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upon receipt of that report (Rule 48.2(g))(54) Title: CATALYST FOR THE MANUFACTURING OF ACRYLIC ACID AND A PROCESS FOR PRODUCING ACRYLIC
ACID BY USING THE CATALYST(57) Abstract: This invention provides a catalyst for producing unsaturated carboxylic acid from unsaturated aldehyde which is ob-
tained by dehydration reaction of alcohol. In particular, this invention provides a catalyst for producing acrylic acid from acrolein
obtained by dehydration reaction of glycerin. This invention provides also a process for producing unsaturated carboxylic acid, espe-
cially acrylic acid by using the catalyst. Catalyst used contains an active ingredient having a composition represented by following
formula (1): $\text{Moi}_2\text{VaWbCu}_c\text{SbdXeYfZgO}_h$ (1), in which Mo, V, W, Cu, Sb and O represent respectively molybdenum, vanadium,
tungsten, copper, antimony and oxygen, X is at least one element selected from a group comprising alkali metals and thallium, Y is
at least one element selected from a group comprising magnesium, calcium, strontium, barium and zinc, Z is at least one element se-
lected from a group comprising niobium, cerium, tin, chromium, manganese, iron, cobalt, samarium, germanium, titanium and arsen-
ic, "a", "b", "c", "d", "e", "f", "g" and "h" each represents an atom ratio of element and satisfies following respective range when a
value for molybdenum atom is considered as 12: "a" is greater than 0 but not greater than 10, "b" is not less than 0 but not greater
than 10, "c" is greater than 0 but not greater than 6, "d" is greater than 0 but not greater than 10, "e" is not less than 0 but not greater
than 0.5, "f" is not less than 0 but not greater than 1, "g" is not less than 0 but less than 6 and "h" is a number of oxygen atom re-
quired for satisfying the valences of above elements.

Description

Title of Invention: CATALYST FOR THE MANUFACTURING OF ACRYLIC ACID AND A PROCESS FOR PRODUCING ACRYLIC ACID BY USING THE CATALYST

Technical Field

- [0001] This invention concerns an oxidation catalyst for producing unsaturated carboxylic acid from unsaturated aldehyde produced by the alcohol catalytic dehydration reaction, and a process for producing acrylic acid by using the catalyst.
- [0002] In particular, this invention concerns a catalyst for producing acrylic acid from acrolein which is produced by catalytic dehydration reaction of glycerin in gas phase or liquid phase, and a process for producing acrylic acid by using the catalyst.

Background Art

- [0003] Acrolein is used in production of methionine and is a derivative for producing amino acid used as an animal feed supplement, which has emerged as a substitute for fishmeal. Acrolein is a synthetic intermediate of acrylic acid and leads, via reaction with methyl vinyl ether then hydrolysis, to glutaraldehyde, which has many uses in leather tanning.
- [0004] Acrylic acid is a material used in a variety of industrial products and is an important monomer and comonomer of industrial polymers such as polyacrylates and polyacrylamide produced by polymerization of acrylic acid and its derivative. One of the important applications of acrylic acid is high water absorption resins prepared by partial neutralization of a mixture of acrylic acid and sodium acrylate or other cation. In practice, acrylic acid is polymerized and the resulting polyacrylic acid is partly neutralized. These polymers or copolymer are utilized widely in various fields such as sanitation, detergent, coating material, varnish, adhesive, paper, fabric and leather.
- [0005] Acrolein and acrylic acid are produced in industrial scale by a process for oxidizing propylene by using a catalyst in the presence of oxygen. Generally, this reaction is carried in gas phase. Acrylic acid is usually produced by two step reactions. In the first step, acrolein-rich product is prepared from propylene but little acrylic acid is produced in this stage. Acrylic acid is obtained by selective oxidation of acrolein in the second step.
- [0006] This two-step reaction is carried out in multi-tubular reactors under two different reaction conditions and catalysts each suitable for each reactor. There is no necessity to effect purification of acrolein obtained in the first step. The present oxidation reaction of propylene to acrolein and acrylic acid is carried out in a fixed bed reactor unlike many other selective oxidation processes.

- [0007] Starting material used in production of acrolein and acrylic acid is derives from petroleum and natural gas which are no regenerable fossil resources. However, it is very important to produce them from renewable sources to reduce the global warming gas. Such change is the responsibility of industry major powers and can contribute to relaxation of the environmental loads and reduction of global warming gas.
- [0008] Glycerin is obtained as by-product when bio-diesel fuel is produced and is considered as one of feedstock for propylene alternative and acrolein can be produced by catalytic dehydration reaction of glycerin. This process route responds to the concept of green chemistry for the environmental protection. Glycerin can be produced by several processes such as fermentation and hydrogenolysis of sugar.
- [0009] This process route is very similar to the propylene oxidation process, because acrolein is prepared in the first step and the second step is carried out in the same reaction condition as the first step. However, actual first step is different from the usual propylene oxidation process. In fact, a different solid catalyst from the propylene oxidation is used in the dehydration reaction in gas phase, and in this process, much water together with acrolein-rich gas is supplied to the second step for producing acrylic acid. Still more, a composition of by-products is very different due to completely different reaction mechanism.
- [0010] Many catalysts have already been reported for producing acrolein by the glycerin dehydration reaction.
- [0011] Patent Document 1 (US 5,387,720) discloses a process for producing acrolein by glycerin dehydration on a variety of solid acids in gas phase and liquid phase. Hammett index is defined as lower than +2, preferably lower than -3, so that corresponding catalyst is for example natural or synthetic silicon compounds such as mordenites, montmorillonite, zeolite, monobasic acids, dibasic acid, tribasic acids supported on alumina and titania, gamma- alumina, $\text{ZnO/Al}_2\text{O}_3$ or heteropoly acids. It is believed that a problem in FR69593 1 of by-products which are generated in case of an iron phosphate catalyst system can be solved.
- [0012] Patent Document 2 (WO2006/087084) shows that strong solid acid having Hammett index from -9 to -18 permits to produce acrolein at high activity by glycerin dehydration and to suppress degradation of catalyst.
- [0013] Patent Document 3 (WO2009/044081) discloses a glycerin dehydration reaction effected in the presence of a catalyst containing oxygen, iron, phosphorus and alkali metal or more than one element selected from a group comprising alkali-earth metals Al, Si, B, Co, Cr, Ni, V, Zn, Zr, Sn, Sb, Ag, Cu, Nb, Mo, Y, Mn, Pt, Rh and rare earth La, Ce and Sm.
- [0014] Patent Document 4 (WO2009/128555) discloses a glycerin dehydration reaction effected in the presence of a catalyst consisting of a compound in which protons in het-

eropolyacid are exchanged with more than one cation of elements selected from a group comprising elements belonging to Group 1 to Group 16 of periodic table.

[0015] Patent Document 5 (WO2010/046227) discloses a glycerin dehydration reaction effected in the presence of a catalyst containing oxygen, phosphorus and at least one element selected from a group comprising vanadium, boron and aluminum.

[0016] However, when acrolein is produced from glycerin, the resulting acrolein is different from acrolein obtained by the oxidation reaction of propylene. In fact, the resulting acrolein produced from glycerin contains a large amount of a variety of by-products such as hydroxy acetone, propionaldehyde, acetaldehyde, acetone, addition products of acrolein added to glycerin, polycondensation products of glycerin, cyclic glycerin ether, phenol, poly aromatic compounds.

[0017] Known documents teaches, in their specification and examples, that catalyst used in production of acrylic acid from acrolein obtained from glycerin can be prepared the conventional technique that were used for producing acrylic acid from acrolein. However, known documents (such as Patent Documents Patent Document 6 (WO2010/074177), Patent Document 7 (US2008/0183013), Patent Document 8 (JP-A 1-2008/53 16283), Patent Document 9 (JP-A 1-2010/5 13422) fail to disclose details of catalysts, their compositions, constituent elements and how to prepare the catalysts including sintering method and shaping method.

Citation List

Patent Literature

- [0018] PTL 1: US Patent No. 5,387,720
 PTL 2: WO2006/087084
 PTL 3: WO2009/04408 1
 PTL 4: WO2009/128555
 PTL 5: WO2010/046227
 PTL 6: WO2010/074177
 PTL 7: U.S. Patent Specification No. US2008/0183013
 PTL 8: JP-A 1-2008/53 16283
 PTL 9: JP-A1-2010/5 13422

Summary of Invention

Technical Problem

[0019] Therefore, an object of this invention is to provide a catalyst for producing unsaturated carboxylic acid from unsaturated aldehyde produced by catalytic dehydration reaction of alcohol in gas phase or in liquid phase.

[0020] Another object of this invention is to provide a process for producing unsaturated carboxylic acid by using the catalyst.

[0021] Still another object of this invention is to provide a catalyst for producing acrylic acid from acrolein produced by catalytic dehydration reaction of glycerin in gas phase or in liquid phase and a process for producing acrylic acid by using the catalyst.

[0022] A further object of this invention is to provide a method for preparing such catalyst.

Solution to Problem

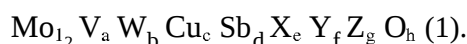
[0023] From the first aspect, this invention provides a catalyst used in production of unsaturated aldehyde and unsaturated carboxylic acid, in particular acrolein and acrylic acid by using alcohol, in particular glycerin which is a material not derived from petroleum in gas phase or in liquid phase at higher yield.

[0024] Further, this invention provides a process for producing acrylic acid by using the catalyst.

[0025] Inventors of this invention tried to solve the problems and found that when unsaturated carboxylic acid is produced by the oxidation of the unsaturated aldehyde which is obtained by catalytic dehydration of alcohol, in particular when acrylic acid is produced by the oxidation of acrolein which is obtained by catalytic dehydration of glycerin, the unsaturated carboxylic acid or acrylic acid can be obtained at a high yield by using a special catalyst prepared from selected materials and by selected method, and completed the present invention.

[0026] Namely, the present invention has following features (1) to (4) taken separately or in combination:

(1) Catalyst for producing unsaturated carboxylic acid from unsaturated aldehyde which is obtained by dehydration reaction of alcohol, in particular, for producing acrylic acid from acrolein obtained by dehydration reaction of glycerin, characterized in that said catalyst contains an active ingredient having a composition represented by following formula (1):



in which Mo, V, W, Cu, Sb and O represent respectively molybdenum, vanadium, tungsten, copper, antimony and oxygen, X is at least one element selected from a group comprising alkali metals and thallium, Y is at least one element selected from a group comprising magnesium, calcium, strontium, barium and zinc, Z is at least one element selected from a group comprising niobium, cerium, tin, chromium, manganese, iron, cobalt, samarium, germanium, titanium and arsenic, "a", "b", "c", "d", "e", "f", "g" and "h" each represents an atom ratio of element and satisfies following respective range when a value for molybdenum atom is considered as 12:

"a" is greater than 0 but not greater than 10,

"b" is not less than 0 but not greater than 10,

"c" is greater than 0 but not greater than 6,

"d" is greater than 0 but not greater than 10,

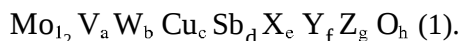
"e" is not less than 0 but not greater than 0.5,

"f" is not less than 0 but not greater than 1,

"g" is not less than 0 but less than 6 and

"h" is a number of oxygen atom required for satisfying the valences of above elements.

(2) Catalyst for producing acrylic acid from acrolein obtained by dehydration reaction of glycerin, characterized in that said catalyst contains an active ingredient having a composition represented by following formula (1):



in which Mo, V, W, Cu, Sb and O represent respectively molybdenum, vanadium, tungsten, copper, antimony and oxygen, X is at least one element selected from a group comprising alkali metals and thallium, Y is at least one element selected from a group comprising magnesium, calcium, strontium, barium and zinc, Z is at least one element selected from a group comprising niobium, cerium, tin, chromium, manganese, iron, cobalt, samarium, germanium, titanium and arsenic, "a", "b", "c", "d", "e", "f", "g" and "h" each represents an atom ratio of element and satisfies following respective range when a value for molybdenum atom is considered as 12:

"a" is greater than 0 but not greater than 10,

"b" is not less than 0 but not greater than 10,

"c" is greater than 0 but not greater than 6,

"d" is greater than 0 but not greater than 10,

"e" is not less than 0 but not greater than 0.5,

"f" is not less than 0 but not greater than 1,

"g" is not less than 0 but less than 6 and

"h" is a number of oxygen atom required for satisfying the valences of above elements.

(3) A process for producing unsaturated carboxylic acid from unsaturated aldehyde which is obtained by dehydration reaction of alcohol, characterized by using the catalyst according to the above Item 1 or 2.

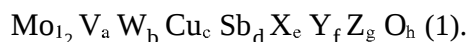
(4) A process for producing acrylic acid from acrolein which is obtained by dehydration reaction of glycerin, characterized by using the catalyst according to the above Item 1 or 2.

Advantageous Effect of Invention

[0027] Unsaturated carboxylic acid can be produced at a high yield by using the catalyst according to this invention, when unsaturated carboxylic acid is produced from unsaturated aldehyde which is obtained by the dehydration of alcohol, in particular, when acrylic acid is produced from acrolein which is obtained by dehydrating glycerin, so that the present invention is very important in industrial production of unsaturated carboxylic acids.

Description of Embodiments

[0028] A catalytic active component of the catalyst according to this invention is represented by following formula (1):



in which Mo, V, W, Cu, Sb and O represent respectively molybdenum, vanadium, tungsten, copper, antimony and oxygen, X is at least one element selected from a group comprising alkali metals and thallium, Y is at least one element selected from a group comprising magnesium, calcium, strontium, barium and zinc, Z is at least one element selected from a group comprising niobium, cerium, tin, chromium, manganese, iron, cobalt, samarium, germanium, titanium and arsenic, "a", "b", "c", "d", "e", "f", "g" and "h" each represents an atom ratio of element and satisfies following respective range when a value for molybdenum atom is considered as 12:

"a" is greater than 0 but not greater than 10,

"b" is not less than 0 but not greater than 10,

"c" is greater than 0 but not greater than 6,

"d" is greater than 0 but not greater than 10,

"e" is not less than 0 but not greater than 0.5,

"f" is not less than 0 but not greater than 1,

"g" is not less than 0 but less than 6 and

"h" is a number of oxygen atom required for satisfying the valences of above elements.

[0029] The catalyst according to this invention can be prepared by providing a mixture of powders of metal elements which constitute the catalyst represented by the formula (1) or powders prepared by drying aqueous solutions (or aqueous dispersions) containing compounds of the above elements, firing the powder mixture and shaping the resulting calcined product together with optional inert components or molding aid, optionally followed by supporting the resulting catalyst on a carrier. The compounds of catalytic active elements may be any compounds that can be converted to oxides after firing or calcination such as chlorides, sulfates, nitrate, ammonium salts of the catalytic active elements. Examples of compound of molybdenum are molybdenum trioxide, molybdic acid or its salts. Examples of compound of vanadium are vanadium pentoxide, vanadyl sulfate, vanadic acid or its salts. Examples of compound of tungsten are tungstic acid or its salts. Examples of compound of copper are copper oxide, copper sulfate, copper nitrate and copper molybdic acid. Among them, copper sulfate is preferable. Examples of compound of antimony are antimony trioxide or antimony acetate. When antimony trioxide is used as a material, antimony trioxide is used without chemical treatment. Namely, antimony trioxide is used as it is with out any chemical treatments which fa-

cilitate dissolution (or dispersion) into water such as contact with acid such as nitric acid and sulfuric acid, oxidizing agent such as hydrogen peroxide or alkalis. Antimony trioxide is used preferably in a form of fine powder. Antimony acetate can be used in place of antimony trioxide to increase mechanical strength and a catalyst having higher activity can be obtained under selected reaction conditions.

[0030] In this invention, an aqueous solution or water dispersion (hereinafter, slurry solution) of the above-mentioned active ingredients or compounds thereof is firstly prepared. The slurry solution can be prepared by mixing the active ingredients with water uniformly. In this invention, the slurry solution is preferably an aqueous solution. Proportions of compounds of the active ingredient in the slurry solution can be selected from suitable ranges, provided that the atom ratio of each active ingredient is within the above-mentioned range. An amount of water is not specially limited but must be sufficient to dissolve (or mixed uniformly) the total of compounds used and is determined with consideration of method and temperature used in a later drying stage. A preferred amount of water is generally 200 to 2000 parts by weight with respect to 100 parts by weight of the total of the compounds. Complete dissolution (or uniform mixing) can not be expected if the quantity of water is short or not sufficient. On the contrary, excessive quantity of water result in problems of increase in energy cost for drying stage and none perfect drying.

[0031] Then, the slurry solution is dried. The drying method is not limited specially, provided that the slurry solution can be dried completely such as drum drying, freeze drying and spray drying. In this invention, the spray drying is preferably used because the slurry solution can be dried up to a powder condition within a short time. Drying temperature depends on a concentration of the slurry solution, a feed seed thereof or the like but a temperature at an exit of a drier is about 85 to 130 degrees Celsius. It is desirable to effect the drying so that the resulting dried powder has an average particle size of 20 to 100 micrometers.

[0032] The resulting dried powder is then fired. This firing or calcination is preferably divided into two steps of preliminary firing step before shaping or molding and of post firing step after shaping molding. The firing or calcination can be carried out by any known technique. The preliminary firing according to the present invention can be effected usually at a temperature between 250 degrees Celsius to 500 degrees Celsius, preferably between 300 degrees Celsius to 450 degrees Celsius for a firing time of 1 to 15 hours, preferably between 3 to 6 hours. The preliminary firing step is desirable to prevent pulverization and peeling off of the catalytic active component when it is poured into a reaction tube and to obtain a catalyst of less wearing.

[0033] The catalyst according to this invention is obtained by shaping or molding granules obtained by the preliminary firing step (hereinafter, preliminary fired granules) directly

or after the granules are crushed. The shaping or molding can be carried out by any known method. For example, the preliminary fired granules mixed optionally with binder are shaped by (A) a tablet making press, (B) an extruder in which the preliminary fired granules are mixed with molding aid such as silica gel, diatomaceous earth and alumina powder and extruded into a shape of ball, cylinder, ring or the like, and (C) coating technique in which the catalyst is coated or supported on spherical carrier. The resulting supported catalyst is then subjected preferably to post-firing step.

[0034] Now, the catalyst coating technique which is a desirable method for the catalyst of this invention will be explained in details. The catalyst coating can be carried out prefer by a roll granulation method. In the roll granulation method, a disk having a flat or uneven surface is placed on a bottom of a fixed container and is rotated at high speed, so that a carrier is stirred strongly in the container by repeated combination motions of rotation and orbital motion. Then, a mixture of the preliminary fired granules and binder with optional molding aid and reinforcement is added onto the carrier, so that the carrier is coated with the mixture. The binder can be added by any method such as (1) the binder is premixed with the mixture, (2) the binder is added at the same time when the mixture is introduced into the container, (3) the binder is added to the mixture after the mixture is introduced into the container, (4) the binder is added to the mixture before the mixture is introduced into the container, (5) the binder and the mixture are added by plural times, or the methods (2) to (5) can be combine before the total amount is added. In case of the method (5), it is preferable to adjust the feed speed in order to assure that a predetermined amount of the mixture is supported on the carrier without adhesion of the mixture onto a wall of the container and to avoid mutual coagulation of the mixture.

[0035] The carrier may be a spherical carrier having a diameter of 2.5 to 10 mm made of silicon carbide, alumina, mullite and alundum. The carrier has preferably a porosity of 30 to 50% and a water absorption of 10 to 30%. A ratio of the powder to be covered on the carrier, namely a ratio of the preliminary fired granules/(the preliminary fired granules + carrier) is usually 10 to 75 % by weight and preferably 15 to 50 % by weight. When the ratio of the coated powder is increased, a reaction activity of the coated catalyst according to this invention increases but a mechanical strength tends to decrease (a wear loss increases). On the contrary, if the proportion of the coated powder decrease, the mechanical strength increase (wear loss decrease) but the reaction activity will become lower.

[0036] When the carrier is coated with preliminary fired powder (obtained by crushing the preliminary fired granules), it is preferable to use a binder. Examples of the binder are water, ethanol, polyalcohol, polyvinyl alcohol of polymer type binder, cellulose such as crystalline cellulose, methyl cellulose and ethyl cellulose, silica sol aqueous solution

of inorganic binder. Among them, cellulose and diol such as ethylene glycol and triol such as glycerin are preferable, and aqueous solutions of cellulose and glycerin having a concentration of higher than 5 % by weight is preferable. Crystalline cellulose is desirable among cellulose. When a suitable amount of cellulose or of aqueous solution of glycerol is used, the moldability and the mechanical strength are improved with high catalytic activity. An amount of binder used is usually 2 to 60 parts by weight with respect to 100 parts by weight of the preliminary fired powder. In case of cellulose, its amount is 2 to 10 parts by weight and preferably 3 to parts by weight. In case of an aqueous solution of glycerol, its amount is 10 to 30 parts by weight.

[0037] Optionally, molding aid such as silica gel, diatomaceous earth, alumina powder can be used. An amount of the molding aid is 5 to 60 parts by weight to 100 parts by weight of the preliminary fired powder.

[0038] It is useful to use inorganic fiber such as ceramic fiber and whisker if necessary as reinforcing material to improve the mechanical strength of catalyst. However, fibers that react with the catalyst component such as potassium titanate whisker and basic magnesium carbonate whisker are not desirable. Preferably, ceramic fiber is preferable. An amount of the fibers is usually 1 to 30 parts by weight to 100 parts by weight of the preliminary fired powder. The preliminary fired powder, molding aid and reinforcement material are used usually in a form of a mixture. Usually, the resulting carrier coated with the preliminary fired powder has a diameter of 3 to 15mm.

[0039] The resulting carrier coated with the preliminary fired powder is then subjected to post-firing to obtain an objective product. The firing temperature is usually 250 to 500 degrees Celsius, preferably 300 to 450 degrees Celsius and the firing time duration is 1 to 50 hours. When other shaping technique than the catalyst coating method, such as tablet press is used, the post-firing is effected usually under such conditions as 250 to 500 degrees Celsius for about 1 to 50 hours.

[0040] The resulting catalyst according to this invention thus obtained is used in a process for producing unsaturated carboxylic acid from unsaturated aldehyde produced by the alcohol catalytic dehydration reaction, and, in particular, is used advantageously in a process for producing acrylic acid from acrolein produced by glycerin dehydration .

[0041] Catalyst used for producing acrylic acid by oxidation of acrolein and a process for producing acrylic acid by oxidation of acrolein are known and described in Japanese patent No. 3786297 and No. 3883755.

[0042] The unsaturated aldehyde used in this invention is obtained by dehydration of alcohol. This alcohol is alcohols having a carbon number of 3 such as 1-propanol, 2-propanol, 1,2-propanediol, 1,3-propanediol and glycerin and includes alcohols having a carbon number of 4 to 6 that can produce the alcohol having a carbon number of 3 by decomposition (such as butanol, isobutanol, pentanol, hexanol, sorbitol).

- [0043] Acrolein as unsaturated aldehyde is obtained by dehydrating the above alcohol having a carbon number of 3. In the present invention, acrylic acid is produced by using the catalyst according to the present invention.
- [0044] This invention provides a catalyst for producing acrylic acid from acrolein which is produced by catalytic dehydration reaction of glycerin, a process for preparing the catalyst and a process for producing acrylic acid.
- [0045] Now, we will show a process for producing acrylic acid from acrolein which is produced by catalytic dehydration reaction of glycerin in details. The process according to the present invention is not limited to the dehydration reaction of glycerin but is applicable to acrolein which is produced by catalytic dehydration reaction of the above-mentioned any alcohol.
- [0046] Catalyst used to produce acrolein by glycerin dehydration can be any known solid acid catalyst which is known as a catalyst for this reaction. Examples of known solid acid are those disclosed in WO2006-087083, WO2006-087084 and Japanese patent No. 3488491.
- [0047] The solid acid catalyst may be acidic zeolite, mono-, di-, tri- and polyacids and heteropolyacid and their salts (polyacid such as tungstic acid, phosphotungstic acid, silicotungstic acid, phosphomolybdic acid and their salts), Nafion composite material (Nafion, Registered trade name), chlorinated alumina, phosphoric acid, boric acid, sulfuric acid and their salts and tungsten oxide. These active ingredient can be supported on carriers such as tantalum oxide, niobium oxide, alumina, titania, zirconia, silica, and silica-alumina.
- [0048] Among these solid acid catalysts, polyacid, heteropolyacid and their salts, namely tungstic acid, phosphotungstic acid and silicotungstic acid and their salts (especially alkali metal salts) described in WO2009-136537, JP-A1-2009-238532 and WO2011-033689 are especially preferable. At least one of these active ingredients are preferably supported on a carrier selected from zirconia, titania, alumina and silica. Preferred examples are CsPW, CsPW/TiO₂ and PW/TiO₂.
- [0049] The dehydration reaction of glycerin can be effected in gas phase and in liquid phase and gas phase is preferable. The gas phase reaction can be carried out in a variety of reactors such as fixed bed, fluidized bed, circulating fluidized bed, movable bed. Among them, the fixed bed is advantageously used. The liquid phase reaction can be carried out in usual liquid phase reaction vessel for solid catalyst.
- [0050] Reaction condition when acrolein is produced by gas phase dehydration reaction of glycerin is such that the reaction temperature is preferably 200 to 450 degrees Celsius. In fact, the catalyst life will be shortened when the reaction temperature is lower than 200 degrees Celsius, since glycerin has high boiling point, so that polymerization or carbonization of glycerin and reaction products will occur. On the contrary, when the

reaction temperature exceeds 450 degrees Celsius, the selectivity of acrolein is lowered due to increase in parallel reaction and successive reactions. More preferable reaction temperature is 250 to 350 degrees Celsius.

- [0051] The reaction pressure is not limited specially but 10 atm or less is desirable at the absolute pressure, more preferable pressure is 6 atm or less. If the pressure is increased, gasified glycerin will be liquidized again. Under higher pressure, carbon deposition will be promoted and the life of catalyst will be shortened.
- [0052] A feed rate of material gas with respect to the catalyst is preferably 500 to 10000 h⁻¹ in term of space velocity GHSV. Under 500h⁻¹ or less, the selectivity will be lowered due to successive reactions and over 10000h⁻¹, the conversion will be lowered.
- [0053] The liquid phase reaction is carried out preferably at a temperature of 150 to 350 degrees Celsius. At low temperatures, the conversion will be lowered but the selectivity will be improved. The pressure is not limited specially but can be increased to 3 atm to 70 atm.
- [0054] A concentration of aqueous solution of glycerol is preferably in a range of from 5 % by weight to 90 % by weight, more preferably from 10 % by weight to 60 % by weight. When the concentration of glycerol becomes lower than 40 % by weight, a feed stock acrolein containing a large amount of water than a feed stock acrolein used in the conventional propylene oxidation process is supplied. In the catalyst according to this invention, however, the performance of catalysis such as activity, selectivity and catalyst life is not spoiled advantageously. Still more, higher glycerol concentration will become undesirable causes of formation of glycerin ether and of reaction between glycerin and unsaturated aldehyde and unsaturated carboxylic acid. Still more, higher energy is required for gasification of glycerin.
- [0055] A concentration of glycerin in the mixed gas which is fed to the glycerin dehydration catalyst is 1 to 30 mol %, preferably 1 to 12 mol %, more preferably 3 to 10 mol %.
- [0056] The glycerin dehydration reaction can be done under inert gas stream such as nitrogen and helium, but is desirably done in the presence of oxygen-containing gas such as oxygen or air. A concentration of oxygen is 1 to 10 mol %, preferably 2 to 7 mol %.
- [0057] Now, we will explain a method for producing acrylic acid from acrolein obtained by the glycerin dehydration in details.
- [0058] When the resulting acrolein obtained by glycerin dehydration in the first step reactor is fed to a second step reactor for producing acrylic acid, acrolein-containing gas obtained in the first step can be fed directly to the second step. However, it is preferable to purify at least a part thereof before feeding to the second step, since acrolein obtained by the glycerin dehydration contain a variety of by-products such as water, unreacted glycerin, acetaldehyde, hydroxyacetone, propionaldehyde, propionic

acid, acrylic acid, glycerin polycondensates, glycerin ether, phenol. Purification can be done in an absorption column as a partial condensation tower. Purification may be effected by other known technique such as temperature control purification such as distillation and crystallization, pressurization condensation purification, extraction purification or their combination, or those equipped with evaporator, heat-exchangers, condensers or the like.

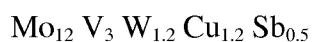
- [0059] Reaction condition for producing acrylic acid from acrolein obtained by glycerin dehydration reaction is a temperature of 200 to 450 degrees Celsius, preferably 220 to 400 degrees Celsius .
- [0060] A pressure is not limited specially but a pressure of 1 atm to 10 atm, preferably from 1 atm to 5 atm is preferable in term of absolute pressure. Much higher pressure will be a cause of excessive oxidization, of promotion of carbon deposition and of shorten of the catalyst life.
- [0061] A feed rate of material gas with respect to the catalyst is 500 to 10000h⁻¹, more preferably 1000 to 5000V¹in term of space velocity GHSV.
- [0062] A concentration of acrolein in the acrolein-containing gas to be fed to the catalyst for acrolein oxidation is 1 to 20 mol %, preferably 3 to 15 mol %.
- [0063] Oxygen or air and inert gas such as nitrogen and helium can be added before the acrolein-containing gas obtained by glycerin dehydration reaction is fed to an acrolein oxidation reactor. A concentration of oxygen is preferably 1 to 15 mol %.

Examples

- [0064] The present invention will be explained in more details in following examples, but the scope of this invention should not be limited to these examples. In example and comparative examples, % means mole %.
- [0065] Example 1(example)
 PW/TiO₂ catalyst was used as a catalyst used for producing acrolein by dehydration reaction of glycerin. This PW/TiO₂ catalyst was prepared as following. Firstly, 13.2 g of phosphotungstic acid (Nippon Inorganic Colour & Chemical Co., Ltd.) were dissolved in 100 ml of pure water. Separately, 100g of anatase TiO₂ pellet (Saint-Gobain, ST 31119: diameter = 3.2 mm, length = 5 mm) was placed in a porcelain dish onto which an aqueous solution of the phosphotungstic acid was added and left for 2 hours. Then, the resulting mixture was evaporation-dried at 120 degrees Celsius for 10 hours and then was fired at 500 degrees Celsius for 3 hours in air atmosphere.
- [0066] Now, a catalyst for producing acrylic acid from acrolein and its preparation method will be shown. In a mixing tank (A) equipped with a stirring motor, 600 parts of deionized water and 16.26 parts of ammonium tungstate were added at 95 degrees

Celsius and stirred. Then, 18.22 parts of ammonium metavanadate and 110 parts of ammonium molybdate were dissolved therein. Then, 7.75 parts of antimony acetate was added further. In a mixing tank (B) in which 96 parts of deionized water was introduced, 15.56 parts of copper sulfate was dissolved therein and the resulting solution was added to mixing tank (A) to obtain a slurry solution. This slurry solution was spray-dried by adjusting air speed so that an outlet temperature of a spray drier becomes to about 100 degrees Celsius. The resulting granules were heated from ambient temperature gradually at an elevation rate of about 60 degrees Celsius per hour and fired in a furnace at a temperature of 390 degrees Celsius for about 5 hour (preliminary firing). The resulting preliminary fired granule was crushed by a ball mill to powder (hereinafter, preliminary fired powder).

- [0067] 36 parts of alundum carrier possessing a porosity of 40%, a diameter of 4mm was placed in a roll granulating machine and 2.4 parts of an aqueous solution of 20 % by weight of glycerin was poured onto the carrier and 12 parts of the preliminary fired powder was fed therein to obtain supported catalyst. The resulting coated carrier was then heated at an elevation rate of about 70 degrees Celsius per hour from ambient temperature and fired in a furnace at a temperature of 390 degrees Celsius for 5 hours to obtain a coated product according to this invention. The resulting catalyst has following proportions in elements of active ingredients other than oxygen:



- [0068] Then, the catalyst for glycerin dehydration was evaluated in a flow-through type fixed bed reactor. 30cc of the catalyst was packed in a SUS reaction tube (diameter of 20 mm). An aqueous solution of glycerin (concentration of 50 % by weight) was fed to an evaporator at a flow rate of 23.4 g/hr by a pump so that glycerin was gasified at 300 degrees Celsius. The resulting gasified glycerin was passed through the fixed catalyst bed together with air. The fixed catalyst bed was heated at a temperature of 290 degrees Celsius. Feed gas had following composition in mol %: glycerin : oxygen : nitrogen : water = 4.7 : 2.8 : 68.5 : 24.0. GHSV was 2020 h⁻¹. Outlet gas had following composition in mol%: acrolein : oxygen : nitrogen : water : acetaldehyde : propionaldehyde : hydroxyacetone = 3.8 : 1.4 : 68.1 : 24.4 : 0.37 : 0.03 : 0.01.

- [0069] Then, the catalyst for acrolein oxidation was evaluated in a flow-through type fixed bed reactor, on the assumption that air and oxygen were added and the water was removed through a condenser with the gas obtained above. Assumed flow rate of added air and oxygen described above was each 0.0087 mol/min and 0.002 l/mol/min, in the case of 30ml of catalyst. Feed gas had following composition in mol %: acrolein : oxygen : nitrogen : water : acetaldehyde : propionaldehyde : hydroxyacetone = 3.4 : 8.1 : 73.0 : 15.1 : 0.34 : 0.03 : 0.03. 30ml of a catalyst was packed in a SUS reaction tube (inner diameter of 28.4mm). Acrolein-containing gas obtained by liquid acrolein

bubbling with nitrogen was added with oxygen, nitrogen, water, and some oxygen-containing compounds (acetaldehyde, propionaldehyde, hydroxyacetone). The reaction was carried out at SV of 2508/hr (space velocity: material gas flow rate per unit time / appearance volume of packed catalyst) at a reaction temperature of 275 degrees Celsius.

[0070] Products were condensed in a condenser and quantitative- analyzed by a gas chromatograph (7890A, DB-WAX column, Agilent). Proportions of products were corrected in factors from the results of the gas chromatograph to determine absolute amounts of products to calculate the conversion of material (glycerin conversion), the selectivity of objective substance (acrylic acid selectivity) and the yield of objective substance (acrylic acid yield).

[0071] The conversion (%) of material = (1 - a mole number of material unreacted / a mole number of material supplied) x 100

The selectivity (%) of objective substance = (a mole number of products obtained / a mole number of material reacted) x 100

The yield (%) of products = (a mole number of products obtained / a mole number of material fed) x 100

The conversion (%) of material (acetaldehyde, propionaldehyde, hydroxyacetone) = (1 - (a mole number of material unreacted - a mole number of material unreacted without feeding impurities) / a mole number of material supplied) x 100

Foliowings are the results of the reaction:

Conversion of acrolein = 98.1%

Selectivity of acrylic acid = 96.5%

Yield of acrylic acid = 94.7%

Conversion of acetaldehyde = 99.5%

Conversion of propionaldehyde = 99.6%

Conversion of hydroxyacetone = 100.0%

[0072] Example 2 (comparative example)

Then, we evaluated the acrolein oxidation catalyst without oxygen-containing compounds in feed gas for comparative evaluation. Feed gas had following composition in mol %: acrolein : oxygen : nitrogen : water = 3.4 : 8.1 : 73.3 : 15.2, and each feed gas flow rate was the same as example 1. 30ml of a catalyst was packed in a SUS reaction tube (inner diameter of 28.4mm). Acrolein-containing gas obtained by liquid acrolein bubbling with nitrogen was added with oxygen, nitrogen, water. The reaction was carried out at SV of 2500/hr.

[0073] Foliowings are the results:

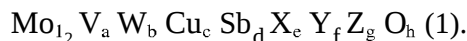
Conversion of acrolein = 98.4%

Selectivity of acrylic acid = 94.7%

Yield of acrylic acid = 93.2%

[0074] Following is the summary of Examples and Comparative examples:

Acrylic acid can be produced at higher yield when a catalyst containing an active ingredient having a composition represented by following formula (1):



(in which Mo, V, W, Cu, Sb and O represent respectively molybdenum, vanadium, tungsten, copper, antimony and oxygen, X is at least one element selected from a group comprising alkali metals and thallium, Y is at least one element selected from a group comprising magnesium, calcium, strontium, barium and zinc, Z is at least one element selected from a group comprising niobium, cerium, tin, chromium, manganese, iron, cobalt, samarium, germanium, titanium and arsenic, "a", "b", "c", "d", "e", "f", "g" and "h" each represents an atom ratio of element and satisfies following respective range when a value for molybdenum atom is considered as 12:

"a" is greater than 0 but not greater than 10,

"b" is not less than 0 but not greater than 10,

"c" is greater than 0 but not greater than 6,

"d" is greater than 0 but not greater than 10,

"e" is not less than 0 but not greater than 0.5,

"f" is not less than 0 but not greater than 1,

"g" is not less than 0 but less than 6 and

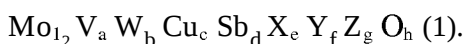
"h" is a number of oxygen atom required for satisfying the valences of above elements)

is used for producing unsaturated carboxylic acid from unsaturated aldehyde which is obtained by dehydration reaction of alcohol, in particular, for producing acrylic acid from acrolein which is obtained by dehydration reaction of glycerol, even when the acrolein contain a larger amount of by-products such as oxygen-containing compounds. No lowering in the acrolein yield was observed even if acrolein containing much water was used as material. The catalyst according to this invention is applicable for producing acrylic acid by using such acrolein as containing various impurities and by using such acrolein material as having a wide range of acrolein concentration.

Claims

[Claim 1]

Catalyst for producing unsaturated carboxylic acid from unsaturated aldehyde which is obtained by dehydration reaction of alcohol, characterized in that said catalyst contains an active ingredient having a composition represented by following formula (1):



in which Mo, V, W, Cu, Sb and O represent respectively molybdenum, vanadium, tungsten, copper, antimony and oxygen, X is at least one element selected from a group comprising alkali metals and thallium, Y is at least one element selected from a group comprising magnesium, calcium, strontium, barium and zinc, Z is at least one element selected from a group comprising niobium, cerium, tin, chromium, manganese, iron, cobalt, samarium, germanium, titanium and arsenic, "a", "b", "c", "d", "e", "f", "g" and "h" each represents an atom ratio of element and satisfies following respective range when a value for molybdenum atom is considered as 12:

"a" is greater than 0 but not greater than 10,

"b" is not less than 0 but not greater than 10,

"c" is greater than 0 but not greater than 6,

"d" is greater than 0 but not greater than 10,

"e" is not less than 0 but not greater than 0.5,

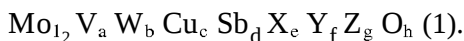
"f" is not less than 0 but not greater than 1,

"g" is not less than 0 but less than 6 and

"h" is a number of oxygen atom required for satisfying the valences of above elements.

[Claim 2]

Catalyst for producing acrylic acid from acrolein obtained by dehydration reaction of glycerin, characterized in that said catalyst contains an active ingredient having a composition represented by following formula (1):



in which Mo, V, W, Cu, Sb and O represent respectively molybdenum, vanadium, tungsten, copper, antimony and oxygen, X is at least one element selected from a group comprising alkali metals and thallium, Y is at least one element selected from a group comprising magnesium, calcium, strontium, barium and zinc, Z is at least one element selected from a group comprising niobium, cerium, tin, chromium, manganese, iron, cobalt, samarium, germanium, titanium and arsenic, "a", "b", "c",

"d", "e", "f", "g" and "h" each represents an atom ratio of element and satisfies following respective range when a value for molybdenum atom is considered as 12:

"a" is greater than 0 but not greater than 10,

"b" is not less than 0 but not greater than 10,

"c" is greater than 0 but not greater than 6,

"d" is greater than 0 but not greater than 10,

"e" is not less than 0 but not greater than 0.5,

"f" is not less than 0 but not greater than 1,

"g" is not less than 0 but less than 6 and

"h" is a number of oxygen atom required for satisfying the valences of above elements.

[Claim 3] A process for producing unsaturated carboxylic acid from unsaturated aldehyde which is obtained by dehydration reaction of alcohol, characterized by using said catalyst according to claim 1 or 2.

[Claim 4] A process for producing acrylic acid from acrolein which is obtained by dehydration reaction of glycerin, characterized by using said catalyst according to claim 1 or 2.