

DESCRIPTION

METHOD OF PREPARING CATALYST FOR PRODUCTION OF METHACRYLIC ACID

TECHNICAL FIELD

[0001] The present invention relates to a method for preparing a catalyst for production of methacrylic acid.

BACKGROUND ART

[0002] As a method for preparing a catalyst, the following method has been generally performed. A catalyst raw material is prepared and mixed in a tank and is, if necessary, heat-treated to obtain catalyst precursor particles. Then, by drying the catalyst precursor particles, catalyst precursor dry powder is obtained, and by performing a heat treatment, the catalytic activity is expressed. In many cases, a raw material solution or raw material slurry may be prepared or mixed generally in a batch-type manner. Further, as the tank, a tank, which is provided with a jacket or electric heating coil so as to regulate a temperature within the tank and heat or cool the tank using a heat medium, is used.

[0003] Meanwhile, for example, as a catalyst for production of methacrylic acid used for preparing methacrylic acid by a gas-phase catalytic oxidation of methacrolein with molecular oxygen, a heteropolyacid-based catalyst containing molybdenum and phosphorus has been known. As such a heteropolyacid-based catalyst, proton-type heteropolyacid having a proton as a counter cation, and alkali metal salts of heteropolyacid in which a part of the proton is substituted with alkali metals such as cesium, rubidium, and potassium have been known. Hereinafter, the proton-type heteropolyacid will also be simply referred to as "heteropolyacid", alkali metal salts of proton-type heteropolyacid and/or heteropolyacid will also be referred to as "heteropolyacid(salts)". Further, the proton-type heteropolyacid is water-soluble, whereas the

alkali metal salts of heteropolyacid are generally poorly water-soluble due to a large ionic radius of the cation (Non-Patent Literature 1).

[0004] As a method of preparing a catalyst synthesized by mixing various materials, various methods different in material composition, a method of adding materials, a method of mixing the materials, and the like have been suggested. For example, Patent Literature 1 describes that, when a surface of a catalyst preparation tank is washed with a basic solution and then a catalyst is prepared using the washed catalyst preparation tank, it is possible to efficiently prepare a catalyst by reducing an influence of a residue on a subsequent production batch.

CITATION LIST

PATENT LITERATURE

[0005] Patent Literature 1: WO 2007/004662 A

NON-PATENT LITERATURE

[0006] Non-Patent Literature 1: Ootake Masayuki, Onoda Takeru, Catalyst, Vol. 18, No. 6 (1976)

SUMMARY OF THE INVENTION

PROBLEM TO BE SOLVED BY THE INVENTION

[0007] In a method of producing a catalyst including sediment formation in which the catalyst is obtained by precipitating insoluble salts such as alkali metal salts of heteropolyacid, a solid matter caused by a catalyst raw material may be deposited on a wall surface of a tank used for production. In particular, in a case where a raw material slurry liquid is heated by supplying a high-temperature heating medium in a tank provided with a jacket, a solvent such as water may evaporate from a heating surface and at this time, a solid matter is likely to be precipitated. It is desirable to remove the solid matter in order to produce a homogeneous catalyst. However, it is difficult to suppress generation of the solid matter or remove the solid matter. Further, if

liquids prepared in a plurality of preparation tanks are mixed in a preparation tank on which a solid matter is deposited, the solid matter may be mixed with catalyst precursor particles to be obtained by mixing the prepared liquids. As a measure against the solid matter, a method of washing a tank as described in Patent Literature 1 may be considered. However, in the case of repeatedly producing a catalyst in an industrial manner, if a preparation tank or the like is chemically washed with an alkali each time, there are many problems that a work-load is increased and a process for waste water is needed.

[0008] An object of the invention is to provide a catalyst with which methacrylic acid can be produced at high selectivity. Further, another object of the invention is to provide a method for preparing a catalyst of a consistent quality during repeated preparation of a catalyst.

MEANS FOR SOLVING PROBLEM

[0009] According to the invention, a method for preparing a catalyst for production of methacrylic acid includes: (a) a step of dividing a catalyst raw material into at least two parts and dispersing or dissolving each of the catalyst raw materials within respectively different preparation tanks to obtain catalyst raw material slurries or catalyst raw material solutions as prepared liquids; and (b) a step of mixing the entire catalyst raw material slurries or catalyst raw material solutions within a single mixing tank, in which the preparation tanks are different from the mixing tank.

[0010] According to the invention, a method for producing methacrylic acid includes: preparing a catalyst for production of methacrylic acid by the method according to the invention; filling a reaction tube with the catalyst; and preparing methacrylic acid by a gas-phase catalytic oxidation of at least one selected from the group consisting of methacrolein, isobutylaldehyde, isobutane, and isobutyric acid.

EFFECT OF THE INVENTION

[0011] According to the invention, it is possible to provide a catalyst with which methacrylic acid can be produced at high selectivity. Further, it is possible to provide a method for preparing a catalyst of a consistent quality during repeated preparation of a catalyst.

MODE(S) FOR CARRYING OUT THE INVENTION

[0012] [Method for preparing catalyst for production of methacrylic acid]

According to the invention, a method for preparing a catalyst for production of methacrylic acid includes: (a) a step of dividing a catalyst raw material into at least two parts and dispersing or dissolving each of the catalyst raw materials within respectively different preparation tanks to obtain catalyst raw material slurries or catalyst raw material solutions as prepared liquids (hereinafter, referred to as "preparation step"); and (b) a step of mixing the entire catalyst raw material slurries or catalyst raw material solutions within a single mixing tank (hereinafter, referred to as "mixing step"), in which the preparation tanks are different from the mixing tank.

[0013] In the method according to the invention, the two or more preparation tanks used in the preparation step are different from the mixing tank used in the mixing step. Preferably, a preparation operation in the preparation step may be performed by heating. The slurry or solution within the preparation tank is heated on a heating surface of the preparation tank and evaporated from the heating surface, so that a solid matter is generated. The solid matter is deposited on an inner wall as the heating surface of the preparation tank. If the preparation tank in this state is also used directly as the mixing tank, the matter deposited on the inner wall is used as a nucleus for crystallization, and thus, a deposition amount of crystals is increased. As a result, a finally obtained catalyst has an unstable composition, and the selectivity of methacrylic acid decreases. Since the preparation tanks used in the method according to the

invention are different from the mixing tank, such an influence can be excluded and the selectivity of methacrylic acid can be improved.

[0014] Further, in the method according to the invention, preferably, the same preparation tanks and the same mixing tank may be used directly, and the catalyst may be produced repeatedly at least one time. That is, preferably, after the catalyst is produced by the method according to the invention, the preparation tanks and the mixing tank used in producing the catalyst may be used directly without performing a washing process and the catalyst may be produced repeatedly by the same method. In a method for preparing a catalyst including a preparation step for preparing a plurality of prepared liquids containing a catalyst raw material and then a mixing step for mixing the prepared liquids, a precipitate generated by the mixing of the prepared liquids and a solid matter generated by evaporation of the solution may be deposited on an inner wall surface of the mixing tank. In this regard, the inventors of the invention found that if a prepared liquid is prepared repeatedly using the mixing tank, in which the solid matter remains, as the preparation tank, the solid matter comes into contact with the prepared liquid and thus a substance different in a structure or composition from a target catalyst is generated, so that the performance of the catalyst, particularly the selectivity with respect to a target product, deteriorates. It is deemed that if the solid matter is present as being in contact with the prepared liquid, a concentration of the raw material is changed; the precipitated solid matter serves as a nucleus and thus generation of particles is accelerated; and a particle size distribution or catalyst composition in the prepared liquid is changed and thus the performance of the catalyst deteriorates. Therefore, if a catalyst is produced repeatedly using a single tank as a preparation tank and a mixing tank, when a prepared liquid is newly prepared, the mixing tank, on which a solid matter is deposited, is used as the preparation tank. Thus, the solid matter may come into contact with the prepared liquid and generation of unnecessary impurities may be promoted. However, if a catalyst is produced repeatedly using different tanks as a preparation tank and a

mixing tank, respectively, when a prepared liquid is prepared, the prepared liquid does not come into contact with a solid matter generated in a mixing step. Therefore, the prepared liquid is not mixed with impurities, and thus, even if a catalyst is produced repeatedly without adding a washing step or the like, it is possible to produce a catalyst of a stable quality.

[0015] The method for preparing a catalyst for production of methacrylic acid according to the invention can be suitably used for preparing a catalyst for production of methacrylic acid used when methacrylic acid is produced by a gas-phase catalytic oxidation of at least one selected from the group consisting of methacrolein, isobutylaldehyde, isobutane, and isobutyric acid with molecular oxygen. Hereinafter, embodiments of the invention will be described in detail. However, the following description about the components is one example of the embodiments of the invention, and the invention is not limited thereto.

[0016] ((a) Preparation step)

In the preparation step, a catalyst raw material is divided into at least two parts and each of the catalyst raw materials is dispersed or dissolved within respectively different preparation tanks to obtain catalyst raw material slurries or catalyst raw material solutions as prepared liquids. A method of dividing the catalyst raw material is not particularly limited as long as the catalyst raw material is divided into at least two parts. For example, the catalyst raw material may be divided by a kind of an element. When the catalyst raw material is divided, an amount of each of the catalyst raw materials is not particularly limited. The catalyst raw material may be divided in the same or different amounts. Preparation tanks of the same number as the divided catalyst raw materials are prepared, and the divided catalyst raw materials are put into the preparation tanks, respectively. Then, solvents are respectively put into the preparation tanks to disperse or dissolve the catalyst raw materials. The solvents put into the preparation tanks may be identical to or different from each other.

[0017] In the preparation step, it is preferable to prepare a prepared liquid 1 containing at least

phosphorus and molybdenum and a prepared liquid 2 containing a cation raw material in order to improve the selectivity of methacrylic acid. That is, preferably, a catalyst raw material containing at least phosphorus and molybdenum may be put into a preparation tank 1 and dispersed or dissolved in a solvent to obtain the prepared liquid 1, and a cation raw material as a catalyst raw material may be put into a preparation tank 2 and dispersed or dissolved in a solvent to obtain the prepared liquid 2. Herein, the cation raw material may be at least one selected from the group consisting of compounds containing an alkali metal, compounds containing an alkali earth metal, compounds containing a transition metal, compounds containing a base metal, and compounds containing nitrogen (including compounds containing ammonium ion, compounds containing alkyl ammonium ion, and nitrogen heterocyclic compounds). Examples of the alkali metal may include lithium, sodium, potassium, rubidium, and cesium. Examples of the alkali earth metal may include magnesium, calcium, strontium, and barium. Examples of the solvent may include water, ethyl alcohol, and acetone. Two or more kinds of solvents may be mixed and used, but it is preferable to use at least water.

[0018] Preferably, the cation raw material may include an element X as at least one element selected from the group consisting of alkali metals and thallium. In this case, it is deemed that a heteropolyacid salt contained in the catalyst is formed of heteropolyacid and a monovalent cation and thus may have a cubic structure which is a superior structure as a catalyst for production of methacrylic acid.

[0019] Further, preferably, the heteropolyacid salt contained in the catalyst may be poorly water-soluble. Therefore, preferably, the cation raw material may be a poorly water-soluble heteropolyacid salt. In this case, the heteropolyacid salt considered as being preferable for selective production of methacrylic acid can be selectively present in the catalyst. The poorly water-soluble heteropolyacid salt may be a salt of at least one element selected from potassium, rubidium, cesium, and thallium of heteropolyacids such as 12-molybdophosphoric acid, 12-

tungstophosphoric acid, 12-molybdosilicic acid, 12-tungstosilicic acid, 12-molybdoarsenic acid, and 12-tungstoarsenic acid, heteropolyacids in which molybdenum and tungsten are partially substituted with vanadium, or heteropolyacids in which molybdenum, tungsten, and vanadium are mixed and coordinated (which are collectively referred to as "heteropolyacid" in the invention).

[0020] Further, in order to reuse the catalyst, it is preferable to use a catalyst for production of methacrylic acid after use as at least a part of the cationraw material and obtain at least a part of the prepared liquid 2 by dispersing or dissolving the catalyst for production of methacrylic acid after use in the solvent. In this case, in the preparation step, it is preferable to also prepare a prepared liquid 3 containing an element lost from the catalyst for production of methacrylic acid after usesuch that a catalyst to be obtained has the same elemental composition as acatalyst for production of methacrylic acid before use in order to obtain a catalyst having a methacrylic acid selectivity equivalent to the catalyst for production of methacrylic acid before use. That is, the prepared liquid 3 containing a lost constituent element may be prepared such that the obtained catalyst has the same elemental composition as the catalyst for production of methacrylic acid before use. The prepared liquid 3 thus obtained may be put into the preparation tank 1 after the prepared liquid 1 is prepared, may be put into the preparation tank 2 after the prepared liquid 2 is prepared, or may be put into the mixing tank so as to be mixed with each preparation liquid. Further, even if the catalyst for production of methacrylic acid after use is used, a catalyst having a different elemental composition from the catalyst for production of methacrylic acid before use may be prepared. Further, the catalyst for production of methacrylic acid after use uses a catalyst for production of methacrylic acid prepared by the method according to the invention and refers to a catalyst obtained after methacrylic acid is produced by the method according to the invention.

[0021] Meanwhile, in the preparation step, it is preferable to preparethe prepared liquid 1 in

which an atomic ratio ($X/(Mo+P)$) of the element X as at least one element selected from the group consisting of alkali metals and thallium to a total amount of phosphorus and molybdenum is 0 to 0.5 and the prepared liquid 2 in which an atomic ratio ($X/(Mo+P)$) of the element X to the total amount of phosphorus and molybdenum is 0.1 to 4.0 in order to precipitate a heteropolyacid salt optimum for a catalytic reaction. More preferably, the atomic ratio ($X/(Mo+P)$) of the prepared liquid 1 may be 0 to 0.2. Further, more preferably, the atomic ratio ($X/(Mo+P)$) of the prepared liquid 2 may be 2.0 to 4.0.

[0022] Further, in the preparation step, it is preferable to prepare the prepared liquid 1 in which an atomic ratio ($X/(Mo+P)$) of the element X as at least one element selected from the group consisting of alkali metals and thallium to a total amount of phosphorus and molybdenum is 0 to 0.5 and the prepared liquid 2 which contains at least a catalyst for production of methacrylic acid after use, an ammonium raw material, and water as a solvent and in which an atomic ratio ($X/(Mo+P)$) of the element X to the total amount of phosphorus and molybdenum is 0.1 to 4.0. It can be seen that if the catalyst for production of methacrylic acid after use is used as a catalyst raw material of the prepared liquid 2, the catalyst for production of methacrylic acid after use loses much of molybdenum by decomposition of heteropolyacid during synthesis of methacrylic acid. Therefore, in order to supply much of molybdenum, it is preferable to prepare the prepared liquid 1 in which an atomic ratio ($X/(Mo+P)$) of the element X to the total amount of phosphorus and molybdenum is 0 to 0.5 and then mix the prepared liquid 1 with the prepared liquid 2. More preferably, the atomic ratio ($X/(Mo+P)$) of the prepared liquid 1 may be 0 to 0.2. Further, more preferably, the atomic ratio ($X/(Mo+P)$) of the prepared liquid 2 may be 2.0 to 4.0.

[0023] Preferably, the prepared liquid 1 may also contain vanadium in order to prepare a catalyst having high methacrylic acid selectivity.

[0024] Further, if the catalyst for production of methacrylic acid contains at least one element

Y selected from the group consisting of copper, antimony, arsenic, silicon, boron, silver, bismuth, iron, cobalt, and cerium, in the preparation step, it is preferable to also prepare a prepared liquid 4 containing at least one element Y selected from the group consisting of copper, antimony, arsenic, silicon, boron, silver, bismuth, iron, cobalt, and cerium and mix the prepared liquid 4 in the mixing tank in order to prepare a catalyst having high methacrylic acid selectivity. [0025] Further, if the catalyst for production of methacrylic acid contains antimony, in the preparation step, it is preferable to also prepare a prepared liquid 5 containing antimony and then mix the prepared liquid 5 in the mixing tank. Antimony may be used as a heteroatom of heteropolyacid, but preferably, antimony may be present as being carried by the heteropolyacid salt in the present catalyst. Therefore, it is preferable to separately prepare antimony in the prepared liquid 5 so as to be then mixed.

[0026] Further, an oxidizer may be used to adjust an oxidation state of the catalyst for production of methacrylic acid. In this case, in the preparation step, it is preferable to also prepare a prepared liquid 6 containing an oxidizer and then mix the prepared liquid 6 in the mixing tank in order to optimize the oxidation number of the catalyst and thus improve an oxidation reaction characteristic. Examples of the oxidizer may include hypochlorous acid, chlorous acid, chloric acid, perchloric acid, halogen, permanganate, cerium ammonium nitrate, chromic acid, dichromic acid, peroxide, and the like. One of them may be used alone, or two or more of them may be used together.

[0027] In the preparation tank 1, it is preferable to perform stirring when the catalyst raw material is dispersed or dissolved in the solvent. Further, preferably, the prepared liquid 1 prepared in the preparation tank 1 may be an aqueous solution or water-soluble slurry containing heteropolyacid in order to improve the selectivity. The preparation tank 1 may be heated preferably to 70 to 150°C, more preferably to 75 to 125°C, and still more preferably to 80 to 100°C to prepare the prepared liquid 1 in the form of an aqueous solution or water-soluble

slurry containing heteropolyacid. When a temperature within the preparation tank 1 is set to 70°C or higher, a reaction rate can be improved. Further, when a temperature within the preparation tank 1 is set to 150°C or lower, heteropolyacid having a target structure can be obtained.

[0028] Further, when the aqueous solution or water-soluble slurry containing heteropolyacid is prepared in the preparation tank 1, it is preferable to prevent evaporation of the solvent. For example, if the preparation tank 1 has a structure in which an upper part is open to the atmosphere and allows steam to volatilize, a lid provided with an exhaust duct may be installed at the upper part of the preparation tank 1 and a device of which a condenser is connected to the exhaust duct to circulate a condensed liquid may be installed. Further, a lid without an exhaust duct may be installed to prevent steam from being open to the atmosphere.

[0029] Further, preferably, a retention time of the prepared liquid 1 after preparation in the preparation tank 1 may be 6 minutes or longer and 900 minutes or shorter. When the retention time is 6 minutes or longer, synthesis of heteropolyacid is sufficiently carried out. Further, when the retention time is 900 or less, synthesis of heteropolyacid sufficiently reaches the equilibrium. The retention time may be in the range of more preferably 60 minutes or longer to 300 minutes or shorter, still preferably 80 minutes or longer to 250 minutes or shorter, and particularly preferably 100 minutes or longer to 200 minutes or shorter.

[0030] In the preparation tank 2, it is preferable to perform stirring when the catalyst raw material is dispersed or dissolved in the solvent. When the prepared liquid 2 is prepared, a temperature within the preparation tank 2 may be preferably 0 to 80°C and more preferably 10 to 40°C. Since the temperature is set in the above-described range, the catalyst raw material is sufficiently dissolved in the solvent. Further, when the temperature is 80°C or lower, the performance of the catalyst can be improved. Although the reason is not clear, it is deemed that when the temperature is higher than 80°C, an element state of the dissolved catalyst raw

material is changed by pyrolysis, and thus, a catalyst slurry required for the mixing step may not be obtained.

[0031] ((b) Mixing step)

All of at least two catalyst raw material slurries or catalyst raw material solutions prepared in the preparation step are mixed in a single mixing tank. The mixing tank used in the invention is different from the preparation tanks used in the preparation step. A liquid transfer method from each of the preparation tanks to the mixing tank is not particularly limited. For example, if both of the prepared liquid 1 and the prepared liquid 2 are transferred to the mixing tank, the prepared liquid 1 and the prepared liquid 2 may be separately transferred to the mixing tank or may be simultaneously transferred to the mixing tank. Further, if a plurality of prepared liquids is put into the mixing tank while the prepared liquids are mixed in the mixing tank, a time required to put each of the prepared liquids can be freely selected.

[0032] In the mixing step, at least two or more prepared liquids are mixed in the mixing tank. However, for example, if antimony is used as a catalyst raw material, the prepared liquid 1 containing at least phosphorus and molybdenum, the prepared liquid 2 containing acation raw material, and the prepared liquid 4 containing antimony can be mixed in the mixing tank.

[0033] In particular, it is preferable to put the prepared liquid 1 into the mixing tank and then put the prepared liquid 2 into the mixing tank. Further, it is preferable to perform stirring when each of the prepared liquids is put into the mixing tank. When the prepared liquids are mixed in the mixing tank, it is preferable to perform the mixing at a maintained temperature of 20 to 120°C since it is possible to generate a desired deposit by mixing the prepared liquids. The temperature may be in the range of more preferably 30 to 110°C, still more preferably 40 to 105°C, and particularly preferably 50 to 100°C. Further, at a temperature of lower than 20°C, the dissolved catalyst component may be out of the solubility range. Thus, it can be

precipitated again. Therefore, when the prepared liquids are mixed, a deposit of a desired catalyst component may not be generated. A temperature control may be performed in the preparation tank 1 before the prepared liquid 1 is put into the mixing tank, or may be performed in the mixing tank after the prepared liquid 1 is put into the mixing tank and before the prepared liquid 2 is put into the mixing tank. Further, when the prepared liquid 1 is put into the mixing tank, the prepared liquid 1 may be put into the mixing tank while a temperature of the preparation tank 1 is controlled using a heat exchanger so as to reach a target temperature for putting the prepared liquid 2. As a heating medium, cooling water, an ethylene glycol aqueous solution, hot water, steam, and the like may be used. In order to prevent the catalyst component from being fixed on a heat transfer surface, it is preferable to use hot water as a heating medium.

[0034] Further, when the catalyst raw material slurries or catalyst raw material solutions are mixed in the mixing tank, it is preferable to prevent evaporation of the solvent. For example, if the mixing tank has a structure in which an upper part is open to the atmosphere and allows steam to volatilize, a lid provided with an exhaust duct may be installed at the upper part of the mixing tank and a device of which a condenser is connected to the exhaust duct to circulate a condensed liquid may be installed. Further, a lid without an exhaust duct may be installed to prevent steam from being open to the atmosphere.

[0035] A mixing time within the mixing tank may be preferably 60 minutes or longer and 320 minutes or shorter. Since the mixing time is 60 minutes or longer, it is possible to homogeneously mix the prepared liquids. Further, since the mixing time is 320 minutes or shorter, it is possible to reduce a processing time. The mixing time may be in the range of more preferably 120 minutes or longer to 280 minutes or shorter, still preferably 140 minutes or longer to 240 minutes or shorter, and particularly preferably 160 minutes or longer to 220 minutes or shorter. Further, the mixing time refers to a time period from when two or more of the prepared liquids 1

and 2 and the rest of the catalyst raw material are put into the mixing tank and come into contact with each other to when a pH control is completed using an ammonium raw material and the entire catalyst raw material is completely mixed. For example, if the prepared liquid 2 or the rest of the catalyst raw material is put into the mixing tank after the prepared liquid 1 is put into the mixing tank, the time when the prepared liquid 2 or the rest of the catalyst raw material is put into the mixing tank is considered as a time of starting the mixing, and if the prepared liquid 1 and the prepared liquid 2 are simultaneously put into the mixing tank, the time when they are simultaneously put into the mixing tank is considered as a time of starting the mixing.

[0036] Further, when the prepared liquids are mixed in the mixing tank, it is preferable to adjust a pH between 0.5 and 7 by further adding an ammonium raw material in order to stabilize a heteropolyacid structure. The pH may be in the range of more preferably 1.5 to 3.5 and still more preferably 2 to 3. Further, the pH is a value obtained by measuring a slurry obtained through the mixing step with Castany-ACTpH meter D-21(trade name, manufactured by HORIBA, Ltd.). Examples of the ammonium raw material may include urea, ammonium salts or ammonia. Examples of the ammonium salts may include ammonium bicarbonate, ammonium carbonate, ammonium nitrate, ammonium phosphate, and the like. One of them may be used alone, or two or more of them may be used together.

[0037] Then, if operations such as aging, concentration, and cooling are needed, an aging step, a concentration step, and a cooling step may be appropriately performed. Although these steps may be performed within the mixing tank, if a solid matter is deposited during these steps, it is preferable to perform the steps using a concentration tank, an aging tank, and a cooling tank, respectively. If the aging step is performed, for example, the mixed liquid may be heated in the aging tank so as to be aged. Preferably, the aging step may be performed by heating for 30 minutes or longer. A temperature for the aging step may be preferably 80 to 103°C. Although it is not necessary to perform the aging step, if the mixed liquid is in the form of

slurry containing deposited particles, the particles can be grown by performing this step and thus stabilized.

[0038] Then, if necessary, a drying step, a molding step, and a heat-treatment step may be performed to prepare a catalyst.

[0039] (Drying step)

In a drying step, the mixing liquid containing the entire catalyst raw material and obtained from the mixing step may be dried to thereby obtain a catalyst dry matter. Conditions such as a drying method or a drying temperature are not particularly limited, and may be suitably selected depending on a shape or a size of a desired dry matter. Examples of the drying method may include a drying method using a box-shaped dryer, a drum drying method, an air-current drying method, an evaporation drying method, and a spray drying method. The drying temperature may be set to, for example, 120 to 500°C and preferably 140 to 400°C. The drying step may be performed until the slurry or solution is dried and hardened.

[0040] (Molding step)

Before a heat-treatment step to be described later is performed to the catalyst dry matter obtained from the above-described drying step, a molding step for molding the catalyst dry matter to thereby obtain a catalyst molding may be performed. A molding method is not particularly limited, and a dry molding method and a wet molding method may be applied. Examples of the molding method may include, tableting, press molding, extrusion molding, and granulation. Also, a shape of the catalyst molding is not particularly limited, and may include, for example, a cylindrical shape, a ring shape, and a spherical shape. Further, during the molding step, it is preferable to perform the molding step without adding a carrier or the like to the catalyst dry matter. However, if necessary, for example, additives such as graphite or talc may be added. If the carrier is used, a kind of the carrier is not particularly limited.

[0041] (Heat-treatment step)

In a heat-treatment step, the catalyst dry matter or the catalyst molding is heat-treated, and thus, the catalytic activity may be expressed. In the heat-treatment step, a heat treatment may be performed under the flow of at least one of air or inert gas. However, it is preferable to perform the heat treatment under the flow of an oxygen-containing gas such as air. Herein, the inert gas refers to a gas that does not inhibit catalytic activity, and may include, for example, nitrogen, a carbon dioxide gas, helium, argon, and the like. One of them may be used alone, or two or more of them may be mixed and used together.

[0042] A shape of a heat-treatment container is not particularly limited. However, it is preferable to use a tubular heat-treatment container having a cross-sectional area of 2 cm² or more and 100 cm² or less. The maximum temperature for the heat treatment may be preferably 300°C or higher and more preferably 320°C or higher. Since the maximum temperature for the heat treatment is 300°C or higher, a leaving component contained in the catalyst may sufficiently leave. Further, the leaving component refers to an anion component contained in the catalyst rawmaterial or an additive added during the molding step. Further, the maximum temperature for the heat treatment may be preferably 700°C or lower and more preferably 500°C or lower. Since the maximum temperature for the heat treatment is 700°C or lower, it is possible to suppress decomposition of the catalyst.

[0043] [Catalyst for production of methacrylic acid]

The catalyst prepared by the method according to the invention is particularly suitable as a catalyst for production of methacrylic acid used for preparing methacrylic acid by a gas-phase catalytic oxidation of methacrolein with molecular oxygen. Preferably, the catalyst prepared by the method according to the invention may have an elemental composition except oxygen as represented by the following Formula (1).

[0044] $\text{Mo}_a\text{P}_b\text{V}_c\text{Cu}_d\text{A}_e\text{B}_f\text{Z}_g\text{O}_h(1)$

In Formula (1), Mo, P, V, Cu, and O are symbols for elements of molybdenum,

phosphorus, vanadium, copper, and oxygen, respectively. A denotes at least one kind of element selected from the group consisting of silicon, titanium, germanium, arsenic, antimony, and cerium, B denotes at least one kind of element selected from the group consisting of bismuth, zirconium, silver, iron, zinc, chromium, magnesium, cobalt, manganese, barium, cerium, and lanthanum, and Z denotes at least one kind of element selected from the group consisting of potassium, rubidium, and cesium. Further, a, b, c, d, e, f, g, and h denote atomic ratios of the respective elements. When a is 12, b is 0.5 to 3, c is 0.01 to 3, d is 0.01 to 2, e is 0 to 3, f is 0 to 3, and g is 0.01 to 3. Further, h is an atomic ratio of oxygen required to satisfy an atomic value of the nucleic element. Furthermore, this elemental composition is calculated from an input amount of the raw material. Herein, e may be preferably 0.1 to 3.

[0045] [Method for producing methacrylic acid]

Preferably, the catalyst prepared by the method according to the invention may be used as a catalyst molding or a catalyst support in a fixed bed, but may be used as granules in a fluid bed. Methacrylic acid may be produced by filling a reaction tube with the catalyst for production of methacrylic acid according to the invention, and preparing methacrylic acid by a gas-phase catalytic oxidation of at least one selected from the group consisting of methacrolein, isobutylaldehyde, isobutane, and isobutyric acid. Hereinafter, embodiments of production of methacrylic acid using the catalyst according to the invention will be described.

[0046] To be specific, methacrylic acid is prepared by bringing at least one selected from the group consisting of methacrolein, isobutylaldehyde, isobutane, and isobutyric acid, a raw material gas containing molecular oxygen, and the catalyst according to the invention into contact with one another. This reaction may be carried out in a fixed bed. A catalyst layer may include a single layer or may include two or more layers. Further, in the case of a high catalytic activity, a radical reaction may occur at an inlet portion for the raw material gas in a fixed bed reactor and a temperature may be increased by heat of the reaction, and thus, the

operation may not be stably performed. Therefore, at the inlet portion, there may be used the catalyst mixed and diluted with a stable substance having no catalytic activity. In this case, the catalyst layer may include two layers, and the catalyst may be diluted for use on an inlet side of a reaction gas. Otherwise, a dilution ratio of the catalyst may be gradationally changed, and the catalyst layer may include two or more layers. Further, a mixture of the catalyst prepared by the method according to the invention and other additives may be used.

[0047] A concentration of at least one selected from the group consisting of methacrolein, isobutylaldehyde, isobutane, and isobutyric acid in the rawmaterial gas is not particularly limited, and may be preferably 1 to 20 vol% and more preferably 3 to 10 vol%. These raw materials may contain impurities in a small amount.

[0048] A concentration of the molecular oxygen in the raw material gas may be preferably 0.4 to 4 mol and more preferably 0.5 to 3 mol with respect to 1 mol of at least one selected from the group consisting of methacrolein, isobutylaldehyde, isobutane, and isobutyric acid. Further, air may be preferable as a source for the molecular oxygen in view of economic efficiency. If necessary, a gas enriched in the molecular oxygen by adding pure oxygen to the air may be used.

[0049] The raw material gas may be a gas obtained by diluting at least one selected from the group consisting of methacrolein, isobutylaldehyde, isobutane, and isobutyric acid and the molecular oxygen source with an inert gas such as nitrogen and a carbon dioxide gas. Further, water vapor may be added to the raw material gas. Since the reaction is carried out in the presence of the water vapor, it is possible to obtain methacrylic acid with higher selectivity. A concentration of the water vapor in the raw material gas may be preferably 0.1 to 50 vol% and more preferably 1 to 40 vol%.

[0050] A contact time between the raw material gas and the catalyst prepared by the method according to the invention may be preferably 1.5 to 15 seconds and more preferably 2 to 5 seconds. A reaction pressure may be preferably 0.1 MPaG(atmospheric pressure) to 1 MPaG.

A reaction temperature may be preferably 200 to 450°C and more preferably 250 to 400°C.

EXAMPLES

[0051] Hereinafter, the invention will be described in detail with reference to Examples and Comparative Examples, but the invention is not limited thereto. In Examples, the term "part" means a part by mass. An analysis of the raw material gas and the product was conducted using gas chromatography. As a result of gas chromatography, the methacrylic acid selectivity was obtained by the following equation.

[0052] Methacrylic acid selectivity (%) = $(B/A) \times 100$

In the equation, A denotes a carbon number of the entire reaction product, and B denotes a carbon number of the produced methacrylic acid.

[0053] [Example 1]

((a) Preparation step)

In a preparation tank 1, 100 parts of molybdenum trioxide, 7.8 parts of ammonium metavanadate, 8.0 parts of a 85 mass% phosphoric acid aqueous solution, 2.1 parts of a 60 mass% arsenic acid aqueous solution, and 5.6 parts of copper (II) nitratetrihydrate were dissolved in 400 parts of pure water. The mixture was increased in temperature to 95°C with stirring, and while a temperature of the liquid was maintained at 95°C, the mixture was stirred for 150 minutes. A water-soluble slurry obtained as such was used as a prepared liquid 1. Further, in a preparation tank 2, 8.5 parts of cesium bicarbonate was added to 20 parts of pure water and stirred to dissolve the cesium bicarbonate. The liquid thus obtained was used as a prepared liquid 2.

[0054] ((b) Mixing step)

The prepared liquid 1 was put into a mixing tank prepared separately from the preparation tanks 1 and 2, and a temperature of the liquid was maintained at 95°C. In the

mixing tank, four baffle plates were installed, and the prepared liquid 2 was added while the prepared liquid 1 was stirred using a rotary stirrer. Then, stirring continued 15 minutes. Then, a solution in which 15 parts of ammonium carbonate was dissolved in 24 parts of pure water was added. Then, stirring continued 15 minutes. Herein, a pH of the slurry was 2.9. Further, the preparation tank 1, the preparation tank 2, and the mixing tank were carefully washed before use, and thus, used without any solid matter deposited therein. In the mixing tank, a mixing time from when addition of the prepared liquid 2 started to when ammonium carbonate was added and stirring was ended was 190 minutes.

[0055] Then, the slurry obtained from the mixing step was transferred to a concentration tank and concentrated at 100°C. Further, the concentrated slurry was transferred to a cooling tank and cooled to 40°C. Then, a spray drying process was performed to the cooled slurry to thereby obtain dry powder. The dry powder was molded, and the catalyst molding was put into a cylindrical firing container made of quartz glass and having an inner diameter of 3 cm. Under the flow of air, the temperature was increased by 10°C/h, and a firing process was performed at 380°C for 15 hours, so that a catalyst was obtained. An elemental composition of the catalyst except oxygen was represented by $\text{Mo}_{1.2}\text{P}_{1.2}\text{V}_{1.2}\text{Cu}_{0.4}\text{As}_{0.2}\text{Cs}_{0.8}$. Further, the elemental composition of the catalyst was calculated from an input amount of the raw material.

[0056] A reaction tube was filled with the obtained catalyst, and a raw material gas consisting of methacrolein of 5 vol%, oxygen of 10 vol%, water vapor of 30 vol%, and nitrogen of 55 vol% was allowed to pass through the tube at a reaction temperature of 300°C for a contact time of 3.6 seconds. A product was collected and analyzed by gas chromatography to thereby calculate methacrylic acid selectivity. A result thereof is shown in Table 1.

[0057] [Example 2]

A catalyst was prepared by the same method as Example 1 by directly using the preparation tank 1, the preparation tank 2, and the mixing tank used for preparation of the

catalyst in Example 1 without performing a washing process thereto. This catalyst was used to produce methacrylic acid, and methacrylic acid selectivity was calculated. Further, in the mixing tank, a mixing time from when addition of the prepared liquid 2 started to when ammonium carbonate was added and stirring was ended was 180 minutes. A pH of the slurry thus obtained was 2.5. A result thereof is shown in Table 1. Further, after the prepared liquid 1 from the preparation tank 1 was put into the mixing tank, an inner wall surface of the preparation tank 1 was observed. As a result, deposition of a solid matter was seen. Further, after the contents were taken out of the mixing tank, an inner wall surface of the mixing tank was observed. As a result, deposition of a solid matter derived from the slurry obtained in the mixing step was seen.

[0058] [Example 3]

The same method as Example 1 was performed up to the washing step by directly using the preparation tank 1, the preparation tank 2, and the mixing tank used for preparation of the catalyst in Example 2 without performing a washing process thereto. Further, in the mixing tank, a mixing time from when addition of the prepared liquid 2 started to when ammonium carbonate was added and stirring was ended was 190 minutes. A pH of the slurry thus obtained was 2.9. Then, the slurry was cooled in the mixing tank to 40°C without performing a concentration process. A catalyst was prepared by the same method as Example 1 except the above description. This catalyst was used to produce methacrylic acid, and methacrylic acid selectivity was calculated. A result thereof is shown in Table 1. Further, after the prepared liquid 1 from the preparation tank 1 was put into the mixing tank, an inner wall surface of the preparation tank 1 was observed. As a result, deposition of a solid matter was seen. Further, after the contents were taken out of the mixing tank, an inner wall surface of the mixing tank was observed. As a result, deposition of a solid matter derived from the slurry obtained in the mixing step was seen.

[0059] [Comparative Example 1]

A prepared liquid 1 and a prepared liquid 2 were prepared in the same manner as Example 1. Further, a preparation tank 1, a preparation tank 2, and a mixing tank were carefully washed before use in the same manner as Example 1, and thus, used without any solid matter deposited therein. Then, the prepared tank 1 was used as a mixing tank. While the prepared liquid 1 was accommodated therein, a temperature of the liquid was maintained at 95°C. Then, the prepared liquid 2 was added thereto with stirring for 15 minutes. Then, a solution in which 15 parts of ammonium carbonate was dissolved in 24 parts of pure water was dropwise added with stirring for 15 minutes. Then, a cesium salt of heteropolyacid was precipitated. A pH of the obtained slurry was 2.6. Further, in the mixing tank, a mixing time from when addition of the prepared liquid 2 started to when ammonium carbonate was added and stirring was ended was 120 minutes. Then, a catalyst was prepared by the same method as Example 1. This catalyst was used to produce methacrylic acid, and methacrylic acid selectivity was calculated. A result thereof is shown in Table 1.

[0060] [Comparative Example 2]

A catalyst was prepared by the same method as Comparative Example 1 by directly using the preparation tank 1 and the preparation tank 2 used for preparation of the catalyst in Comparative Example 1 without performing a washing process thereto. This catalyst was used to produce methacrylic acid, and methacrylic acid selectivity was calculated. Further, in a mixing tank, a mixing time from when addition of the prepared liquid 2 started to when ammonium carbonate was added and stirring was ended was 180 minutes. A pH of the obtained slurry was 2.3. A result thereof is shown in Table 1. Further, after the contents were taken out of the preparation tank 1, an inner wall surface of the preparation tank 1 was observed. As a result, deposition of a solid matter derived from a slurry obtained during a previous preparation was seen.

[0061] [Example 4]

((a) Preparation step)

In a preparation tank 1, 100 parts of molybdenum trioxide, 7.8 parts of ammonium metavanadate, 6.8 parts of a 85 mass% phosphoric acid aqueous solution, 5.1 parts of antimony trioxide, and 5.6 parts of copper (II) nitratetrihydrate were dissolved in 400 parts of pure water. The mixture was increased in temperature to 95°C with stirring, and while a temperature of the liquid was maintained at 95°C, the mixture was stirred for 180 minutes. Then, the temperature of the liquid was set to 50°C, and a water-soluble slurry obtained as such was used as a prepared liquid 1. Further, in a preparation tank 2, 8.5 parts of cesium nitrate was added to 20 parts of pure water and stirred at 50°C to dissolve the cesium nitrate. The liquid thus obtained was used as a prepared liquid 2.

[0062] ((b) Mixing step)

The prepared liquid 1 was put into a mixing tank prepared separately from the preparation tanks 1 and 2, and a temperature of the liquid was maintained at 50°C. In the mixing tank, four baffle plates were installed, and the prepared liquid 2 was added while the prepared liquid 1 was stirred using a rotary stirrer. Then, 25.3 parts of a 25 mass% ammonia aqueous solution was added thereto. Further, a solution in which 4.2 parts of iron nitrate was dissolved in 3.0 parts of pure water was dropwise added, and stirring continued 15 minutes. Herein, a pH of the slurry was 3.2. In the mixing tank, a mixing time from when addition of the prepared liquid 2 started to when the iron acetate solution was added and stirring was ended was 200 minutes. Further, the preparation tank 1, the preparation tank 2, and the mixing tank were carefully washed before use, and thus, used without any solid matter deposited therein.

[0063] Then, a catalyst was prepared by the same method as Example 1. This catalyst was used to produce methacrylic acid, and methacrylic acid selectivity was calculated. Further, an elemental composition of the obtained catalyst except oxygen was represented by

$\text{Mo}_{12}\text{P}_1\text{V}_{1.2}\text{Cu}_{0.4}\text{Sb}_{0.3}\text{Fe}_{0.3}\text{Cs}_{0.8}$. Further, the elemental composition of the catalyst was calculated from an input amount of the raw material. A result thereof is shown in Table 1.

[0064] [Example 5]

A catalyst was prepared by the same method as Example 4 by directly using the preparation tank 1, the preparation tank 2, and the mixing tank used for preparation of the catalyst in Example 4 without performing a washing process thereto. This catalyst was used to produce methacrylic acid, and methacrylic acid selectivity was calculated. Further, in the mixing tank, a mixing time from when addition of the prepared liquid 2 started to when the iron nitratesolution was added and stirring was ended was 200 minutes. A pH of the slurry thus obtained was 3.7. A result thereof is shown in Table 1. Further, after the prepared liquid 1 from the preparation tank 1 was put into the mixing tank, an inner wall surface of the preparation tank 1 was observed. As a result, deposition of a solid matter was seen. Further, after the contents were taken out of the mixing tank, an inner wall surface of the mixing tank was observed. As a result, deposition of a solid matter derived from the slurry obtained in the mixing step was seen.

[0065] [Example 6]

The same method as Example 4 was performed up to the washing step by directly using the preparation tank 1, the preparation tank 2, and the mixing tank used for preparation of the catalyst in Example 5 without performing a washing process thereto. In the mixing tank, a mixing time from when addition of the prepared liquid 2 started to when the iron nitratesolution was added and stirring was ended was 200 minutes. A pH of the slurry thus obtained was 3.7. Then, the slurry was cooled in the mixing tank to 40°C without performing a concentration process. A catalyst was prepared by the same method as Example 4 except the above description. This catalyst was used to produce methacrylic acid, and methacrylic acid selectivity was calculated. A result thereof is shown in Table 1. Further, after the prepared

liquid 1 from the preparation tank 1 was put into the mixing tank, an inner wall surface of the preparation tank 1 was observed. As a result, deposition of a solid matter was seen. Further, after the contents were taken out of the mixing tank, an inner wall surface of the mixing tank was observed. As a result, deposition of a solid matter derived from the slurry obtained in the mixing step was seen.

[0066] [Comparative Example 3]

A prepared liquid 1 and a prepared liquid 2 were prepared in the same manner as Example 4. Further, a preparation tank 1, a preparation tank 2, and a mixing tank were carefully washed before use in the same manner as Example 4, and thus, used without any solid matter deposited therein. Then, the prepared tank 1 was used as a mixing tank. While the prepared liquid 1 was accommodated therein, a temperature of the liquid was set to 50°C. Then, the prepared liquid 2 was added thereto with stirring for 15 minutes. Then, 25.3 parts of a 25 mass% ammonia aqueous solution was added. Further, a solution in which 4.2 parts of iron nitrate was dissolved in 3.0 parts of pure water was dropwise added. In the mixing tank, a mixing time from when addition of the prepared liquid 2 started to when the iron nitrate solution was added and stirring was ended was 150 minutes. Herein, a pH of the slurry was 3.6. Then, a catalyst was prepared by the same method as Example 4. This catalyst was used to produce methacrylic acid, and methacrylic acid selectivity was calculated. A result thereof is shown in Table 1.

[0067] [Comparative Example 4]

A catalyst was prepared by the same method as Comparative Example 3 by directly using the preparation tank 1 and the preparation tank 2 used for preparation of the catalyst in Comparative Example 3 without performing a washing process thereto. This catalyst was used to produce methacrylic acid, and methacrylic acid selectivity was calculated. In a mixing tank, a mixing time from when addition of the prepared liquid 2 started to when the iron nitrate solution

was added and stirring was ended was 150 minutes. A pH of the obtained slurry was 3.7. A result thereof is shown in Table 1. Further, after the contents were taken out of the preparation tank 1, an inner wall surface of the preparation tank 1 was observed. As a result, deposition of a solid matter derived from a slurry obtained during a previous preparation was seen.

[0068] [Example 7]

((a) Preparation step)

In a preparation tank 1, 98 parts of a catalyst for production of methacrylic acid after use as the catalyst of Example 4 for calculation of methacrylic acid selectivity for about 1000 hours was dispersed in 400 parts of pure water. The mixture was increased in temperature to 95°C with stirring, and while a temperature of the liquid was maintained at 95°C, the mixture was stirred for 150 minutes. A water-soluble slurry obtained as such was used as a prepared liquid 1. Further, in a preparation tank 2, 20 parts of molybdenum trioxide and 1.1 parts of cesium bicarbonate were added to 20 parts of pure water and dispersed therein with stirring. The liquid thus obtained was used as a prepared liquid 2.

[0069] ((b) Mixing step)

The prepared liquid 1 was put into a mixing tank prepared separately from the preparation tanks 1 and 2, and a temperature of the liquid was maintained at 95°C. In the mixing tank, four baffle plates were installed, and the prepared liquid 2 was added while the prepared liquid 1 was stirred using a rotary stirrer. Then, stirring continued for 15 minutes. Then, a solution in which 15 parts of ammonium plate was dissolved in 24 parts of pure water was added. Then, stirring continued for 15 minutes. Herein, a pH of the slurry was 1.9. In the mixing tank, a mixing time from when addition of the prepared liquid 2 started to when ammonium carbonate was added and stirring was ended was 190 minutes. Then, a catalyst was prepared by the same method as Example 1. This catalyst was used to produce methacrylic acid, and methacrylic acid selectivity was calculated. Further, an elemental

composition of the obtained catalyst except oxygen was represented by $\text{Mo}_{12}\text{P}_1\text{V}_{1.2}\text{Cu}_{0.4}\text{Cs}_{0.8}$.

Further, the elemental composition of the catalyst was calculated from an input amount of the raw material. A result thereof is shown in Table 1.

[0070] [Table 1]

[Table 1]

	Preparation tank 1		Mixing tank			Selectivity
	Temperature [°C]	Retention time [min]	Temperature [°C]	Retention time [min]	pH	[%]
Example 1	95	150	95	190	2.9	82.1
Example 2	95	150	95	180	2.5	82.3
Example 3	95	150	95	190	2.9	83.0
Comparative Example 1	95	150	95	120	2.6	80.1
Comparative Example 2	95	150	95	180	2.3	78.9
Example 4	95	180	50	200	3.2	85.3
Example 5	95	180	50	200	3.7	85.4
Example 6	95	180	50	200	3.7	85.1
Comparative Example 3	95	180	50	150	3.6	81.5
Comparative Example 4	95	180	50	150	3.7	80.7
Example 7	95	150	95	190	1.9	81.2

[0071] In Example 1, the prepared liquids 1 and 2 were prepared in the preparation tanks 1 and 2, respectively, and then mixed in the mixing tank different from the preparation tanks. Consequently, as shown in Comparative Example 1, the catalyst having higher selectivity than the catalyst prepared using the preparation tank 1 as a mixing tank could be prepared.

[0072] In Examples 2 and 3, the catalyst was prepared by directly using the preparation tank 1, the preparation tank 2, and the mixing tank used in Example 1 and deposition of a solid matter on the inner wall surface of the preparation tank 1 was seen. However, even when a catalyst was produced repeatedly, the selectivity was not decreased and the catalyst could be stably prepared. Meanwhile, in Comparative Example 2, the same preparation tanks used in Comparative Example 1 were used directly and the preparation tank 1 was used as a mixing tank. Therefore, a solid matter derived from the slurry was deposited on the inner wall surface of the preparation tank 1. It is deemed that the catalyst could not be stably prepared by an influence of the deposited solid matter and the selectivity was decreased accordingly.

[0073] In Example 4, the prepared liquids 1 and 2 were prepared in the preparation tanks 1 and 2, respectively, and then mixed in the mixing tank different from the preparation tanks. Consequently, as shown in Comparative Example 3, the catalyst having higher selectivity than the catalyst prepared using the preparation tank 1 as a mixing tank could be prepared.

[0074] Also, in Example 5, the catalyst was prepared by directly using the preparation tank 1, the preparation tank 2, and the mixing tank used in Example 4 and deposition of a solid matter on the inner wall surface of the preparation tank 1 was seen. However, even when a catalyst was produced repeatedly, the selectivity was not decreased and the catalyst could be stably prepared. Meanwhile, in Comparative Example 4, the same preparation tanks used in Comparative Example 3 were used directly and the preparation tank 1 was used as a mixing tank. Therefore, a solid matter derived from the slurry was deposited on the inner wall surface of the preparation tank 1. It is deemed that the catalyst could not be stably prepared by an influence of the

deposited solid matter and the selectivity was decreased accordingly.

[0075] This application claims the benefit of Japanese Patent Application No. 2013-188195 filed on September 11, 2013, the disclosures of which are incorporated herein by reference.

[0076] Although the invention has been described with reference to the embodiments and Examples, the invention is not limited to the above-described embodiments and Examples. The configuration or details of the invention may be changed or modified, as can be understood by those skilled in the art, within the scope of the invention.

INDUSTRIAL APPLICABILITY

[0077] The method for preparing a catalyst for production of methacrylic acid according to the invention makes it possible to repeatedly prepare a catalyst having high methacrylic acid selectivity in a stable manner and is thus useful for industrial use.

CLAIMS

1. A method for preparing a catalyst for production of methacrylic acid, comprising:
 - (a) a step of dividing a catalyst raw material into at least two parts and dispersing or dissolving each of the catalyst raw materials within respectively different preparation tanks to obtain catalyst raw material slurries or catalyst raw material solutions as prepared liquids; and
 - (b) a step of mixing the entire catalyst raw material slurries or catalyst raw material solutions within a single mixing tank,wherein the preparation tanks are different from the mixing tank.
2. The method for preparing a catalyst for production of methacrylic acid according to claim 1, wherein in the step (a), a prepared liquid 1 containing at least phosphorus and molybdenum and a prepared liquid 2 containing a cationraw material are prepared.
3. The method for preparing a catalyst for production of methacrylic acid according to claim 2, wherein the cationraw material includes an element X as at least one element selected from the group consisting of alkali metals and thallium.
4. The method for preparing a catalyst for production of methacrylic acid according to claim 2 or 3, wherein at least a part of the prepared liquid 2 is obtained by dispersing or dissolving a catalyst for production of methacrylic acid after use.
5. The method for preparing a catalyst for production of methacrylic acid according to claim 4, wherein in the step (a), a prepared liquid 3 containing an element lost from the catalyst for production of methacrylic acid after use is also prepared such that a catalyst to be obtained has the same elemental composition as a catalyst for production of methacrylic acid before use.

6. The method for preparing a catalyst for production of methacrylic acid according to claim 2, wherein the cationraw material is a poorly water-soluble heteropolyacid salt.
7. The method for preparing a catalyst for production of methacrylic acid according to any one of claims 2 to 6, wherein the prepared liquid 1 also contains vanadium.
8. The method for preparing a catalyst for production of methacrylic acid according to any one of claims 2 to 7, wherein in the step (a), a prepared liquid 4 containing at least one element Y selected from the group consisting of copper, antimony, arsenic, silicon, boron, silver, bismuth, iron, cobalt, and cerium is also prepared.
9. The method for preparing a catalyst for production of methacrylic acid according to any one of claims 2 to 8, wherein in the step (a), a prepared liquid 5 containing antimony is also prepared.
10. The method for preparing a catalyst for production of methacrylic acid according to any one of claims 2 to 9, wherein in the step (a), a prepared liquid 6 containing an oxidizer is also prepared.
11. The method for preparing a catalyst for production of methacrylic acid according to claim 1, wherein in the step (a), the prepared liquid 1 in which an atomic ratio ($X/(Mo + P)$) of the element X as at least one element selected from the group consisting of alkali metals and thallium to a total amount of phosphorus and molybdenum is 0 to 0.5 and the prepared liquid 2 in which an atomic ratio ($X/(Mo+P)$) of the element X to the total amount of phosphorus and

molybdenum is 0.1 to 4.0 are prepared.

12. The method for preparing a catalyst for production of methacrylic acid according to claim 1, wherein in the step (a), the prepared liquid 1 in which an atomic ratio ($X/(Mo+P)$) of the element X as at least one element selected from the group consisting of alkali metals and thallium to a total amount of phosphorus and molybdenum is 0 to 0.5 and the prepared liquid 2 which contains at least a catalyst for production of methacrylic acid after use, an ammonium raw material, and water as a solvent and in which an atomic ratio ($X/(Mo+P)$) of the element X to the total amount of phosphorus and molybdenum is 0.1 to 4.0 are prepared.

13. The method for preparing a catalyst for production of methacrylic acid according to any one of claims 2 to 12, wherein in the step (a), when the prepared liquid 1 is obtained, an aqueous solution or water-soluble slurry containing heteropolyacid is prepared by heating at 70 to 150°C.

14. The method for preparing a catalyst for production of methacrylic acid according to any one of claims 2 to 13, wherein in the step (a), a retention time of the prepared liquid 1 after preparation in the preparation tank is 6 minutes or longer and 900 minutes or shorter, and in the step (b), a mixing time in the mixing tank is 60 minutes or longer and 320 minutes or shorter.

15. The method for preparing a catalyst for production of methacrylic acid according to any one of claims 1 to 14, wherein the same preparation tanks and the same mixing tank are used directly, and the catalyst is produced repeatedly at least one time.

16. The method for preparing a catalyst for production of methacrylic acid according to any

one of claims 1 to 15, wherein in the step (b), the mixing is performed at a maintained temperature of 20 to 120°C.

17. The method for preparing a catalyst for production of methacrylic acid according to any one of claims 1 to 16, wherein in the step (b), a pH is adjusted between 0.5 and 7 by further adding an ammonium raw material.

18. The method for preparing a catalyst for production of methacrylic acid according to any one of claims 1 to 17, further comprising:

a step of drying the mixed liquid containing the entire catalyst raw material and obtained from the step (b) to thereby obtain a catalyst dry matter.

19. The method for preparing a catalyst for production of methacrylic acid according to claim 18, further comprising:

a step of molding the catalyst dry matter to thereby obtain a catalyst molding.

20. The method for preparing a catalyst for production of methacrylic acid according to claim 19, further comprising:

a step of heat-treating the catalyst molding.

21. A method for producing methacrylic acid, comprising:

preparing a catalyst for production of methacrylic acid by the method according to any one of claims 1 to 20;

filling a reaction tube with the catalyst; and

preparing methacrylic acid by a gas-phase catalytic oxidation of at least one selected

from the group consisting of methacrolein, isobutylaldehyde, isobutane, and isobutyric acid.