

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

5

FIELD OF THE INVENTION

[0001] The present invention relates to a method for regenerating a catalyst for the production of methacrylic acid by subjecting a deteriorated catalyst (spent catalyst) comprising a heteropolyacid compound containing phosphorus, molybdenum and at least one element X selected from the group consisting of potassium, rubidium, cesium and thallium to a regeneration treatment, and a method for producing methacrylic acid using a regenerated catalyst obtained by such a regeneration method.

BACKGROUND ART

15 [0002] It is known that the catalytic activity of a catalysts for producing methacrylic acid comprising a heteropolyacid compound containing phosphorus, molybdenum and at least one element X selected from the group consisting of potassium, rubidium, cesium and thallium is reduced due to heat load or the like, 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 a deteriorated catalyst, JP-A-2008-80232, JP-A-2008-86928 and JP-A-2008-93595 disclose methods for regenerating a deteriorated catalyst comprising the steps of mixing the deteriorated catalyst with a nitrate ion and an ammonium ion to obtain an aqueous slurry, drying the slurry to obtain a dried catalyst and then calcinating the dried catalyst.

25 [0004] However, regenerated catalysts obtained by the conventional methods are not always satisfactory in the catalytic activity.

SUMMARY OF THE INVENTION

[0005] An object of the present invention is to provide a method for regenerating a catalyst for the production of methacrylic acid, which can satisfactorily restore the catalytic activity of such a catalyst.

[0006] Another object of the present invention is to provide a method for preparing methacrylic acid in a high conversion and a high selectivity using a regenerated catalyst obtained by the regeneration method of the present invention.

[0007]

To achieve the above objects, the present invention provides a method for regenerating a catalyst for the production of methacrylic acid comprising a heteropolyacid compound containing phosphorus, molybdenum and at least one element X selected from the group consisting of potassium, rubidium, cesium and thallium, wherein the method comprises following Steps (I) to (III), and an atomic ratio of the element X to molybdenum (X:Mo) in a heteropolyacid compound constituting a regenerated catalyst is from 0.5 : 12 to 2 : 12:

Step (I): mixing a deteriorated catalyst recovered from a production process of methacrylic acid, a nitrate ion, an ammonium ion and water to form aqueous slurry A in which an atomic ratio of the element X to molybdenum (X:Mo) is adjusted from 2 : 12 to 4 : 12;

Step (II): mixing starting compounds of the heteropolyacid compound and water to form aqueous slurry B in which an atomic ratio of the element X to molybdenum (X:Mo) is adjusted from 0 : 12 to 0.5 : 12;

Step (III): mixing aqueous slurry A obtained in Step (I) and aqueous

slurry B obtained in Step (II), and then drying and calcining the mixture.

[0008] In a preferred embodiment, aqueous slurry A obtained in Step (I) contains 0.1 to 3.0 moles of the ammonium ion per one mole of the nitrate ion.

5 [0009] In another preferred embodiment, the liquid phase of aqueous slurry A obtained in Step (I) has pH of 8 or less.

[0010] In a further preferred embodiment, the heteropolyacid compound further comprises vanadium, and at least one element selected from the group consisting of copper, arsenic, antimony, boron, silver, bismuth, iron,
10 cobalt, lanthanum and cerium.

[0011] The present invention also provides a process for preparing methacrylic acid comprising the steps of:

regenerating a catalyst for the production of methacrylic acid by the regeneration method according the present invention, and then

15 subjecting at least one 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.

[0012] When a catalyst for the production of methacrylic acid is regenerated
20 according to the present invention, the catalytic activity can be satisfactorily restored. Also, when a regenerated catalyst obtained by the regeneration method of the present invention is used, methacrylic acid can be produced in a high conversion and a high selectivity.

25 DETAILED DESCRIPTION OF THE INVENTION

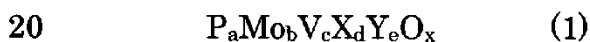
[0013] Hereinafter, the present invention will be described in detail.

[0014] The method for regenerating a catalyst for the production of methacrylic acid of the present invention comprises subjecting a spent

catalyst, that is, a deteriorated catalyst which is recovered from a preparation method of methacrylic acid, to a regeneration treatment, whereby a regenerated catalyst is obtained.

[0015] 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") is a catalyst comprising a heteropolyacid compound containing phosphorus, molybdenum and at least one element X selected from the group consisting of potassium, rubidium, cesium and thallium. 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. Preferably, the heteropolyacid compound further contains vanadium, and at least one element selected from the group consisting of copper, arsenic, antimony, boron, silver, bismuth, iron, cobalt, lanthanum and cerium (hereinafter sometimes refers to as "element Y").

[0016] 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, the following composition formula (1):



wherein P, Mo and V represent phosphorus, molybdenum and vanadium, respectively; X represents at least one element (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 copper, arsenic, antimony, boron, silver, bismuth, iron, cobalt, lanthanum and cerium; O represents oxygen; a, b, c, d and e are numbers satisfying $0 < a \leq 3$, $0 \leq c \leq 3$, $0 < d \leq 3$ and $0 \leq e \leq 3$, when b is 12; and x is a value determined depending on the oxidation states of other elements.

[0017] In particular, the atomic ratio of the element X to molybdenum (X:Mo) is preferably from 0.5 : 12 to 2 : 12 in the composition of the heteropolyacid compound which constitutes the catalyst for the production of methacrylic acid (object catalyst).

- 5 [0018] The catalyst for the production of methacrylic acid (object catalyst) may be produced by any conventional method, for example, a method comprising the steps of mixing 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,
- 10 a nitrate, a carbonate, a bicarbonate, a hydroxide or a halide of each element), molding the mixture into a desired shape, and calcining the molded mixture. 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
- 15 ammonium molybdate, molybdenum oxide, molybdenum chloride and the like; examples of a compound containing vanadium include vanadic acid, vanadates (metavanadate) such as ammonium vanadate (ammonium metavanadate), vanadium oxide, vanadium chloride and the like; and examples of a compound containing the element X include oxides such as
- 20 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 carbonate, hydroxides such as potassium hydroxide, rubidium
- 25 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.

[0019] In general, when the object catalyst having a preferable catalyst composition as described above in a fresh catalyst state before use is used in the production of methacrylic acid, the catalytic activity may sometimes
5 decreases due to heat load and the like. According to the regeneration method of the present invention, such a deteriorated catalyst with decreased catalytic activity is used as a catalyst to be subjected to the regeneration treatment, two kinds of aqueous slurries, that is, slurry A and slurry B, are mixed, and the mixture is dried and calcined, thereby adjusting the atomic
10 ratio of the element X to molybdenum (X:Mo) in the range described above.

[0020] According to the regeneration method of the present invention, a regenerated catalyst is obtained through Steps (I) to (III) described above.

[0021] In Step (I), a deteriorated catalyst, a nitrate ion, an ammonium ion and water are mixed to prepare slurry A with adjusting the atomic ratio of
15 the element X to molybdenum (X:Mo) in the resulting slurry in a range from 2 : 12 to 4 : 12, preferably from 2.5 : 12 to 3.5 : 12. The conversion and selectivity achieved by the resulting regenerated catalyst are improved by mixing the nitrate ion and the ammonium ion in this step.

[0022] For supplying the nitrate ion, for example, nitric acid and nitrates
20 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,
25 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 nitrate ion and the ammonium ion in a range described below.

[0023] In aqueous slurry A prepared in Step (I), 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. When the amount of the ammonium ion is outside the above range, the catalytic activity may be unsatisfactorily restored.

[0024] When aqueous slurry A is prepared, the atomic ratio of the element X to molybdenum contained in aqueous slurry A (X:Mo) should be adjusted in the range described above (the ratio of X to Mo in aqueous slurry A).

Specifically, the atomic ratio may be adjusted by adding at least one of a compound containing element X (element X-containing compound) and a molybdenum compound. The amount of such a compound may be determined by analyzing a catalyst composition (the kinds and amounts of the constituent elements) of the deteriorated catalyst before regeneration with a fluorescent X-ray analysis, an ICP emission spectrometry, etc., and adjusting the atomic ratio of the element X to molybdenum (X:Mo) in a composition after the addition of the element X-containing compound and/or molybdenum compound in the range described above, based on the catalyst composition of the deteriorated catalyst. Usually, the element X-containing compound is added by taking the amount of molybdenum in the deteriorated catalyst into account. The composition of the deteriorated catalyst may sometimes fall within the range of the X:Mo ratio in aqueous slurry A described above, depending on the decreased amounts of the element X and/or molybdenum, even if molybdenum scatters or dissipates due to heat load and the like caused by using the catalyst for a long time in the production of methacrylic acid,. In such a case, neither the element X-containing compound nor molybdenum compound may be added.

[0025] One or more compounds may be suitably selected from the molybdenum-containing compounds and the element X-containing compounds which can be used in the production of the object catalyst described above, as the molybdenum compound and the element

- 5 X-containing compound which are supplied for the preparation of aqueous slurry A.

[0026] When aqueous slurry A is prepared, a compound containing an element constituting the catalyst other than molybdenum and the element X may be added if necessary, based on the composition of the deteriorated catalyst. As the compound containing an element constituting the catalyst
10 other than molybdenum and the element X, one or more compounds may be suitably selected from the compounds containing each element, which are used in the production of the object catalyst.

[0027] Deionized water may be usually used as water to be supplied for the preparation of aqueous slurry A. The amount of water supplied is usually
15 from 1 to 20 parts by weight based on one part by weight of molybdenum in resulting aqueous slurry A, that is, the total weight of molybdenum contained in the deteriorated catalyst and molybdenum contained in the molybdenum compound supplied.

20 [0028] When aqueous slurry A is prepared, the mixing order of each component described above is not particularly limited, and may be arbitrarily set.

[0029] When aqueous slurry A is prepared, the deteriorated catalyst may be mixed as such, or may be thermally pretreated.

25 [0030] A temperature of the thermal pretreatment of the deteriorated catalyst is not particularly limited, and is preferably from 350 to 600°C. The treatment time for the thermal treatment is not particularly limited, and is usually from 0.1 to 24 hours, preferably 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.

[0031] When the deteriorated catalyst used in the preparation of aqueous slurry A is a molded catalyst, the molded catalyst may be used as such, or
5 may be previously pulverized by a conventional method, if necessary. When fibers or the like for reinforcing the catalyst are contained in the molded catalyst (deteriorated molded catalyst), it is preferable to adjust a degree of pulverization so that the fibers or the like are not cut or broken, because the
10 strength of the catalyst may be deteriorated if the fibers or the like are cut or broken.

[0032] When the deteriorated catalyst used in the preparation of aqueous slurry A is subjected to both the pulverization treatment and the thermal pretreatment, the order of these treatments is not particularly limited, while
15 the pulverization treatment is usually carried out prior to thermal pretreatment.

[0033] The liquid phase of aqueous slurry A obtained in Step (I) preferably has pH of 8 or less. When the liquid phase of aqueous slurry A has pH exceeding 8, the catalytic activity may not be satisfactorily restored.

[0034] In Step (II), the starting compounds of the heteropolyacid compound constituting the object catalyst and water are mixed so that the atomic ratio of the element X to molybdenum (X:Mo) in the resulting slurry is adjusted in the range from 0 : 12 to 0.5 : 12, preferably from 0 : 12 to 0.3 : 12 to prepare aqueous slurry B.

[0035] In the preparation of aqueous slurry B, at least a compound containing molybdenum and optionally a compound containing the element X is used as the starting compounds of the heteropolyacid compound, so that the atomic ratio of the element X to molybdenum in the compound containing

molybdenum (X:Mo) is within the range described above (the X to Mo ratio in aqueous slurry B). Accordingly, if the atomic ratio of the element X to molybdenum (X:Mo) is adjusted to 0 : 12, the compound containing the element X is not necessarily mixed.

5 [0036] As the molybdenum compound and the element X-containing compound supplied in the preparation of aqueous slurry B, one or more compounds may be suitably selected from the molybdenum-containing compounds and the element X-containing compounds which can be used in the production of the object catalyst.

10 [0037] When aqueous slurry B is prepared, a compound containing an element constituting the catalyst other than molybdenum and the element X may be added, if necessary. As the compound containing an element forming the catalyst other than molybdenum and the element X, one or more compounds may be suitably selected from the compounds containing each
15 element, which are used in the production of the object catalyst.

[0038] Deionized water may be usually used as water to be supplied in the preparation of 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 resulting aqueous slurry B.

20 [0039] When aqueous slurry B is prepared, the mixing order of each component described above is not particularly limited, and may be arbitrarily set.

[0040] In Step (III), firstly, aqueous slurry A obtained in Step (I) and aqueous slurry B obtained in Step (II) are mixed. The mixing ratio of
25 aqueous slurry A and aqueous slurry B may be adjusted so that the atomic ratio of the element X to molybdenum in the heteropolyacid compound constituting the finally obtained regenerated catalyst (X:Mo) is from 0.5 : 12 to 2 : 12 by taking into account the amounts of molybdenum and the element

X contained in both of the slurries.

[0041] The mixing order, the temperature and the stirring conditions are not particularly limited, and may be arbitrarily set, when aqueous slurry A and aqueous slurry B are mixed.

5 [0042] When aqueous slurry A and aqueous slurry B are mixed, or when or after the mixture of aqueous slurries A and B is aged as described below, a compound containing an element constituting the object catalyst, in particular, a compound containing the element Y may be mixed, if necessary. In such a case, it is preferable to add the compound containing an element
10 constituting the catalyst such as the compound containing element Y, and the like) in the form of an aqueous suspension of such a compound. The amounts thereof may be suitably selected so that the heteropolyacid compound constituting the finally obtained regenerated catalyst has a preferable composition of the object catalyst in the state of a fresh catalyst
15 before use.

[0043] In Step (III), secondly, the mixed slurry obtained by mixing aqueous slurry A and aqueous slurry B is dried. The drying method is not particularly limited, and a method usually used in this art field, such as evaporation to dryness, spray drying, drum drying and flash drying may be
20 employed. The drying conditions are not particularly limited, and they may be suitably selected so as to satisfactorily decrease a water content in the mixed slurry. For example, the drying temperature is usually lower than 300°C.

[0044] The mixed slurry obtained by mixing aqueous slurry A and aqueous
25 slurry B is preferably aged by heating the mixed slurry at a temperature of 100°C or more in a closed vessel, prior to drying described above. When the mixed slurry is aged, the catalytic activity can be effectively restored. The upper limit of the aging temperature is preferably 200°C or less, more

preferably 150°C or less. The aging time is usually 0.1 hour or more, preferably 2 hours or more, in order to satisfactorily restore the catalytic activity, while it is preferably 20 hours or less from the viewpoint of productivity.

- 5 [0045] In Step (III), 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 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 at a calcination temperature of, usually, 10 300°C or higher. Preferably, the calcination is carried out by a multi-step process in an atmosphere of oxidizing gas or non-oxidizing gas in order to satisfactorily restore the catalyst life. More preferably, a two-step process including the first calcination step which is carried out in an atmosphere of oxidizing gas and the second calcination step which is carried out in an 15 atmosphere of non-oxidizing gas is employed.

- [0046] The oxidizing gas used in the calcination process contains an oxidizing material. A preferred example of such a gas is oxygen-containing gas. The concentration of oxygen in the oxygen-containing gas is usually from about 1 to about 30% by volume. As a source of oxygen, an air or pure 20 oxygen may be 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. Usually, the calcination carried out in the atmosphere of the oxidizing gas is carried out in the stream of the 25 oxidizing gas. A temperature in the calcination step carried out in the atmosphere of the oxidizing gas is usually from 360 to 410°C, preferably from 380 to 400°C.

[0047] The non-oxidizing gas used in the calcination process contains

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

10 [0048] Prior to the calcination process, the dried product obtained after drying is preferably heat-treated (pre-calcined) in an atmosphere of oxidizing gas or non-oxidizing gas at a temperature of about 180 to 300°C.

[0049] The dried product obtained after drying may be molded into a desired shape such as a ring, a pellet, a sphere, a cylinder and the like before
15 calcination or pre-calcination, if necessary. The molding may be carried out by any conventional method 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. Example of the molding aid include ammonium nitrate as well as ceramic fiber and glass fiber. In particular, ammonium
20 nitrate is preferably used since it function as a pore-forming agent besides a molding aid.

[0050] Preferably, the molded catalyst obtained by the previous molding process is subsequently subjected to temperature-humidity conditioning. When the molded catalyst is subjected to the temperature-humidity
25 conditioning before calcination or pre-calcination, a more stable catalyst can be obtained. In particular, the temperature-humidity conditioning is carried out by exposing the molded catalyst to an atmosphere having a temperature of 40 to 100°C and a relative humidity of 10 to 60% for about 0.5

to 10 hours. 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.

[0051] The regeneration method of the present invention can produce a regenerated catalyst having a satisfactorily restored catalytic activity. The regenerated catalyst contains 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. 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, and preferably the catalyst has the same preferable composition as that of the object catalyst described above.

[0052] In general, the method for regenerating a catalyst for the production of methacrylic acid of the present invention applies to a deteriorated catalyst which has been used in the production of methacrylic acid. Furthermore, the 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. In such a case, excellent effects can be attained as in the case where a deteriorated catalyst is regenerated.

[0053] The method 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 "raw material for methacrylic acid") 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. Methacrylic acid can be produced in a high conversion and a high selectivity using the regenerated catalyst which is regenerated by the method of the present invention.

[0054] Methacrylic acid is usually prepared by charging the catalyst in a fixed-bed multitubular reactor and supplying a starting gas mixture containing oxygen and the raw material for methacrylic acid, although a reaction system such as a fluidized bed or a moving bed may also be used. As an oxygen source, an air 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, etc.

[0055] The raw material for methacrylic acid may not necessarily be a purified material with a high purity. For example, methacrolein may be a methacrolein-containing reaction product gas obtained by a gas phase catalytic oxidization reaction of isobutylene or tert-butyl alcohol. The starting gas mixture may contain one raw material for methacrylic acid or two or more raw materials for methacrylic acid.

[0056] 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 a raw material, 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 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 to 350°C, and a reaction pressure is 0.1 to 0.3 MPa.

When isobutane is used as a raw material for methacrylic acid, the reaction is carried out usually under conditions such that a concentration of isobutane in the starting gas 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 to 400°C, and a reaction pressure is 0.1 to 1 MPa. When isobutylaldehyde 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.

10

EXAMPLES

[0057] Hereinafter, the present invention is explained in more detail by making reference to the Examples, which do not limit the scope of the present invention in any way.

15 [0058] An air used in the Examples contains 3.5% by volume of water (corresponding to the water content of an atmosphere), and nitrogen used in the Examples is substantially free of water.

[0059] The catalysts obtained in the following Examples were analyzed and evaluated as follows.

20 [0060] A catalyst composition (ratio of elements constituting catalyst) was determined by analyzing a catalyst by fluorescent X-ray analysis using a fluorescent X-ray analyzer, ZSX Primus II manufactured by Rigaku Corporation.

[0061] Activity Test of Catalyst

25 [0062] Nine grams (9 g) of a catalyst were charged into a glass micro-reactor having an inner diameter of 16 mm, and a starting gas 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 a reaction was carried out at a furnace temperature (the temperature of a furnace used for heating the micro-reactor) of 355°C for one hours. Then, the starting gas having the same composition as above
 5 was fed to the micro-reactor at the same space velocity as above, and the reaction was re-started at a furnace temperature of 280°C . After carrying out the reaction for 1 hour from the re-start of the reaction, an exit gas (a gas after reaction) was sampled and analyzed by gas chromatography, and a conversion of methacrolein (%), a selectivity of methacrylic acid (%) and a
 10 yield of methacrylic acid were calculated by the following equations.

$$\text{[0063] Conversion (\%)} = \frac{\text{[(moles of methacrolein reacted)]}}{\text{[(moles of methacrolein fed)]}} \times 100$$

$$\text{[0064] Selectivity (\%)} = \frac{\text{[(moles of methacrylic acid generated)]}}{\text{[(moles of methacrolein reacted)]}} \times 100$$

$$\text{15 [0065] Yield (\%)} = \frac{\text{[(moles of methacrylic acid generated)]}}{\text{[(moles of methacrolein supplied)]}} \times 100$$

REFERENCE EXAMPLE 1

[0066] Preparation of Fresh Catalyst

20 [0067] In 224 kg of ion-exchange water heated to 40°C , 38.2 kg of cesium nitrate $[\text{CsNO}_3]$, 27.4 kg of 75 wt% orthophosphoric acid, and 25.2 kg of 70 wt% nitric acid were dissolved to prepare Liquid a. Separately, 297 kg of ammonium molybdate tetrahydrate $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}]$ was dissolved in 330 kg of ion-exchange water heated to 40°C , followed by suspending 8.19 kg
 25 of ammonium metavanadate $[\text{NH}_4\text{VO}_3]$ therein to prepare Liquid b.

[0068] After Liquid a was dropwise added to Liquid b while stirring and maintaining the temperature of Liquids a and b at 40°C , the mixture was further stirred for 5.8 hours at 120°C in a closed vessel, and then a

suspension of 10.2 kg of antimony trioxide [Sb_2O_3] and 10.2 kg of copper nitrate trihydrate [$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$] 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. The resulting slurry was dried with a spray dryer. To
5 100 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
10 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.

[0069] The fresh catalyst comprised a heteropolyacid compound containing
15 phosphorus, molybdenum, vanadium, antimony, copper and cesium at an atomic ratio of 1.5, 12, 0.50, 0.5, 0.3 and 1.4 respectively. The results of the activity test of the fresh catalyst are shown in Table 1.

REFERENCE EXAMPLE 2

20 [0070] Preparation of Deteriorated (spent) Catalyst

[0071] The fresh catalyst prepared in Reference Example 1 was used in a gas phase catalytic oxidation reaction of methacrolein for a specified time to give a deteriorated catalyst. The heteropolyacid compound constituting the deteriorated catalyst contained phosphorus, molybdenum, vanadium,
25 antimony, copper and cesium at an atomic ratio of 1.3, 9.6, 0.48, 0.5, 0.3 and 1.4 respectively (other than oxygen). The results of the activity test of the deteriorated catalyst are shown in Table 1.

EXAMPLE 1

[0072] Step (I): Preparation of Aqueous Slurry A

[0073] One hundred grams (100 g) of the deteriorated catalyst obtained in Reference Example 2 was added to 200g of ion-exchange water, and the
5 mixture was stirred. Next, to compensate for the deficient elements of the deteriorated catalyst in comparison to the fresh catalyst, 15.8 g of molybdenum trioxide (MoO_3) as a molybdenum source, 1.3 g of 75 wt.% orthophosphoric acid as a phosphorus source, and 0.1 g of ammonium metavanadate as a vanadium source were added thereto, followed by the
10 addition of 17.9 g of cesium nitrate and 27.0 g of ammonium nitrate (NH_4NO_3). The mixture was heated to 70°C , and the mixture was kept at the same temperature for one hour. Then, 6.23 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 to
15 form Aqueous Slurry A1. The molar ratio of the ammonium ion to the nitrate ion in Aqueous Slurry A1 was 1.0 : 1, and the liquid phase of Aqueous Slurry A1 had pH of 2.8. 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, 0.3 and 3.2,
20 respectively, and the atomic ratio of cesium to molybdenum was 3.2 : 12.

[0074] Step (II): Preparation of Aqueous Slurry B

[0075] 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 form Liquid a. Separately, in 165 g of ion-exchange water heated to 40°C ,
25 139 g of ammonium molybdate tetrahydrate was dissolved, and then 3.85 g of ammonium metavanadate was suspended therein to form Liquid b. To Liquid b, Liquid a was dropwise added while stirring and maintaining the temperatures of Liquid a and Liquid b at 40°C to form Aqueous Slurry B1.

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 cesium to molybdenum was 0 : 12.

5 [0076] Step (III): Mixing of Aqueous Slurry A and Aqueous Slurry B .

[0077] The whole quantity of Aqueous Slurry B1 was mixed with the whole quantity of Aqueous Slurry A1, and then the mixture was stirred in a closed vessel at 120°C for 5 hours. Then, to the mixture, the suspension of 4.80 g of antimony trioxide and 4.76 g of copper nitrate trihydrate in 11.0 g of
10 ion-exchange water was added, and the mixture was further stirred in a closed vessel at 120°C for 5 hours. The thus obtained mixed slurry was dried at 135°C. To 100 parts by weight of the dried product obtained, 2 parts by weight of ceramic fiber, 14 parts by weight of ammonium nitrate and 7.4 parts by weight of ion-exchange water were added, and the mixture
15 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, and then calcined catalyst at 390°C in an air stream for 4 hours and further at 435°C in a nitrogen stream for 4 hours, and finally the molded catalyst was
20 recovered to obtain Regenerated Catalyst (1).

[0078] Regenerated Catalyst (1) comprised a heteropolyacid compound, and the atomic ratios of the metal elements other than oxygen, i.e., phosphorus, molybdenum, vanadium, antimony, copper and cesium contained in the heteropolyacid compound were 1.5, 12, 0.50, 0.5, 0.3 and 1.4, respectively,
25 and the atomic ratio of cesium to molybdenum was 1.4 : 12. The results of activity test of Regenerated Catalyst (1) are shown in Table 1.

EXAMPLE 2

[0079] Aqueous Slurry A2 was prepared in the same manner as in Step (I) of Example 1 except that the amount of 25 wt.% aqueous ammonia used in the preparation of Aqueous Slurry A in Step (I) of Example 1 was changed from 6.23 g to 2.74 g. The molar ratio of the ammonium ion to the nitrate ion in Aqueous Slurry A2 was 0.9 : 1, and the liquid phase of Aqueous Slurry A2 had pH of 1.6. The atomic ratios of the metal elements contained in Aqueous Slurry A2 (atomic ratio of cesium to molybdenum) were the same as those in Aqueous Slurry A1 prepared in Example 1.

[0080] Next, Regenerated Catalyst (2) was prepared in the same manner as in Step (III) of Example 1 using Aqueous Slurry A2 and Aqueous Slurry B1, which was prepared in the same manner as in Step (II) of Example 1.

[0081] Regenerated Catalyst (2) comprised a heteropolyacid compound, the atomic ratio of metal elements other than oxygen, i.e., phosphorus, molybdenum, vanadium, antimony, copper and cesium in the heteropolyacid compound were 1.5, 12, 0.50, 0.5, 0.3 and 1.4, respectively, and the atomic ratio of cesium to molybdenum was 1.4 : 12. The results of activity test of Regenerated Catalyst (2) are shown in Table 1.

EXAMPLE 3

[0082] One hundred grams (100 g) of the deteriorated catalyst prepared in Reference Example 2 was added to 200 g of ion-exchange water, and the mixture was stirred. To compensate for the deficient elements of the deteriorated catalyst in comparison to the fresh catalyst, 15.8 g of molybdenum trioxide as a molybdenum source, 1.3 g of 75 wt.% orthophosphoric acid as a phosphorus source, and 0.1 g of ammonium metavanadate as a vanadium source were added thereto, and then the mixture was heated to 40°C. After that, 37.6 g of 25 wt.% aqueous ammonia was added and the mixture was kept at 40°C for one hour, 19.1 g of

67.5 wt.% nitric acid was added and the mixture was kept at 40°C for one hour. Then, an aqueous solution of 17.9 g of cesium nitrate dissolved in 54 g of ion-exchange water, which was heated to 40°C, was added to the mixture, and the mixture was kept at 40°C for 15 minutes to form Aqueous Slurry A3.

5 The molar ratio of the ammonium ion to the nitrate ion in Aqueous Slurry A3 was 1.9 : 1, and the liquid phase of Aqueous Slurry A3 had pH of 6.3. The atomic ratios of the metal elements, i.e., phosphorus, molybdenum, vanadium, antimony, copper and cesium contained in Aqueous Slurry A3 were 1.5, 12, 0.50, 0.5, 0.3 and 3.2, respectively, and the atomic ratio of
10 cesium to molybdenum was 3.2 : 12.

[0083] Next, Regenerated Catalyst (3) was prepared in the same manner as in Step (III) of Example 1, using Aqueous Slurry A3 and Aqueous Slurry B1, which was prepared in the same manner as in Step (II) of Example 1.

[0084] Regenerated Catalyst (3) comprised a heteropolyacid compound, the
15 atomic ratio of metal elements other than oxygen, i.e., phosphorus, molybdenum, vanadium, antimony, copper and cesium in the heteropolyacid compound were 1.5, 12, 0.50, 0.5, 0.3 and 1.4, respectively, and the atomic ratio of cesium to molybdenum was 1.4 : 12. The results of activity test of Regenerated Catalyst (3) are shown in Table 1.

20

COMPARATIVE EXAMPLE 1

[0085] Two hundred grams (200 g) of the deteriorated catalyst prepared in Reference Example 2 was added to 400 g of ion-exchange water, and the mixture was stirred. Next, to compensate for the deficient elements of the
25 deteriorated catalyst in comparison to the fresh catalyst, 31.5 g of molybdenum trioxide as a molybdenum source, 2.7 g of 75 wt.% orthophosphoric acid as a phosphorus source and 0.2 g of ammonium metavanadate as a vanadium source were added thereto, followed by the

addition of 69.2 g of ammonium nitrate. The mixture was heated to 70°C, and kept at the same temperature for one hour. After that, 41.2 g of 25 wt.% aqueous ammonia was added, and the mixture was kept at 70°C for one hour. The mixture was stirred in a closed vessel at 120°C for 5 hours to
5 form Aqueous Slurry C1. The molar ratio of the ammonium ion to the nitrate ion in Aqueous Slurry C1 was 1.7 : 1, and the liquid phase of Aqueous Slurry C1 had pH of 4.2. 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, 0.5, 0.5, 0.3 and 1.4,
10 respectively, and the atomic ratio of cesium to molybdenum was 1.4 : 12. [0086] Aqueous Slurry C1 was dried at 135°C to obtain a dried product. To 100 parts by weight of the dried product, 2 parts by weight of ceramic fiber, 14 parts by weight of ammonium nitrate and 7.4 parts by weight of ion-exchange water were added, and the mixture was kneaded and then
15 extruded into cylinders each having a diameter of 5 mm and a height of 6 mm. The obtained molded catalyst was dried at a temperature of 90°C and a relative humidity of 30% for 3 hours, and then calcined at 390°C in an air stream for 4 hours and further at 435°C in a nitrogen stream for 4 hours. After that, the molded catalyst was recovered to obtain Regenerated Catalyst
20 (C1) for comparison. [0087] Regenerated Catalyst (C1) comprised a heteropolyacid compound, the atomic ratios of the metal elements other than oxygen, i.e., phosphorus, molybdenum, vanadium, antimony, copper and cesium in the heteropolyacid compound were 1.5, 12, 0.5, 0.5, 0.3 and 1.4, respectively, and the atomic
25 ratio of cesium to molybdenum was 1.4 : 12. The results of activity test of Regenerated Catalyst (C1) are shown in Table 1.

TABLE 1

		Aqueous slurry A		Activity test		
		Amount of ammonium ion per mole of nitrate ion (moles)	pH of liquid phase	Conversion (%)	Selectivity (%)	Yield (%)
Ref. Ex. 1	Fresh catalyst	---	---	88	83	73
Ref. Ex. 2	Deteriorated catalyst	---	---	31	84	26
Ex. 1	Regenerated catalyst (1)	1.0	2.8	91	82	74
Ex. 2	Regenerated catalyst (2)	0.9	1.6	90	81	75
Ex. 3	Regenerated catalyst (3)	1.9	6.3	93	82	76
Comp. Ex. 1	Regenerated catalyst (C1)	---	---	78	87	68

CLAIMS

1. A method for regenerating a catalyst for the production of methacrylic acid comprising a heteropolyacid compound containing phosphorus, molybdenum and at least one element X selected from the group consisting of potassium, rubidium, cesium and thallium, wherein the method
5 comprises following Steps (I) to (III), and an atomic ratio of the element X to molybdenum (X:Mo) in a heteropolyacid compound constituting a regenerated catalyst is from 0.5 : 12 to 2 : 12:

Step (I): mixing a deteriorated catalyst recovered from a preparation
10 process of methacrylic acid, a nitrate ion, an ammonium ion and water to form aqueous slurry A in which an atomic ratio of the element X to molybdenum (X:Mo) is adjusted from 2 : 12 to 4 : 12;

Step (II): mixing starting compounds of the heteropolyacid compound and water to form aqueous slurry B in which an atomic ratio of the element
15 X to molybdenum (X:Mo) is adjusted from 0 : 12 to 0.5 : 12;

Step (III): mixing aqueous slurry A obtained in Step (I) and aqueous slurry B obtained in Step (II), and then drying and calcining the mixture.

2. The method according to claim 1, wherein aqueous slurry A obtained in Step (I) contains 0.1 to 3.0 moles of the ammonium ion per one
20 mole of the nitrate ion.

3. The method according to claim 1 or 2, wherein a liquid phase of aqueous slurry A obtained in Step (I) has pH of 8 or less.

4. The method according to any one of claims 1 to 3, wherein the heteropolyacid compound further comprises vanadium, and at least one
25 element selected from the group consisting of copper, arsenic, antimony, boron, silver, bismuth, iron, cobalt, lanthanum and cerium.

5. A process for preparing methacrylic acid comprising the steps of: regenerating a catalyst for the production of methacrylic acid by the

method according to claim 1 and then

subjecting at least one 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

5 catalyst.