid is produced at a high yield for
a long time with the use of the regenerated catalyst obtained by the method.

Detailed Description of the Invention

[0010]

25 Hereinafter, the present invention will be described in detail. A
method for regenerating a catalyst for the production of methacrylic acid of
the present invention comprises subjecting a used catalyst for the production
of methacrylic acid used for the production of methacrylic acid to a
regeneration treatment, whereby a specific regenerated catalyst is obtained.

30 [0011]

 The catalyst for the production of methacrylic acid which can be
regenerated by the regeneration method of the present invention
(hereinafter sometimes referred to as an "object catalyst") may be a catalyst
comprising a heteropolyacid compound containing phosphorus, molybdenum
35 and copper. The catalyst may comprise a free heteropolyacid or a salt of a

heteropolyacid. Among these, a catalyst comprising an acidic salt (a partially neutralized salt) of a heteropolyacid is preferable, and a catalyst comprising an acidic salt of a Keggin type heteropolyacid is more preferable. [0012]

5 Further, the heteropolyacid compound preferably contains at least one element X selected from the group consisting of potassium, rubidium, cesium and thallium, and more preferably contains the element X, vanadium and at least one element (hereinafter referred to as "element Y") selected from the group consisting of copper, arsenic, antimony, boron, silver, bismuth, iron, cobalt, lanthanum and cerium. [0013]

The heteropolyacid compound which constitutes the catalyst for the production of methacrylic acid (object catalyst) preferably has, in the state of a fresh catalyst before use for the production of methacrylic acid, the following composition formula (i):



wherein P, Mo, Cu and V represent phosphorus, molybdenum, copper and vanadium, respectively; X represents at least one element X selected from the group consisting of potassium, rubidium, cesium and thallium; Y represents at least one element (element Y) selected from the group consisting of arsenic, antimony, boron, silver, bismuth, iron, cobalt, lanthanum and cerium; O represents oxygen; a, b, c, d, e and f are numbers satisfying $0 < a \leq 3$, $0 < c \leq 3$, $0 \leq d \leq 3$, $0 \leq e \leq 3$ and $0 \leq f \leq 3$, when b is 12; x is a value determined depending on the oxidation states of other elements; and, in the case where each of X and Y represents two or more elements, a ratio of the total of two or more elements is required to satisfy $0 < e \leq 3$ and $0 < f \leq 3$, when b is 12.

[0014]

In particular, from the viewpoint of a yield of methacrylic acid and catalyst life, the atomic ratio of copper to molybdenum (Cu : Mo) is preferably from 0.01 : 12 to 0.50 : 12 in the composition of the heteropolyacid compound which constitutes the fresh catalyst. Also, from the viewpoint of a yield of methacrylic acid and catalyst life, the element X is preferably contained in the heteropolyacid compound which constitutes the fresh catalyst, and, in such a case, the atomic ratio of the element X to

molybdenum (X : Mo) is preferably from 0.5 : 12 to 2 : 12.

[0015]

The fresh catalyst may be those which are produced by any conventional method, for example, a method comprising the steps of mixing
5 compounds each containing the respective element among the elements described above which constitute the heteropolyacid compound (for example, an oxo acid, an oxo acid salt, an oxide, a nitrate, a carbonate, a bicarbonate, a hydroxide, a halide or an ammine complex of each element), molding the mixture into a desired shape, and calcining the molded mixture.

10 Among compounds containing the respective element, examples of a compound containing phosphorus include phosphoric acid, phosphates and the like; examples of a compound containing molybdenum include molybdic acid, molybdates such as ammonium molybdate, molybdenum oxide, molybdenum chloride and the like; examples of a compound containing
15 copper include copper oxide, copper nitrate, tetraamminecopper dinitrate, copper carbonate, copper hydroxide, copper chloride and the like; examples of a compound containing vanadium include vanadic acid, vanadates (metavanadates) such as ammonium vanadate (ammonium metavanadate), vanadium oxide, vanadium chloride and the like; and examples of a
20 compound containing the element X include 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 hydrogen carbonate and cesium hydrogen
25 carbonate, hydroxides such as potassium hydroxide, rubidium hydroxide and cesium hydroxide, halides such as potassium chloride, rubidium chloride, cesium fluoride, cesium chloride, cesium bromide and cesium iodide; and the like. Examples of a compound containing the element Y include an oxo acid, an oxo acid salt, an oxide, a nitrate, a carbonate, a hydroxide and a halide.

30 [0016]

In general, when the fresh catalyst having the above-described preferable catalyst composition is used for producing methacrylic acid, the catalytic activity may sometimes decrease due to heat load and the like. According to the regeneration method of the present invention, such a used
35 catalyst with decreased catalytic activity is subjected to the regeneration

treatment in which the atomic ratio of copper to molybdenum (Cu : Mo) is adjusted to from 0.05 : 12 to 0.25 : 12 by mixing two kinds of aqueous slurries, and then drying and calcining the mixture. When the Cu : Mo ratio in the regenerated catalyst is from 0.05 : 12 to 0.25 : 12, it is possible to produce the methacrylic acid with satisfactory conversion and selectivity for a long time. Further, in the regeneration method of the present invention, the atomic ratio of the element X to molybdenum (X : Mo) in the regenerated catalyst is preferably from 0.5 : 12 to 2 : 12 from the viewpoints of catalytic activity and catalyst life.

10 [0017]

According to the regeneration method of the present invention, the regenerated catalyst is obtained through steps (1) to (3).

In step (1), an aqueous slurry A is obtained by mixing the used catalyst, a nitrate ion, an ammonium ion and water, and adjusting the atomic ratio of copper to molybdenum (Cu : Mo) in the obtained slurry to from 0.10 : 12 to 0.50 : 12, preferably from 0.20 : 12 to 0.40 : 12. Further, from the viewpoint of effectively restoring the catalytic activity in the regenerated catalyst to be obtained, the atomic ratio of the element X to molybdenum (X : Mo) in the aqueous slurry A is preferably adjusted to from 2 : 12 to 4 : 12, more preferably from 2.5 : 12 to 3.5 : 12. The conversion and selectivity in the production of methacrylic acid using the resulting regenerated catalyst are improved by mixing the nitrate ion and the ammonium ion.

[0018]

25 For supplying the nitrate ion, for example, nitric acid and nitrates such as ammonium nitrate may be used as a nitrate ion source, besides nitrates containing the elements which constitute the object catalyst. For supplying the ammonium ion, for example, ammonia and ammonium salts such as ammonium nitrate, ammonium carbonate, ammonium hydrogen carbonate and ammonium acetate may be used as an ammonium ion source, besides ammonium salts containing the elements which constitute the object catalyst. Preferably, nitrates and ammonium salts containing the elements which constitute the object catalyst are used as the nitrate ion source and the ammonium ion source. More preferably, nitric acid, ammonia and ammonium nitrate are used so as to adjust the ratio of the ammonium ion to

the nitrate ion within the range described below.

[0019]

5 In the aqueous slurry A prepared in step (1), as to the ratio of the ammonium ion to the nitrate ion, the amount of the ammonium ion per mole of the nitrate ion is preferably 0.1 to 3.0 moles, more preferably 0.5 to 2.5 moles in view of effectively restoring the catalytic activity in the regenerated catalyst to be obtained.

[0020]

10 When preparing the aqueous slurry A, the atomic ratio of copper to molybdenum (Cu : Mo) contained in the aqueous slurry A should be adjusted within the above-specified range (Cu : Mo in aqueous slurry A). Specifically, the atomic ratio may be adjusted by adding at least one of a compound containing copper (copper-containing compound) and a compound containing molybdenum (molybdenum-containing compound). An amount of such a
15 compound may be determined so as to keep the atomic ratio of copper to molybdenum (Cu : Mo) in the aqueous slurry A after the addition of the copper-containing compound and/or molybdenum-containing compound within the above-specified range, based on a catalyst composition (kinds and amounts of constituent elements) of the used catalyst. The catalyst
20 compositions of the fresh catalyst and the used catalyst may sometimes be different from each other since molybdenum in the catalyst for the production of methacrylic acid scatters or dissipates due to heat load and the like caused by long period of use of the catalyst in the production of methacrylic acid. Therefore, a catalyst composition (kinds and amounts of
25 constituent elements) of the used catalyst before regeneration is preferably analyzed by fluorescent X-ray analysis, inductively-coupled plasma (ICP) emission spectrometry or the like. When the Cu : Mo ratio in the used catalyst before regeneration is within the above-specified range of Cu : Mo ratio in the aqueous slurry A, neither the copper-containing compound nor
30 the molybdenum-containing compound may be added, or the copper-containing compound and/or the molybdenum-containing compound may be added insofar as the Cu : Mo ratio in the aqueous slurry A is kept within the above-specified range.

[0021]

35 When preparing the aqueous slurry A, the atomic ratio of the

element X to molybdenum (X : Mo) contained in the aqueous slurry A is preferably adjusted within the above-specified range (X : Mo ratio in the aqueous slurry A). Specifically, the atomic ratio may be adjusted by adding at least one of a compound containing the element X (element X-containing
5 compound) and a molybdenum-containing compound. An amount of such a compound may be determined so as to keep the atomic ratio of the element X to molybdenum (X : Mo) in the composition after the addition of the element X-containing compound and/or the molybdenum-containing compound within the above-specified range, based on a catalyst composition of the used
10 catalyst before regeneration, which is detected by the above-described analysis. When the X : Mo ratio in the used catalyst before regeneration is within the above-specified range of X : Mo ratio in the aqueous slurry A, neither the element X-containing compound nor the molybdenum-containing compound may be added, or the element X-containing compound and/or the
15 molybdenum-containing compound may be added insofar as the Cu : Mo ratio and the X : Mo ratio in the aqueous slurry A are kept within the above-specified range.

[0022]

As the molybdenum-containing compound and the copper-containing
20 compound to be mixed in the preparation of the aqueous slurry A, one or more compounds may be suitably selected from the compounds containing molybdenum and the compounds containing copper which are usable for the production of fresh catalyst as described above.

[0023]

Also, when preparing the aqueous slurry A, a compound containing
25 an element constituting the catalyst other than molybdenum and copper may be added if necessary, based on the composition of the used catalyst. As the compound containing an element constituting the catalyst other than molybdenum and copper, one or more compounds may be suitably selected
30 from the compounds containing each element, which are used in the production of fresh catalyst.

[0024]

Deionized water may be usually used as water to be supplied for the
preparation of the aqueous slurry A. The amount of water supplied is
35 usually from 1 to 20 parts by weight based on one part by weight of

molybdenum in the resulting aqueous slurry A, that is, the total weight of molybdenum contained in the used catalyst and molybdenum contained in the molybdenum-containing compound supplied.

[0025]

5 When preparing the aqueous slurry A, the mixing order of each component described above is not particularly limited and may be arbitrarily set.

[0026]

10 When preparing the aqueous slurry A, the used catalyst may be mixed as such or may be thermally pretreated.

[0027]

15 A temperature of the thermal pretreatment of the used catalyst is not particularly limited and is preferably from 350°C to 600°C. Treatment time for the thermal treatment is not particularly limited and is usually from 0.1 to 24 hours, preferably from 0.5 to 10 hours. The thermal pretreatment may be carried out in an atmosphere of oxidizing gas such as oxygen-containing gas or in an atmosphere of non-oxidizing gas such as nitrogen.

[0028]

20 When the used catalyst used in the preparation of the aqueous slurry A is a molded catalyst, the molded catalyst may be used as such or may be previously pulverized by a conventional method, if necessary. When the used catalyst used in the preparation of the aqueous slurry A is subjected to both of the pulverization treatment and the thermal pretreatment, the order of these treatments is not particularly limited, while the pulverization treatment is usually carried out prior to the thermal pretreatment.

[0029]

25 The liquid phase of the aqueous slurry A obtained in step (1) preferably has pH of 8 or less. When pH of the liquid phase of the aqueous slurry A exceeds 8, the catalytic activity may not be satisfactorily restored.

[0030]

30 In step (2), the aqueous slurry B is obtained by mixing at least the compound containing molybdenum among the compounds containing the constituent elements of the heteropolyacid compound consisting the objective catalyst with water so that the atomic ratio of copper to molybdenum (Cu :

Mo) in the resulting slurry is from 0 : 12 to 0.25 : 12.

[0031]

In the preparation of the aqueous slurry B, at least the molybdenum-containing compound is used as starting compounds of the heteropolyacid compound, and the copper-containing compound is used so as to keep the atomic ratio of copper to molybdenum in the compound containing molybdenum (Cu : Mo) within the above-specified range (Cu : Mo ratio in the aqueous slurry B). Accordingly, when the atomic ratio of copper to molybdenum (Cu : Mo) is adjusted to 0 : 12, there is no need to mix the copper-containing compound.

[0032]

As the molybdenum-containing compound and the copper-containing compound supplied in the preparation of the aqueous slurry B, one or more compounds may be suitably selected from the above-described molybdenum-containing compounds and the copper-containing compounds which can be used in the production of the object catalyst.

[0033]

When preparing the aqueous slurry B, a compound containing an element constituting the catalyst other than molybdenum and copper may be added, if necessary. As the compound containing an element constituting the catalyst other than molybdenum and copper, one or more compounds may be suitably selected from the compounds containing each element, which are used in the production of the object catalyst. Among the compounds, a compound containing the element X is preferably added. The atomic ratio of the element X to molybdenum (X : Mo) in the aqueous slurry B is preferably adjusted to from 0 : 12 to 0.5 : 12, more preferably from 0 : 12 to 0.3 : 12.

[0034]

Deionized water may be usually used as water to be supplied in the preparation of the aqueous slurry B. The amount of water mixed is usually from 1 to 20 parts by weight based on one part by weight of molybdenum present in the resulting aqueous slurry B.

[0035]

When preparing the aqueous slurry B, the mixing order of each component described above is not particularly limited and may be arbitrarily

set.

[0036]

In step (3), the aqueous slurry A obtained in step (1) and the aqueous slurry B obtained in step (2) are mixed to obtain an aqueous slurry C. A
5 mixing ratio between the aqueous slurry A and the aqueous slurry B is not particularly limited and may be adjusted so that the atomic ratio of copper to molybdenum (Cu : Mo) in the heteropolyacid compound constituting the finally-obtained regenerated catalyst is from 0.05 : 12 to 0.25 : 12 by taking
10 into account the amounts of molybdenum and copper contained in the aqueous slurry C. Specifically, it is possible to attain the Cu : Mo ratio of from 0.05 : 12 to 0.25 : 12 in the heteropolyacid compound constituting the finally-obtained regenerated catalyst by, for example, adjusting the mixing ratio of the aqueous slurry A and the aqueous slurry B to attain the atomic ratio of copper to molybdenum contained in the aqueous slurry C of from
15 0.05 : 12 to 0.25 : 12 and then drying and calcining the obtained aqueous slurry C.

[0037]

The mixing order, the temperature and the stirring conditions are not particularly limited and may be arbitrarily set, when the aqueous slurry
20 C is prepared.

[0038]

In the preparation of the aqueous slurry C, when mixing the aqueous slurry A with the aqueous slurry B, or when or after the heat treatment described later in this specification is carried out, a compound containing an
25 element constituting the object catalyst and water may be added, if necessary, and the copper-containing compound is preferably added. It is possible to effectively restore the catalytic activity by mixing the compound containing copper in the preparation of the aqueous slurry C. In such a case, the compound containing an element constituting the catalyst in the form of an
30 aqueous suspension is preferably added. The mixing ratio thereof may be suitably selected so that the heteropolyacid compound constituting the finally-obtained regenerated catalyst has a composition which satisfies the above-described formula (i), and that the atomic ratio of copper to molybdenum (Cu : Mo) is from 0.15 : 12 to 0.25 : 12. Specifically, when the
35 aqueous slurry C is obtained by mixing the aqueous slurry A, the aqueous

slurry B and the compound containing copper, for example, it is possible to attain the Cu : Mo ratio of from 0.05 : 12 to 0.25 : 12 in the heteropolyacid compound constituting the finally-obtained regenerated catalyst by adjusting the mixing ratio of the aqueous slurry A, the aqueous slurry B and the compound containing copper within the range by which the atomic ratio of copper to molybdenum (Cu : Mo) contained in the aqueous slurry C is kept to from 0.05 : 12 to 0.25 : 12, and then drying and calcining the obtained aqueous slurry C.

[0039]

10 In the preparation of the aqueous slurry C, the atomic ratio of the element X to molybdenum (X : Mo) is preferably adjusted so that the atomic ratio in the heteropolyacid compound constituting the finally-obtained regenerated catalyst is from 0.5 : 12 to 2 : 12 by taking into account the amounts of molybdenum and the element X contained in the aqueous slurry C. Specifically, it is possible to attain the Cu : Mo ratio of from 0.05 : 12 to 0.25 : 12 and the X : Mo ratio of from 0.5 : 12 to 2 : 12 in the heteropolyacid compound constituting the finally-obtained regenerated catalyst by, for example, adjusting the mixing ratio of the aqueous slurry A and the aqueous slurry B so that the atomic ratio (X : Mo) of the element X to molybdenum contained in the aqueous slurry C is within the range of from 0.5 : 12 to 2 : 12 when the atomic ratio of copper to molybdenum (Cu : Mo) contained in the aqueous slurry C is kept to from 0.05 : 12 to 0.25 : 12, and then drying and calcining the obtained aqueous slurry C. Here, for the purpose that the Cu : Mo ratio and the X : Mo ratio satisfy the above-specified ranges, at least one of the compound containing the element X (element X-containing compound) and the molybdenum-containing compound may be added to the aqueous slurry C as required.

[0040]

30 When newly adding water in the preparation of the aqueous slurry C, deionized water may be usually used as the water to be added.

[0041]

In step (3), the aqueous slurry C is then dried. The drying method is not particularly limited, and a method usually employed in this art field, such as evaporation-to-dryness, spray drying, drum drying and flash drying may be employed. The drying conditions are not particularly limited and

may be suitably selected so as to satisfactorily decrease a water content in the mixed slurry. For example, the drying temperature is usually below 300°C.

[0042]

5 The aqueous slurry C is preferably subjected to a heat treatment at 100°C or more prior to the drying described above since the heat treatment enables to stably obtain methacrylic acid at a high yield for a long time. As the heat treatment, for example, the aqueous slurry C is aged by heating at a temperature of 100°C or more in a closed vessel. When such a heat
10 treatment is performed on the aqueous slurry C, the catalytic activity is effectively restored. An upper limit of the heating temperature in the heat treatment is preferably 200°C or less, more preferably 150°C or less. Heating time in the heat treatment is usually 0.1 hour or more, preferably 2 hours or more, in order to attain a satisfactory effect of restoring the
15 catalytic activity, while it is preferably 20 hours or less from the viewpoint of productivity. When obtaining the aqueous slurry C by mixing the aqueous slurry A, the aqueous slurry B and the compound containing copper, the heat treatment of the aqueous slurry C at 100°C or more may be performed, for example, by employing (A) a method of performing the heat treatment at
20 100°C or more on the mixed slurry of the aqueous slurry A, the aqueous slurry B and the compound containing copper, (B) a method of performing the heat treatment at 100°C or more on the mixed slurry of the aqueous slurry A and the aqueous slurry B, and then adding the compound containing copper, followed by performing heat treatment at 100°C or more on the
25 resulting mixed slurry, or the like.

[0043]

 The dried product obtained after the drying may be molded into a desired shape such as a ring, a pellet, a sphere or a cylinder before calcination or pre-calcination described later, if necessary. The molding
30 may be carried out by a method ordinarily employed in this art field, such as tableting or extrusion molding. For molding, water, a molding aid or a pore-forming agent may be added to the dried product, if necessary. Examples of the molding aid include ammonium nitrate as well as ceramic fiber and glass fiber. In particular, ammonium nitrate functions as a
35 pore-forming agent besides a molding aid.

[0044]

Preferably, the molded catalyst (hereinafter sometimes referred to as a "dried product") obtained by the above-described molding process is subsequently subjected to temperature-humidity conditioning. When the
5 molded catalyst is subjected to the temperature-humidity conditioning before calcination or pre-calcination, a uniform and more stable catalyst is obtained. In particular, the temperature-humidity conditioning is carried out by exposing the molded catalyst to an atmosphere having a temperature of 40°C to 100°C and a relative humidity of 10% to 60% for about 0.5 to 10 hours.

10 The conditioning may be carried out, for example, in a container having controlled temperature and humidity or by blowing a gas having controlled temperature and humidity to the molded catalyst. An air is usually used as an atmosphere gas when carrying out the conditioning, while an inert gas such as nitrogen may be used.

15 [0045]

The dried product obtained after drying is preferably treated (pre-calcined) in an atmosphere of oxidizing gas or non-oxidizing gas at a temperature of about 180°C to 300°C prior to the calcination described below.

[0046]

20 In step (3), the dried product obtained after drying is subsequently calcined. The calcination can be carried out by a method usually used in this art field and the method is not particularly limited. For example, it may be carried out in an atmosphere of oxidizing gas such as oxygen or in an atmosphere of non-oxidizing gas such as nitrogen. A calcination
25 temperature is usually 300°C or more. In order to satisfactorily restore the catalyst life, the calcination is carried out preferably by a multi-step process in an atmosphere of oxidizing gas or non-oxidizing gas, more preferably by a two-step process comprising the first calcination step which is carried out in an atmosphere of oxidizing gas and the second calcination step which is
30 carried out in an atmosphere of non-oxidizing gas.

[0047]

The oxidizing gas used in the calcination process contains an oxidizing material, and examples of such a gas include oxygen-containing gas. When the oxygen-containing gas is used, the concentration of oxygen
35 in the oxygen-containing gas is usually from about 1 to 30% by volume. As

a source of oxygen, an air or pure oxygen may be usually used, and it may be diluted with an inert gas, if necessary. The oxidizing gas may optionally contain water. However, the concentration of water in the oxidizing gas is usually 10% by volume or less. The oxidizing gas is preferably an air.

5 Usually, the calcination in the atmosphere of oxidizing gas is carried out in the stream of the above-described oxidizing gas. A temperature in the calcination carried out in the atmosphere of the oxidizing gas is usually from 360°C to 410°C, preferably from 380°C to 400°C.

[0048]

10 The non-oxidizing gas used in the calcination contains substantially no oxidizing material such as oxygen. Specific examples of the non-oxidizing gas include an inert gas such as nitrogen, carbon dioxide, helium and argon. The non-oxidizing gas may optionally contain water. However, the concentration of water in the non-oxidizing gas is usually 10%
15 by volume or less. In particular, nitrogen gas is preferably used as the non-oxidizing gas. Usually, the calcination in the atmosphere of non-oxidizing gas is carried out in the stream of the above-described non-oxidizing gas. A temperature in the calcination carried out in the atmosphere of the non-oxidizing gas is usually from 420°C to 500°C,
20 preferably from 420°C to 450°C.

[0049]

In the method for regenerating a catalyst for the production of methacrylic acid of the present invention, at least one of the aqueous slurry A and the aqueous slurry C is preferably subjected to a wet pulverization
25 treatment from the viewpoint of effectively restoring catalytic activity and catalyst life.

[0050]

The wet pulverization treatment is a treatment which is performed for pulverizing a solid content in the slurry and is usually performed by
30 using a wet pulverization treatment apparatus. Examples of the wet pulverization treatment apparatus include a ball mill, an oscillating ball mill, a rod mill, a medium stirring type mill, an oscillation rod mill and a jet mill. In the wet pulverization treatment, the pulverization is preferably performed so as to attain a particle diameter of 5.0 μm or less, more
35 preferably 2.0 μm or less. The particle diameter in the present invention

means an average particle diameter of a solid content in an aqueous slurry, and can be obtained, for example, by measuring a volume-basis median diameter with a laser diffraction/scattering type particle size distribution measurement apparatus.

5 [0051]

A solid content concentration in the aqueous slurry before the wet pulverization treatment is preferably 20 to 60 wt.% from the viewpoint of attaining high pulverizing efficiency. In order to satisfy the concentration range, the slurry may be concentrated or diluted, while concentrating
10 conditions and diluting conditions are not particularly limited.
[0052]

The wet pulverization treatment is performed during preparation of at least one of the aqueous slurry A and the aqueous slurry C. From the viewpoint of a degree of restoration of catalyst life among others, only the
15 aqueous slurry A or both of the aqueous slurry A and the aqueous slurry C are preferably subjected to the wet pulverization treatment. In order to subject only the aqueous slurry A to the wet pulverization treatment, for example, in steps (1) to (3), the aqueous slurry A after the wet pulverization treatment and the aqueous slurry B are mixed to obtain the aqueous slurry
20 C; and then the aqueous slurry C is dried and calcined. In order to subject the aqueous slurry A and the aqueous slurry C to the wet pulverization treatment, for example, in steps (1) to (3), the aqueous slurry A after the wet pulverization treatment and the aqueous slurry B are mixed to obtain a mixed slurry; the wet pulverization treatment is performed on the mixed
25 slurry to obtain the aqueous slurry C; and the obtained aqueous slurry is subjected to drying and calcination.
[0053]

When performing the heat treatment at 100°C or more on the aqueous slurry C, the wet pulverization treatment may be performed before
30 the heat treatment or may be performed after the heat treatment. The wet pulverization treatment is preferably performed after the heat treatment.
[0054]

It is possible to obtain the regenerated catalyst having satisfactory catalytic activity and catalyst life as described above. The regenerated
35 catalyst comprises a heteropolyacid compound, like the object catalyst, and

may comprise a free heteropolyacid or the salt of a heteropolyacid. Among these, a catalyst comprising an acidic salt of a heteropolyacid is preferable, and a catalyst comprising an acidic salt of a Keggin type heteropolyacid is more preferable. In the heteropolyacid compound constituting the
5 regenerated catalyst, the atomic ratio of copper to molybdenum (Cu : Mo) is from 0.05 : 12 to 0.25 : 12, and the Cu : Mo ratio is preferably from 0.15 : 12 to 0.25 : 12. Also, the heteropolyacid compound constituting the regenerated catalyst preferably has the composition which satisfies the formula (i), and the atomic ratio of the element X to molybdenum (X : Mo) is
10 preferably from 0.5 : 12 to 2 : 12.
[0055]

In general, the method for regenerating a catalyst for the production of methacrylic acid of the present invention applies to a used catalyst which has been used in the production of methacrylic acid. Further, the
15 regeneration method of the present invention may be applied to, for example, a catalyst which has not been used in the production of methacrylic acid, such as loss powder produced during the production of a fresh catalyst, or a catalyst which does not have desired properties. Excellent effects which are attained in the regeneration of used catalyst are also attained in these cases.
20 [0056]

The process for preparing methacrylic acid according to the present invention comprises subjecting a compound selected from the group consisting of methacrolein, isobutyl aldehyde, isobutane and isobutyric acid (hereinafter sometimes referred to as a "raw material for methacrylic acid")
25 to a gas phase catalytic oxidation reaction in the presence of a catalyst for the production of methacrylic acid which is regenerated by the regeneration method of the present invention. With the use of the regenerated catalyst of the present invention as described above, it is possible to produce methacrylic acid while maintaining high conversion and high selectivity for a
30 long time.
[0057]

Methacrylic acid is usually prepared by charging the catalyst for the production of methacrylic acid in a fixed-bed multitubular reactor, and supplying a starting gas mixture containing oxygen and the raw material for
35 methacrylic acid to the reactor, although a reaction system such as a

fluidized bed or a moving bed may also be used. As an oxygen source, an air or pure oxygen is usually used. Besides oxygen and the raw material for methacrylic acid, the starting gas mixture may contain nitrogen, carbon dioxide, carbon monoxide, water vapor and the like.

5 [0058]

The raw material for methacrylic acid, which is contained in the starting gas mixture, does not necessarily have to be a purified material of high purity. For example, as methacrolein, a methacrolein-containing reaction product gas obtained by a gas phase catalytic oxidization reaction of isobutylene or tert-butyl alcohol may be used without purifying the reaction product gas to high purity methacrolein. The starting gas mixture may contain one raw material for methacrylic acid or two or more raw materials for methacrylic acid.

[0059]

15 The reaction conditions of the method for preparing methacrylic acid may arbitrarily selected depending on the kind of the raw material for methacrylic acid contained in the starting gas mixture, etc. For example, when methacrolein is used as the raw material for methacrylic acid, the reaction is carried out usually under conditions such that a concentration of methacrolein in the starting gas mixture is 1 to 10% by volume, the
20 concentration of water vapor is 1 to 30% by volume, a molar ratio of oxygen to methacrolein is 1 to 5, a space velocity is 500 to 5000 h⁻¹ (based on the normal state), a reaction temperature is 250°C to 350°C, and a reaction pressure is 0.1 to 0.3 MPa. When isobutane is used as a raw material for
25 methacrylic acid, the reaction is carried out usually under conditions such that a concentration of isobutane in the starting gas mixture is 1 to 85% by volume, a water vapor concentration is 3 to 30% by volume, a molar ratio of oxygen to isobutane is 0.05 to 4, a space velocity is 400 to 5000 h⁻¹ (based on the normal state), a reaction temperature is 250°C to 400°C, and a reaction
30 pressure is 0.1 to 1 MPa. When isobutyl aldehyde or isobutyric acid is used as a raw material for methacrylic acid, substantially the same reaction conditions as those employed when methacrolein is used as the raw material are adopted. The space velocity may be determined by dividing an amount of the starting gas mixture passing through the reactor per one hour (L/h) by
35 a catalyst volume (L) in the reactor.

Examples

[0060]

Hereinafter, the present invention is explained in more detail in
5 conjunction with examples, which do not limit the scope of the present
invention in any way.

An air used in the examples contains 3.5% by volume of water
(corresponding to water content of atmosphere), and nitrogen used in the
examples is substantially free of water.

10 [0061]

The catalyst composition analysis and catalyst property evaluation of
the catalysts obtained in the following examples were performed as follows.

[0062]

Catalyst Composition (ratio of elements constituting catalyst)

15 A catalyst composition was determined by analyzing a catalyst by
fluorescent X-ray analysis using a fluorescent X-ray analyzer, ZSX Primus II
manufactured by Rigaku Corporation.

[0063]

Particle Diameter

20 An average particle diameter (a volume-basis median diameter) of a
solid content in a slurry was measured by using a laser diffraction/scattering
type particle size distribution measurement apparatus, LA-920
manufactured by Horiba, Ltd. Water was used as a dispersion medium, and
the measurement was performed at a relative refractive index of 1.80 (value
25 relative to water).

[0064]

Activity Test of Catalyst

Nine grams (9 g) of a catalyst was charged into a glass micro-reactor
having an inner diameter of 16 mm, and a furnace temperature
30 (temperature of furnace for heating micro-reactor) was raised to 355°C.
Subsequently, a starting gas mixture composed of 4% by volume of
methacrolein, 12% by volume of molecular oxygen, 17% by volume of water
vapor and 67% by volume of nitrogen, prepared by mixing methacrolein, air,
steam and nitrogen, was fed to the reactor at a space velocity of 670 h⁻¹, and
35 a reaction was carried out for one hour to artificially deteriorate the catalyst.

Then, after lowering the furnace temperature to 280°C, the starting gas mixture having the same composition as above was fed to the micro-reactor at the same space velocity as above, and the reaction was started. After carrying out the reaction for one hour from the start of the reaction at the furnace temperature of 280°C, an exit gas (gas after reaction) was sampled and analyzed by gas chromatography, and conversion of methacrolein (%), selectivity of methacrylic acid (%) and a yield of methacrylic acid (%) were calculated by the following equations.

$$\text{Conversion (\%)} = [(\text{moles of methacrolein reacted}) / (\text{moles of methacrolein fed})] \times 100$$

$$\text{Selectivity (\%)} = [(\text{moles of methacrylic acid generated}) / (\text{moles of methacrolein reacted})] \times 100$$

$$\text{Yield (\%)} = [\text{conversion (\%)} \times \text{selectivity (\%)}] / 100$$

[0065]

15 Reference Example 1

Preparation of Fresh Catalyst

In 224 kg of ion-exchange water heated to 40°C, 38.2 kg of cesium nitrate [CsNO₃], 27.4 kg of 75 wt.% orthophosphoric acid and 25.2 kg of 70 wt.% nitric acid were dissolved to prepare Liquid α. Separately, 297 kg of ammonium molybdate tetrahydrate [(NH₄)₆Mo₇O₂₄·4H₂O] was dissolved in 330 kg of ion-exchange water heated to 40°C, followed by suspending 8.19 kg of ammonium metavanadate [NH₄VO₃] therein to prepare Liquid β.

[0066]

After Liquid α was dropwise added to Liquid β while stirring and maintaining the temperature of Liquids α and β to 40°C, the mixture was further stirred at 120°C for 5.8 hours in a closed vessel, and then a suspension of 10.2 kg of antimony trioxide [Sb₂O₃] and 10.2 kg of copper nitrate trihydrate [Cu(NO₃)₂·3H₂O] in 23 kg of ion-exchange water was added thereto. Thereafter, the mixture was stirred at 120°C for 5 hours in the closed vessel. Of the resulting slurry, a particle diameter of a solid content was 1.9 μm. The resulting slurry was dried with a spray dryer. To 100 parts by weight of the resulting dried powder, 4 parts by weight of ceramic fibers, 13 parts by weight of ammonium nitrate and 9.7 parts by weight of ion-exchange water were added, and the resulting mixture was kneaded and extrusion-molded into cylinders each having a diameter of 5

mm and a height of 6 mm. The molded product was dried at a temperature of 90°C and a relative humidity of 30% for 3 hours, and then calcined at 435°C in a nitrogen stream for 3 hours and further at 390°C in an air stream for 3 hours. After that, the molded catalyst was recovered and used as a

fresh catalyst.

[0067]

The fresh catalyst comprised a heteropolyacid compound containing phosphorus, molybdenum, vanadium, antimony, copper and cesium at ~~an~~ the atomic ratio of 1.5, 12, 0.50, 0.5, 0.30 and 1.4, respectively. The results of the activity test of the fresh catalyst are shown in Table 1.

[0068]

Reference Example 2

Preparation of Used (Spent) Catalyst

The fresh catalyst prepared in Reference Example 1 was used in a gas phase catalytic oxidation reaction of methacrolein for a predetermined time to give a used catalyst.

The heteropolyacid compound constituting the used catalyst contained phosphorus, molybdenum, vanadium, antimony, copper and cesium at the atomic ratio of 1.3, 9.9, 0.49, 0.5, 0.29 and 1.4, respectively (other than oxygen). The results of the activity test of the used catalyst are shown in Table 1.

[0069]

Example 1

Step (1): Preparation of Aqueous Slurry A1

To 376 g of ion-exchange water, 200 g of the used catalyst obtained in Reference Example 2 was added, followed by stirring. Next, to compensate for the deficient elements of the used catalyst in comparison to the fresh catalyst, 30.6 g of molybdenum trioxide (MoO_3) as a molybdenum source, 2.4 g of 75 wt.% orthophosphoric acid as a phosphorus source, and 0.2 g of ammonium metavanadate as a vanadium source were added, and then an aqueous solution obtained by dissolving 32.6 g of ammonium nitrate (NH_4NO_3) in 108 g of ion-exchange water was added, followed by heating to 70°C. The mixture was kept at the same temperature for one hour. Then, 47.1 g of 25 wt.% aqueous ammonia was added thereto, and the mixture was kept at 70°C for one hour. Thereafter, the mixture was stirred in a closed

vessel at 120°C for 5 hours. The mixture was stirred and then cooled to 40°C. Then, an aqueous solution of 40°C obtained by dissolving 35.7 g of cesium nitrate in 107 g of ion-exchange water was added to the mixture to obtain Aqueous Slurry A1. Of Aqueous Slurry A1, a particle diameter of a solid content was 14.3 μm , a molar ratio of the ammonium ion to the nitrate ion was 1.9, and a liquid phase had pH of 6.1. The atomic ratios of the metal elements, i.e. phosphorus, molybdenum, vanadium, antimony, copper and cesium, contained in Aqueous Slurry A1 were 1.5, 12, 0.50, 0.5, 0.29 and 3.2, respectively, the atomic ratio of copper to molybdenum was 0.29 : 12, and the atomic ratio of cesium to molybdenum was 3.2 : 12.

[0070]

Preparation of Aqueous Slurry A2

Aqueous slurry A1 was diluted by adding ion exchange water to the whole quantity thereof to obtain 950 g of a slurry (solid content concentration: 29 wt.%). The obtained slurry was poured into an alumina container together with 1870 g of alumina balls each having a diameter of 15 mm, a pulverization was carried out by continuously rotating the container with the use of a rotational ball mill at a speed of 53 rpm for 16 hours, and Aqueous Slurry A2 was obtained. Of Aqueous Slurry A2, a particle diameter of a solid content was 1.3 μm , a molar ratio of the ammonium ion to the nitrate ion was 1.9, and a liquid phase had pH of 6.4. The atomic ratios of the metal elements, i.e. phosphorus, molybdenum, vanadium, antimony, copper and cesium, contained in Aqueous Slurry A2 were 1.5, 12, 0.50, 0.5, 0.29 and 3.2, respectively, the atomic ratio of copper to molybdenum was 0.29 : 12, and the atomic ratio of cesium to molybdenum was 3.2 : 12.

[0071]

Step (2): Preparation of Aqueous Slurry B1

In 105 g of ion-exchange water heated to 40°C, 12.9 g of 75 wt.% orthophosphoric acid and 12.3 g of 67.5 wt.% nitric acid were dissolved to prepare Liquid a. Separately, in 165 g of ion-exchange water heated to 40°C, 139 g of ammonium molybdate tetrahydrate was dissolved, and then 3.85 g of ammonium metavanadate was suspended therein to prepare Liquid b. To Liquid a, Liquid b was dropwise added while stirring to obtain Aqueous Slurry B1 containing a heteropolyacid compound. The atomic ratios of the metal elements, i.e. phosphorus, molybdenum and vanadium, contained in

Aqueous slurry B1 were 1.5, 12 and 0.50, respectively, while the ratios of antimony, copper and cesium were all zero (0), and thus the atomic ratio of copper to molybdenum and the atomic ratio of cesium to molybdenum were both 0 : 12.

5 [0072]

Step (3): Preparation of Aqueous Slurry C1

475 g of Aqueous Slurry A2 was taken out and mixed with the whole quantity of Aqueous Slurry B1, and then the mixture was stirred in a closed vessel at 120°C for 5 hours. Then, a suspension of 4.80 g of antimony trioxide and 1.59 g of copper nitrate trihydrate in 3.67 g of ion-exchange water was added to the mixture, and the mixture was further stirred in the closed vessel at 120°C for 5 hours to obtain Aqueous Slurry C1. Of Aqueous Slurry C1, a particle diameter of a solid content was 1.4 μm . The atomic ratios of the metal elements, i.e. phosphorus, molybdenum, vanadium, antimony, copper and cesium, contained in Aqueous Slurry C1 were 1.5, 12, 0.50, 0.5, 0.19 and 1.4, respectively, the atomic ratio of copper to molybdenum was 0.19 : 12, and the atomic ratio of cesium to molybdenum was 1.4 : 12.

[0073]

20 Drying and Calcination of Aqueous Slurry C1

The thus-obtained Aqueous Slurry C1 was dried at 135°C. To 100 parts by weight of the dried product obtained, 2 parts by weight of ceramic fiber, 13 parts by weight of ammonium nitrate and 7 parts by weight of ion-exchange water were added, and the mixture was kneaded and extruded into cylinders each having a diameter of 5 mm and a height of 6 mm. The resulting molded catalyst was dried at a temperature of 90°C and a relative humidity of 30% for 3 hours. After the drying, the catalyst was calcined by maintaining it in an air stream at 220°C for 22 hours, then at 250°C for one hour, then in an air stream at 390°C for 4 hours and further in a nitrogen stream at 435°C for 4 hours, and finally the molded catalyst was recovered to obtain Regenerated Catalyst (R1). The atomic ratios of metal elements, i.e. phosphorus, molybdenum, vanadium, antimony, copper and cesium, contained in Regenerated Catalyst (R1) were 1.5, 12, 0.50, 0.5, 0.19 and 1.4, respectively, the atomic ratio of copper to molybdenum was 0.19 : 12, and the atomic ratio of cesium to molybdenum was 1.4 : 12. The results of activity

test of Regenerated Catalyst (R1) are shown in Table 1.

[0074]

Example 2

Steps (1) and (2): Preparation of Aqueous Slurries A2 and B1

5 Aqueous Slurries A2 and B1 were obtained in the same manner as in Example 1.

[0075]

Step (3): Preparation of Aqueous Slurry C2

10 475 g of Aqueous Slurry A2 was taken out and mixed with the whole quantity of Aqueous Slurry B1, and then the mixture was stirred in a closed vessel at 120°C for 5 hours. Then, a suspension of 4.80 g of antimony trioxide and 3.18 g of copper nitrate trihydrate in 7.34 g of ion-exchange water was added to the mixture, and the mixture was further stirred in the closed vessel at 120°C for 5 hours to obtain Aqueous Slurry C2. Of Aqueous
15 Slurry C2, a particle diameter of a solid content was 1.4 μm . The atomic ratios of the metal elements, i.e. phosphorus, molybdenum, vanadium, antimony, copper and cesium, contained in Aqueous Slurry C2 were 1.5, 12, 0.50, 0.5, 0.24 and 1.4, respectively, the atomic ratio of copper to molybdenum was 0.24 : 12, and the atomic ratio of cesium to molybdenum
20 was 1.4 : 12.

[0076]

Drying and Calcination of Aqueous Slurry C2

 Aqueous Slurry C2 was dried and calcined in the same manner as in Drying and Calcination of Aqueous Slurry C1 of Example 1 to obtain
25 Regenerated Catalyst (R2). The atomic ratios of metal elements, i.e. phosphorus, molybdenum, vanadium, antimony, copper and cesium, contained in Regenerated Catalyst (R2) were 1.5, 12, 0.50, 0.5, 0.24 and 1.4, respectively, the atomic ratio of copper to molybdenum was 0.24 : 12, and the atomic ratio of cesium to molybdenum was 1.4 : 12. The results of activity
30 test of Regenerated Catalyst (R2) are shown in Table 1.

[0077]

Example 3

Steps (1) and (2): Preparation of Aqueous Slurries A2 and B1

35 Aqueous Slurries A2 and B1 were obtained in the same manner as in Example 1.

[0078]

Steps (3): Preparation of Aqueous Slurry C3

475 g of Aqueous Slurry A2 was taken out and mixed with the whole quantity of Aqueous Slurry B1, and then the mixture was stirred in a closed
 5 vessel at 120°C for 5 hours. Then, a suspension of 4.80 g of antimony trioxide and 0.80 g of copper nitrate trihydrate in 1.83 g of ion-exchange water was added to the mixture, and the mixture was further stirred in the closed vessel at 120°C for 5 hours to obtain Aqueous Slurry C3. Of Aqueous
 10 Slurry C3, a particle diameter of a solid content was 1.4 μm . The atomic ratios of the metal elements, i.e. phosphorus, molybdenum, vanadium, antimony, copper and cesium, contained in Aqueous Slurry C3 were 1.5, 12, 0.50, 0.5, 0.16 and 1.4, respectively, the atomic ratio of copper to molybdenum was 0.16 : 12, and the atomic ratio of cesium to molybdenum was 1.4 : 12.

15 [0079]

Drying and Calcination of Aqueous Slurry C3

Aqueous Slurry C3 was dried and calcined in the same manner as in Drying and Calcination of Aqueous Slurry C1 of Example 1 to obtain Regenerated Catalyst (R3). The atomic ratios of metal elements, i.e.
 20 phosphorus, molybdenum, vanadium, antimony, copper and cesium, contained in Regenerated Catalyst (R3) were 1.5, 12, 0.50, 0.5, 0.16 and 1.4, respectively, the atomic ratio of copper to molybdenum was 0.16 : 12, and the atomic ratio of cesium to molybdenum was 1.4 : 12. The results of activity test of Regenerated Catalyst (R3) are shown in Table 1.

25 [0080]

Example 4

Steps (1) and (2): Preparation of Aqueous Slurries A1 and B1

Aqueous Slurries A1 and B1 were obtained in the same manner as in Example 1.

30 [0081]

Step (3): Preparation of Aqueous Slurry C4

Aqueous Slurry A1 was diluted by adding ion-exchange water to the whole quantity thereof to obtain 950 g of a slurry (solid content concentration: 29 wt.%). 475 g of the obtained slurry was taken out and
 35 mixed with the whole quantity of Aqueous Slurry B1, and then the mixture

was stirred in a closed vessel at 120°C for 5 hours. Then, a suspension of 4.80 g of antimony trioxide and 1.59 g of copper nitrate trihydrate in 3.67 g of ion-exchange water was added to the mixture, and the mixture was further stirred in the closed vessel at 120°C for 5 hours to obtain Aqueous Slurry C4.

5 Of Aqueous Slurry C4, a particle diameter of a solid content was 11.4 μm . The atomic ratios of the metal elements, i.e. phosphorus, molybdenum, vanadium, antimony, copper and cesium, contained in Aqueous Slurry C4 were 1.5, 12, 0.50, 0.5, 0.19 and 1.4, respectively, the atomic ratio of copper to molybdenum was 0.19 : 12, and the atomic ratio of cesium to molybdenum

10 was 1.4 : 12.

[0082]

Drying and Calcination of Aqueous Slurry C4

Aqueous Slurry C4 was dried and calcined in the same manner as in Drying and Calcination of Aqueous Slurry C1 of Example 1 to obtain

15 Regenerated Catalyst (R4). The atomic ratios of metal elements, i.e. phosphorus, molybdenum, vanadium, antimony, copper and cesium, contained in Regenerated Catalyst (R4) were 1.5, 12, 0.50, 0.5, 0.19 and 1.4, respectively, the atomic ratio of copper to molybdenum was 0.19 : 12, and the atomic ratio of cesium to molybdenum was 1.4 : 12. The results of activity

20 test of Regenerated Catalyst (R4) are shown in Table 1.

[0083]

Example 5

Steps (1) and (2): Preparation of Aqueous Slurries A2 and B1

Aqueous Slurries A2 and B1 were obtained in the same manner as in

25 Example 1.

[0084]

Step (3): Preparation of Aqueous Slurry C5

475 g of Aqueous Slurry A2 was taken out and mixed with the whole quantity of Aqueous Slurry B1, and then, a suspension of 4.80 g of antimony trioxide and 1.59 g of copper nitrate trihydrate in 3.67 g of ion-exchange

30 water was added to the mixture. Then, the mixture was stirred in a closed vessel at 120°C for 5 hours to obtain Aqueous Slurry C5. Of Aqueous Slurry C5, a particle diameter of a solid content was 1.3 μm . The atomic ratios of the metal elements, i.e. phosphorus, molybdenum, vanadium, antimony,

35 copper and cesium, contained in Aqueous Slurry C3 were 1.5, 12, 0.50, 0.5,

0.19 and 1.4, respectively, the atomic ratio of copper to molybdenum was 0.19 : 12, and the atomic ratio of cesium to molybdenum was 1.4 : 12.

[0085]

Drying and Calcination of Aqueous Slurry C5

5 Aqueous Slurry C5 was dried and calcined in the same manner as in Drying and Calcination of Aqueous Slurry C1 of Example 1 to obtain Regenerated Catalyst (R5). The atomic ratios of metal elements, i.e. phosphorus, molybdenum, vanadium, antimony, copper and cesium, contained in Regenerated Catalyst (R5) were 1.5, 12, 0.50, 0.5, 0.19 and 1.4, respectively, the atomic ratio of copper to molybdenum was 0.19 : 12, and the atomic ratio of cesium to molybdenum was 1.4 : 12. The results of activity test of Regenerated Catalyst (R5) are shown in Table 1.

[0086]

Comparative Example 1

15 Steps (1) and (2): Preparation of Aqueous Slurries A2 and B1

Aqueous Slurries A2 and B1 were obtained in the same manner as in Example 1.

[0087]

Step (3): Preparation of Aqueous Slurry C6

20 475 g of Aqueous Slurry A2 was taken out and mixed with the whole quantity of Aqueous Slurry B1, and then the mixture was stirred at 120°C for 5 hours in a closed vessel. Then, a suspension of 4.80 g of antimony trioxide and 4.77 g of copper nitrate trihydrate in 11.0 g of ion-exchange water was added to the mixture, and the mixture was stirred in the closed vessel at 120°C for 5 hours to obtain Aqueous Slurry C6. Of Aqueous Slurry C6, a particle diameter of a solid content was 1.5 μm . The atomic ratios of the metal elements, i.e. phosphorus, molybdenum, vanadium, antimony, copper and cesium, contained in Aqueous Slurry C6 were 1.5, 12, 0.50, 0.5, 0.29 and 1.4, respectively, the atomic ratio of copper to molybdenum was 0.29 : 12, and the atomic ratio of cesium to molybdenum was 1.4 : 12.

[0088]

Drying and Calcination of Aqueous Slurry C6

Aqueous Slurry C6 was dried and calcined in the same manner as in Drying and Calcination of Aqueous Slurry C1 of Example 1 to obtain Regenerated Catalyst (R6). The atomic ratios of metal elements, i.e.,

phosphorus, molybdenum, vanadium, antimony, copper and cesium, contained in Regenerated Catalyst (R6) were 1.5, 12, 0.50, 0.5, 0.29 and 1.4, respectively, the atomic ratio of copper to molybdenum was 0.29 : 12, and the atomic ratio of cesium to molybdenum was 1.4 : 12. The results of activity test of Regenerated Catalyst (R6) are shown in Table 1.

[0089]

TABLE 1

	Cu : Mo ratio in aqueous slurry (atomic ratio)		Cu : Mo ratio in catalyst (atomic ratio)	Activity test result		
	Aqueous slurry A	Aqueous slurry B		Conversion (%)	Selectivity (%)	Yield (%)
Ref. Ex. 1	---	---	0.30 : 12	90	82	74
Ref. Ex. 2	---	---	0.29 : 9.9	31	84	26
Ex. 1	0.29 : 12	0 : 12	0.19 : 12	94	82	77
Ex. 2	0.29 : 12	0 : 12	0.24 : 12	93	82	76
Ex. 3	0.29 : 12	0 : 12	0.16 : 12	94	82	77
Ex. 4	0.29 : 12	0 : 12	0.19 : 12	93	83	77
Ex. 5	0.29 : 12	0 : 12	0.19 : 12	96	79	76
Comp. Ex. 1	0.29 : 12	0 : 12	0.29 : 12	93	80	74

[0090]

As shown in Table 1, it is found that each of the catalysts obtained in Examples 1 to 5 enables to obtain methacrylic acid at a high yield after the artificial deterioration and to produce methacrylic acid at a satisfactory yield for a long time as compared to the catalyst obtained in Comparative Example 1.

CLAIMS

1. A method for regenerating a catalyst for the production of methacrylic acid comprising a heteropolyacid compound containing
5 phosphorus, molybdenum and copper, wherein the method comprises the following steps (1) to (3), and wherein the atomic ratio of copper to molybdenum (Cu : Mo) in the heteropolyacid compound constituting a regenerated catalyst is from 0.05 : 12 to 0.25 : 12,
step (1): mixing a used catalyst used for the production of
10 methacrylic acid, a nitrate ion, an ammonium ion and water to form an aqueous slurry A in which the atomic ratio of copper to molybdenum (Cu : Mo) has been adjusted to from 0.10 : 12 to 0.50 : 12,
step (2): mixing at least a compound containing molybdenum among compounds containing constituent elements of the heteropolyacid compound
15 with water to form an aqueous slurry B in which the atomic ratio of copper to molybdenum (Cu : Mo) has been adjusted to from 0 : 12 to 0.25 : 12, and
step (3): mixing the aqueous slurry A obtained in step (1) with the aqueous slurry B obtained in step (2) to form an aqueous slurry C, and then drying and calcining the aqueous slurry C.
20
2. The method according to claim 1, wherein
the heteropolyacid compound further contains at least one element X selected from the group consisting of potassium, rubidium, cesium and thallium,
25 the atomic ratio of the element X to molybdenum (X : Mo) in the heteropolyacid compound constituting the regenerated catalyst is from 0.5 : 12 to 2 : 12,
the atomic ratio of the element X to molybdenum (X : Mo) contained in the aqueous slurry A in step (1) is from 2 : 12 to 4 : 12, and
30 the atomic ratio of the element X to molybdenum (X : Mo) contained in the aqueous slurry B in step (2) is from 0 : 12 to 0.5 : 12.
3. The method according to claim 1, wherein
the aqueous slurry C obtained in step (3) is a slurry obtained by
35 mixing the aqueous slurry A obtained in step (1), the aqueous slurry B

obtained in step (2) and a compound containing copper.

4. The method according to claim 3, wherein
the aqueous slurry A, the aqueous slurry B and the compound
5 containing copper are mixed so that the atomic ratio of copper to
molybdenum (Cu : Mo) contained in the aqueous slurry C is within the range
of from 0.05 : 12 to 0.25 : 12.

5. The method according to any one of claims 1 to 4, wherein
10 at least one of the aqueous slurry A obtained in step (1) and the
aqueous slurry C obtained in step (3) is a slurry subjected to a wet
pulverization treatment.

6. The method according to any one of claims 1 to 4, wherein
15 the aqueous slurry C obtained in step (3) is a slurry subjected to a
heat treatment at 100°C or more.

7. The method according to any one of claims 1 to 4, wherein
the aqueous slurry A obtained in step (1) contains 0.1 to 3.0 moles of
20 the ammonium ion per one mole of the nitrate ion.

8. The method according to any one of claims 1 to 4, wherein
the pH of a liquid phase of the aqueous slurry A obtained in step (1) is
8 or less.

9. The method according to any one of claims 1 to 4, wherein
the heteropolyacid compound further contains vanadium and at least
one element selected from the group consisting of arsenic, antimony, boron,
silver, bismuth, iron, cobalt, lanthanum and cerium.

10. A process for preparing methacrylic acid, the process comprising
the steps of:

regenerating a catalyst for the production of methacrylic acid by the
regeneration method according to any one of claims 1 to 4, and
35 subjecting a compound selected from the group consisting of

methacrolein, isobutylaldehyde, isobutane and isobutyric acid to a gas phase catalytic oxidation reaction in the presence of the regenerated catalyst.