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(54) Title: PROCESS FOR MANUFACTURING ACROLEIN FROM GLYCEROL

(57) Abstract: The subject of the present invention is a process for preparing acrolein and/or acrylic acid by dehydration of glycerol in the presence of molecular oxygen in an amount chosen so as to be outside the flammability range at any point in the plant, characterized in that said dehydration is carried out in the presence of a catalyst comprising as a main component, a mixed oxide containing niobium oxide NbOx and at least one element taken from the group of tungsten, molybdenum and chromium. The process according to the invention permits to obtain acrolein at higher yield.



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PROCESS FOR MANUFACTURING ACROLEIN FROM GLYCEROL

Background of the Invention

Field of the invention

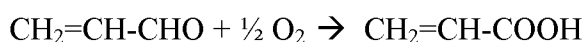
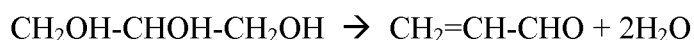
5 The present invention relates to a process for producing acrolein and/or acrylic acid from glycerol and, more particularly, to a process for preparing acrolein by dehydration of glycerol in the presence of a novel catalyst based on niobium oxide.

Description of related art

10 Fossil resources, such as oil cuts, for the chemical industry will be exhausted in a few decades. Resources of natural and renewable origin as alternative raw materials are consequently being studied more and more.

 Acrolein (also called 2-propenal), an important synthetic intermediate for the chemical industry is currently produced industrially by oxidation, in the gas phase, of propylene via the oxygen in the air in the presence of catalyst systems based on mixed
15 oxides based on Molybdenum-Bismuth-Iron and several other metals. Glycerol, derived from animal fat or vegetable oils in the production of bio diesel fuels or oleochemicals is one of the substitutes envisaged for propylene, glycerol being able to produce acrolein when subjected to a catalytic dehydration reaction. Such a process makes it possible to thus respond to the concept of green chemistry within a more
20 general context of environment protection and renewable chemicals. Glycerin and Glycerol words are used indifferentially in this application and in the literature although formally Glycerine should be used for a water containing Glycerol mixture, since Glycerol corresponds to the molecule itself or to the pure product.

 A method for preparing acrylic acid in one step process by the oxydehydration
25 reaction of glycerol in the presence of molecular oxygen is disclosed in WO 06/114506. The principle of the method is based on the two consecutive dehydration and oxidation reactions:



30 The presence of oxygen serves to carry out an oxidation reaction, following the glycerol dehydration reaction, leading to the formation of acrylic acid from the glycerol

in a single step. This method can be implemented in the gas phase or the liquid phase, with concentrated or dilute aqueous solutions of glycerol. This method for producing acrylic acid directly from glycerol is particularly advantageous because it allows synthesis in a single reactor. However, it is necessary to introduce all the molecular
5 oxygen from the dehydration stage. This has many drawbacks, in particular the reaction in the first dehydration step risks running out of control by combustion, and furthermore, when the source of molecular oxygen is air, the reactor must be much larger because of the presence of nitrogen in the air.

The use of an aqueous solution of glycerol in a two-step method has the
10 drawback of producing, at the outlet of the first stage, a stream containing not only the acrolein produced and the by-products, but also a large quantity of water, originating partly from the glycerol solution, and partly from the water produced by the dehydration reaction. Use of aqueous solutions of glycerol, however, is preferable from economic reasons. This stream is sent to the second reactor, where the acrolein is oxidized to
15 acrylic acid in the presence of a catalyst. The conventional catalysts for this oxidation reaction are generally solids containing at least one element selected from Mo, V, W, Re, Cr, Mn, Fe, Co, Ni, Cu, Zn, Sn, Te, Sb, Bi, Pt, Pd, Ru, Rh, present in metal form or oxide, nitrate, carbonate, sulphate or phosphate form. Certain elements, such as molybdenum, tellurium or rhenium, are volatile, particularly in the presence of water.
20 This means that the second stage catalyst loses its efficiency and its mechanical strength rapidly in the presence of the stream of water, making the maintenance of the method difficult. Moreover, the acrylic acid, produced in a dilute aqueous solution, requires separation and concentration steps that are generally complicated and fairly costly.

25 Numerous catalyst systems have already been the subject of studies for the dehydration reaction of glycerol to acrolein.

A process is known from French Patent FR 695 931 for preparing acrolein from glycerol according to which acid salts having at least three acid functional groups or mixtures of these salts are used as catalysts. The preparation of these catalysts consists
30 in impregnating, for example with iron phosphate, pumice that has been reduced to pea-sized fragments. According to the teaching of the patent, the yield obtained with this type of catalyst is greater than 80%.

In US Patent US 2,558,520, the dehydration reaction is carried out in gas/liquid phase in the presence of diatomaceous earths impregnated with phosphoric acid salts, in suspension in an aromatic solvent. A degree of conversion of glycerol to acrolein of 72.3% is obtained under these conditions.

5 US Patent US 5,387,720 discloses a process for producing acrolein by dehydration of glycerol in liquid phase or in gas phase at a temperature ranging up to 340°C, over acidic solid catalysts that are defined by their Hammett acidity. The catalysts must have a Hammett acidity below +2 and preferably below -3. These catalysts correspond, for example, to natural or synthetic siliceous materials, such as
10 mordenite, montmorillonite and acidic zeolites; supports, such as oxides or siliceous materials, for example alumina (Al_2O_3), titanium oxide (TiO_2), covered by monobasic, dibasic or tribasic inorganic acids; oxides or mixed oxides such as gamma-alumina, $\text{ZnO}/\text{Al}_2\text{O}_3$ mixed oxide, or heteropolyacids. The use of these catalysts would make it possible to solve the problem of formation of secondary products generated with the
15 iron phosphate type catalysts described in the aforementioned document FR 695,931.

According to International Application WO2006/087084, the strongly acidic solid catalysts whose Hammett acidity H_0 is between -9 and -18 have a strong catalytic activity for the dehydration reaction of glycerol to acrolein and are deactivated less quickly.

20 However, the catalysts recommended in the prior art for producing acrolein from glycerol generally lead to the formation of by-products such as hydroxypropanone, propanaldehyde, acetaldehyde, acetone, addition products of acrolein to glycerol, polycondensation products of glycerol, cyclic glycerol ethers, but also phenol and polyaromatic compounds which originate from the formation of coke on the catalyst
25 and therefore from its deactivation. The presence of the by-products in acrolein, especially propanaldehyde, poses numerous problems for the separation of acrolein and requires separation and purification steps which lead to high costs for the recovery of the purified acrolein. Furthermore, for example when acrolein is used for producing acrylic acid, the propanaldehyde present may be oxidized to propionic acid that is
30 difficult to separate from acrylic acid, especially by distillation. These impurities that are present greatly reduce the field of application of the acrolein produced by dehydration of glycerol since the same issues apply also for other applications of

acrolein.

The Applicant Company has therefore sought to improve the production of acrolein from glycerol, by using more selective catalysts that make it possible to obtain high yields of acrolein and that have an activity over long durations. In the field of catalysts, French Patent FR 2 657 792 discloses a catalyst of general formula $\text{FeP}_x\text{Me}_y\text{O}_z$, in which:

- Me represents at least one of the following elements: Li, Na, K, Rb, Cs, Mg, Ca, Sr and Ba;
- x has a value of 0.2 to 3.0;
- 10 - y has a value of 0.1 to 2.0; and
- z is the amount of oxygen bonded to the other elements and that corresponds to their oxidation state,

this catalyst being combined with a support, characterized by the fact that said support is a fully impregnable macroporous support having a specific surface area less than or equal to $1 \text{ m}^2/\text{g}$, a pore volume between 0.2 and $1 \text{ cm}^3/\text{g}$ and an average pore diameter greater than or equal to 1 micron, and that the active material is deposited on the surface of all the pores of said support, said catalyst being in the form of support grains impregnated with active material, which have a size between 0.5 and 10 mm.

WO2007/058221 discloses a process for producing acrolein by dehydration reaction of glycerin in gas-phase in the presence of heteropolyacid used as a solid acid catalyst. The heteropolyacid is those of Group 6 element such as tungstosilicic acid, tungstophosphoric acid and phosphomolybdic acid. These heteropolyacids are supported on bi-elemental pore silica carrier and produce acrolein at a yield of 86%. This dehydration reaction of glycerin, however, is effected without oxidation gas but using nitrogen stream as carrier gas, so that deposition of carbon increase seriously and hence there is a problem of deterioration in time of stability, activity and selectivity of the catalysis.

Tsukida et al. "Production of acrolein from glycerol over silica-supported heteropoly acid" CATALYSIS COMMUNICATIONS, vol. 8, no. 9, 21 July 2007, pp 1349-1353, and Chai et al., "Sustainable production of acrolein: gas phase dehydration of glycerol over 12-tungstophosphoric acid supported on ZrO_2 and SiO_2 ", GREEN CHEMISTRY, vol.10, 2008, pp.1087-1093, and Chai et al.,

“Sustainable production of acrolein: preparation and characterization of zirconia-supported 12-tungstophosphoric acid catalyst for gas phase dehydration of glycerol”, APPLIED CATALYST A: GENERAL, vol. 353, 2009, pp.213-222 disclose that silica or zirconia-supported heteropoly acid is effective as a catalyst
5 for dehydration of glycerol.

In WO2006/087083, oxygen is introduced to prevent degradation of the catalyst in the gas-phase reaction of glycerin. In WO2006/087084, the catalyst possessing the acid strength of H_o of -9 to -18 is used. A variety of solid acid catalysts such as phosphoric acid/zirconia, Nafion/silica, sulfuric acid/zirconia,
10 tungsten/zirconia are used in Examples and the highest yield of acrolein of 74% was obtained when tungstated zirconia catalyst was used.

However, there is no catalyst usable in the industrial scale at higher performance.

Inventors of this application have made a variety of studies to solve the
15 problems and found that acrolein can be produced at high yield by using a niobium based mixed oxide, in which niobium oxide is combined with at least one metal oxide taken from the group of tungsten, molybdenum, chromium.

An object of this invention is to provide a process for producing acrolein and acrylic acid from glycerin that is a material not derived from petroleum, at a
20 high yield.

Summary of the Invention

This invention is characterized by following features (1) to (20) taken separately or in combination:

(1) Process for preparing acrolein by dehydration of glycerin in the presence of
25 molecular oxygen in an amount chosen so as to be outside the flammability range at any point in the plant characterized in that said dehydration is carried out in the presence of a catalyst comprising as a main component, a mixed oxide containing niobium oxide NbO_x and at least one element taken from the group of tungsten, molybdenum and chromium.

30 (2) The catalyst is represented by the general formula (1):



in which :

A is at least one member selected from elements belonging to Group 1 to Group 16 of the Periodic Table of Elements and ammonium,

5 B is at least one element selected from W, Mo and Cr,

Nb is niobium,

$a \geq 0$, $b > 0$, x is a number determined by oxidation numbers of the elements and n is a any positive number.

(3) To the catalyst is added at least one salt of elements belonging to Group 1 to Group 16 of the Periodic Table of Elements and ammonium.

(4) The member selected from elements belonging to Group 1 to Group 16 of the Periodic Table of Elements is preferaly selected from the group comprising alkali metals such as cesium, potassium or rubidium, alkaline earth metals, rare earths, V, Ti, Ta, Mn, Fe, Co, Ni, Cu, Zn, Ga, In, Tl, Sn and Pb

(5) The catalyst is exchanged partially with at least on element selected from elements belonging to Group 1 to Group 16 of the Periodic Table of Elements and ammonium, preferably one alkali metal cation.

(6) the X-ray diffraction pattern (Cu-K α , $\lambda = 1.5428$ nm) of said niobium oxide (NbO $_x$) based catalyst has two peaks at $2\theta = 22.6 \pm 0.4$, preferably ± 0.2 , $2\theta = 46.1 \pm 0.4$, preferably ± 0.2 .

(7) The catalyst is supported on a carrier.

(8) The catalyst is prepared by hydrothermal synthesis method.

(9) The catalyst is prepared by oxidizing a niobium containing compound which will be changed to an oxide when heated by hydrothermal synthesis technique.

(10) The catalyst is prepared by a method comprising the steps of adding a solution of at least one metal selected from elements belonging to the Group Tungsten, Molybdenum, Chromium to a solution of niobium precursor , and of calcinating the resulting solid mixture.

(11) The catalyst is prepared by coprecipitation synthesis technique.

(12) The calcination is carried out under an atmosphere of air, inert gas or a

mixture of oxygen and inert gas.

- (13) The calcination is effected at a temperature of 150 to 900 °C for 0.5 to 10 hours.
- (14) Molecular oxygen is in the form of air or in the form of a mixture of gases containing molecular oxygen, and the oxygen content is chosen so as to be more than 0.4% and not to exceed 7% relative to the mixture of gases entering the reaction (mixture of glycerol/H₂O/oxygen/inert gases).
- (15) The process is effected in the presence of a gas containing propylene, as disclosed for example in WO 07/090990 and WO 07/090991, that is say to carry out the glycerol dehydration stage beneath the propylene oxidation reactor of the conventional process, taking benefit of the high temperature of the gas coming out of that stage containing mainly acrolein and some remaining propylene..
- (16) The process is performed in a reactor of the plate heat exchanger type, or in a fixed bed reactor or in a fluidized bed type reactor or in a circulating fluidized bed or in a moving bed.
- (17) The resulting acrolein prepared by the process according to this invention can be further oxidized to produce acrylic acid
- (18) A process for preparing acrylic acid from glycerol comprises a first step of the dehydration reaction of glycerol to acrolein, in which an intermediate step of partial condensation of the water and heavy by-products issuing from the dehydration step is implemented, as described for example in WO 08/087315.
- (19) The process according to this invention can be used in a followed second step of ammoxidation of acrolein to acrylonitrile, as described for example in WO 08/113927, or in a followed second step of amidification of acrolein to acrylamide.
- (20) the resulting acrolein prepared by present invention is utilized effectively to prepare glutaraldehyde, pyridine, methionine, or acrolein polymers or copolymers.

According to one particular embodiment of the invention, it is possible to

place, upstream of the catalyst system based on a mixed oxide of niobium and at least one metal chosen from W, Mo or Cr, a first active catalyst bed, or a first reactor enabling the dehydration reaction of glycerol to acrolein to be carried out. The gaseous reaction mixture is thus sent to a first catalyst, in contact with which the dehydration reaction of glycerol is at least partially carried out generally resulting in secondary compounds such as propanaldehyde. The reaction mixture thus obtained is then in contact with the catalyst system on which the dehydration reaction of unreacted glycerol may continue at the same time as the conversion of propanaldehyde to acrolein. The first catalyst bed may operate at a lower or higher temperature than the second catalyst bed, thus optimizing the energy balance of the process. The acrolein obtained according to this embodiment contains a minimized amount of propanaldehyde, which widens its field of application. This configuration of reactors is possible according to various technologies, for example as an adiabatic fixed bed, but also as a multitubular fixed bed, or else, for example, as a compartmentalized fluidized bed. This configuration is also possible in the case where the first reactor operates in the liquid phase and the second, containing the mixed Nb based oxides catalyst operates in the gas phase.

Description of the Preferred Embodiments

The dehydration catalyst according to this invention is used in dehydration of glycerin to produce acrolein and acrylic acid and comprises a mixed oxide containing niobium oxide NbO_x and at least one element taken from the group of tungsten, molybdenum and chromium, preferably tungsten.

The catalyst is represented by the general formula (1):



in which :

A is at least one member selected from elements belonging to Group 1 to Group 16 of the Periodic Table of Elements and ammonium,

B is at least one element selected from W, Mo and Cr,

Nb is niobium,

$a \geq 0$, $b > 0$, preferably $10 > a \geq 0$ and $10 > b > 0$

x is a number determined by oxidation numbers of the elements and n is a any positive number.

In a preferred embodiment, the member selected from elements belonging to Group 1 to Group 16 of the Periodic Table of Elements is selected from the group comprising alkali metals such as cesium, potassium or rubidium, and V, Mn, Fe, Co, Ni, Cu, Sn and Pb.

In a preferred embodiment, the glycerin dehydration catalyst according to this invention is prepared by hydrothermal synthesis. This type glycerin dehydration catalyst permits to produce acrolein and acrylic acid at high yield.

Hydrothermal synthesis is usually done in autoclaves, i.e. pressurized vessels. Reactants either solids or solubilized salts are mixed with a solvent, usually water, in an appropriate molar ratio. The autoclave can be purged with an inert gas in order to control the oxidation conditions during the hydrothermal synthesis. The autoclave is then heated for a given time. Depending on reaction conditions the autoclave can be left standing or can be mixed. There are several ways of mixing the reaction medium, among which an internal stirrer mechanically connected to an engine or magnetically connected to avoid risks of gas leakage. The autoclave can also be installed in a rotating device that will shake the reaction medium. Crystals or solids are being produced by chemical dissolutions-reactions in the autoclave. With this particular method of catalyst preparation, the solid which is formed does not usually have the same composition that the molar ratio of reactants introduced in the autoclave. There is a preferred cristallisation. After the hydrothermal synthesis which usually lasts for several hours, or days, the autoclave is being cooled to room temperature and the solid is recovered, washed, dried and eventually calcined. Hydrothermal synthesis is very common for zeolites preparation for example, and for mixed oxides like the Mo-V-Te-Nb-O or Mo-V-Sb-Nb-O catalysts used for propane oxidation to acrylic acid. Solids prepared by hydrothermal synthesis can be treated with acidic solutions or basic solutions in order to exchange at least partially some of their ionic constituents.

In a preferred embodiment, the glycerin dehydration catalyst according to

this invention is prepared by a coprecipitation synthesis method. This type glycerin dehydration catalyst permits also to produce acrolein and acrylic acid at high yield.

Coprecipitation method is very common in catalyst preparation procedures. According to this method, reactants are solubilized at least partially and mixed together under agitation in order to generate a solid in suspension or a gel. To obtain an homogeneous material, the pH can be controlled or not, by adding acids and/or bases. Reactants can be mixed one into the other, or added simultaneously in the coprecipitation vessel. There are many other ways of combining the reactants in order to generate a coprecipitation. The solid or gel produced can then be filtered, washed, dried and calcined. The solids prepared according to this method have generally the same metal molar composition than the reactants introduced, except if during washing a constituent is more soluble than others. Coprecipitation procedure is a preferred method in the catalyst industry since it is usually faster than the hydrothermal synthesis.

Usually both methods lead to different type of solids, but there are examples where similar catalysts, with similar catalytic activity, have been obtained like for the Mo-V-Te(Sb)-Nb(Ta) type catalysts for propane oxidation.

The catalyst used in the present invention can be prepared by the following method: For example, an aqueous solution of niobium oxalate is prepared firstly. Then an aqueous solution of tungsten, and/or molybdenum and/or chromium is prepared for example from ammonium metatungstate or ammonium paratungstate, from ammonium heptamolybdate, from chromium nitrate or chromium chloride. To the aqueous solution of tungsten and or molybdenum and/or chromium, an aqueous solution niobium oxalate is added. From a resulting mixture, a solid component is separated by suitable treatment such as evaporation drying, filtering, spray drying and vacuum drying. The resulting solid component is finally fired or calcinated to obtain the catalyst for glycerin dehydration reaction according to the present invention.

The solids obtained after hydrothermal synthesis, or coprecipitation, are in an ionic form meaning that they contain cations such as ammonium cations.

In a preferred embodiment, the dehydration catalyst for producing acrolein

and acrylic acid from glycerin according to the present invention comprises one salt of elements belonging to Group 1 to Group 16 of the Periodic Table of Elements and ammonium, or is exchanged partially with at least one element belonging to Group 1 to Group 16 of the Periodic Table of Elements and ammonium.

The elements can be partially or totally exchanged with other cations such as protons or Cs^+ , K^+ or Rb^+ . A usual procedure consists in washing the solid with an aqueous solution of the cation, for example an acid solution of HCl , or HNO_3 or H_2SO_4 , and/or an aqueous solution of NaOH , KOH , CsOH or RbOH .

The type of compound used is selected in such a way that the solubility of the compound to be formed like NH_4OH is high enough in the reaction condition to ensure that it will not remain in the solid being exchanged.

In the process to prepare the catalyst, the calcination can be carried out in air and/or under inert gas such as nitrogen, helium and argon or under an atmosphere of mixed gases of oxygen and inert gas, usually in a furnace such as muffle furnace, rotary kiln, fluidized bed furnace. Type of the furnace is not limited specially. The calcination can be effected even in a reaction tube that is used for the glycerin dehydration reaction. The firing temperature is usual 150 to 900 °C, preferably 200 to 600 °C and more preferably 200 to 500 °C. The calcination is continued usually for 0.5 to 10 hours.

The glycerin dehydration catalyst according to this invention, can be supported on a carrier ("supported catalyst"). Examples of the carrier are silica, diatomaceous earth, alumina, silica alumina, silica magnesia, zirconia, titania, magnesia, zeolite, silicon carbide and carbon. The catalyst can be supported on a single carrier or a complex or mixture of at least two carriers. By supporting the active material on carrier, active components can be used effectively. An amount of the active material is 5 to 200 % by weight, preferably 5 to 150 % by weight to the weight of the carrier.

The catalyst may have any shape and can be granule or powder. In case of gas phase reactions, however, it is preferable to mold the catalyst into a shape of sphere, pellets, cylinder, hollow cylinder, bar or the like, optionally with adding a molding aide. The catalyst can be shaped into the above-configurations together

with carrier and optional auxiliary agents. The molded catalyst may have a particle size of for example 1 to 10 mm for a fixed bed and of less than 1 mm for a fluidized bed.

The dehydration reaction of glycerin according to this invention can be carried out in gas phase or in liquid phase and the 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 and moving bed. Among them, the fixed bed and the fluidized bed are preferable. Regeneration of catalyst can be effected outside or inside the reactor. When the catalyst is taken out of a reactor for regeneration, the catalyst is regenerated in air or in oxygen-containing gas, or in hydrogen-containing gas. In case of liquid phase reaction, usual general type reactors for liquid reactions for solid catalysts can be used. Since a difference in boiling point between glycerin (290°C) and acrolein (53°C) and acrylic acid is big, the reaction is effected preferably at relatively lower temperatures so as to distil out acrolein continuously.

The reaction temperature for producing acrolein and acrylic acid by dehydration of glycerin in gas phase is effected preferably at a temperature of 450°C to 200°C. If the temperature is lower than 200°C, the life of catalyst will be shortened due to polymerization and to carbonization of glycerin and of reaction products because the boiling point of glycerin is high. On the contrary, if the temperature exceeds 450°C, the selectivity of acrolein and acrylic acid will be lowered due to increment in parallel reactions and consecutive reactions. Therefore, more preferable reaction temperature is 250 ° C to 350 ° C. The pressure is not limited specially but is preferably lower than 5 atm and more preferably lower than 3 atm. Under higher pressures, gasified glycerin will be re-liquefied and deposition of carbon will be promoted by higher pressure so that the life of catalyst will be shortened.

A feed rate of a reactant gas is preferably 500 to 10,000 h⁻¹ in term of the space velocity of GHSV (gaz hourly space velocity). If the GHSV becomes lower than 500 h⁻¹, the selectivity will be lowered due to successive reactions. On the contrary, if the GHSV exceeds 10,000h⁻¹, the conversion will be lowered.

The reaction temperature of the liquid phase reaction is preferably from

150 °C to 350 °C. The selectivity will be spoiled under lower temperatures although the conversion is improved. The reaction pressure is not limited specially but the reaction can be carried, if necessary, under a pressurized condition of 3 atm to 70 atm.

5 The material of glycerin is easily available in a form of aqueous solution of glycerin. Concentration of the aqueous solution of glycerin is from 5 % to 90 % by weight and more preferably 10 % to 50 % by weight. Too high concentration of glycerin will result in such problems as production of glycerin ethers or undesirable reaction between the resulting acrolein or acrylic acid and
10 material glycerin. Still more, the energy that is necessary to gasify glycerin is increased.

 The process according to the present invention is effected in the presence of molecular oxygen. The molecular oxygen may be in a form of air or in a form of a mixture of gasses containing molecular oxygen. The presence of oxygen
15 reduces the formation of aromatic compounds such as phenol and by-products originating from a hydrogenation of dehydrated products such as propanaldehyde and acetone or from hydroxypropanone. The oxygen content in the process according to the invention will generally be chosen so as not to exceed 7% relative to the mixture of gases entering the reaction (mixture of
20 glycerol/H₂O/oxygen/inert gases).

 In the process of the invention, the reactant gas may also contain gas such as nitrogen, argon, carbon dioxide, sulfur dioxide.

 The process according to the present invention can be effected in the presence of a gas containing propylene. In fact, the process according to the
25 present invention is advantageously carried out in the presence of a reaction gas issued from an oxidation of propylene to acrolein. This reaction gas is generally a mixture of non-reacted propylene, propane initially present in the propylene, inert gas, water vapour, oxygen, CO, CO₂, by products such as acrylic acid, acid or the like.

30 According to one particular embodiment of the invention, the process is performed in a reactor of the plate heat exchanger type. This reactor consists of plates forming between themselves circulation channels that can contain a catalyst. This

technology has many advantages in terms of heat exchange, associated with high heat exchange capacity. Thus, this type of reactor is particularly suitable for removing heat easily in the case of exothermic reactions, or for supplying heat in the start-up phases of reactions or in the case of endothermic reactions. More particularly, this reactor makes
5 it possible either to heat or to cool the catalyst. The heat exchange is particularly efficient with the circulation of a heat-exchange fluid in the system. The plates may be assembled in modules, which give greater flexibility, whether as regards the size of the reactor, its maintenance or the replacement of the catalyst. Systems that may be suitable for the process of the invention are, for example, the reactors described in documents
10 EP 995 491 or EP 1 147 807, the content of which is incorporated by reference.

These reactors are particularly suitable for the catalytic conversion of reaction media, specifically gaseous reaction media, such as those used in the present invention. The plate heat exchanger used for the preparation of (meth)acrolein or (meth)acrylic acid via catalytic oxidation of C3 or C4 precursors, described in document US
15 2005/0020851, may also be suitable for the process according to this invention.

The resulting acrolein prepared by the process according to this invention can be further oxidized to produce acrylic acid.

In a preferred embodiment according to the present invention, a process for preparing acrylic acid from glycerol comprising a first step of the dehydration
20 reaction of glycerol to acrolein, in which an intermediate step of partial condensation of the water and heavy by-products issuing from the dehydration step is implemented. In fact, the presence of water in the dehydration reactor serves to promote the gas phase glycerol dehydration reaction by limiting the deactivation of the dehydration catalyst. This process for synthesizing acrylic
25 acid from glycerol can overcome the drawbacks of prior methods, while allowing the use of dilute aqueous solutions of glycerol that enhance the dehydration reaction while being economical. The solution provided by the invention constitutes an optimization between the quantity of water fed to the first stage dehydration reactor and the quantity of water introduced into the second stage
30 oxidation reactor. The solution consists in at least partly condensing the water present in the stream issuing from the dehydration reaction of the aqueous glycerol solution, to prevent the second stage catalyst from being deactivated too

rapidly, on the one hand, and to prevent the acrylic acid solution produced from being too dilute, on the other.

More precisely, the present invention relates to a method for preparing acrylic acid from an aqueous solution of glycerol, comprising a first step of dehydration of the glycerol to acrolein, carried out in the gas phase in the presence of a catalyst and under a pressure of between 1 and 5 bar, and a second step of oxidation of the acrolein to acrylic acid, in which an intermediate step, consisting in at least partly condensing the water and heavy by-products present in the stream issuing from the first dehydration step is implemented. The expression at least partly condensing means that 20% to 95%, preferably 40% to 90%, of the water present in the stream issuing from the first step is removed in the intermediate step before being sent to the second stage reactor.

Simultaneously to the removal of water heavier products like unconverted glycerol, polyglycerol, glycerol acetals, acrylic acid, acetic acid and others are also extracted.

In order to avoid entrainment of heavy products downstream, the separation equipment can include a mist elimination device, such a demister. A demister is a device often fitted to vapor liquid separator vessels to enhance the removal of liquid droplets entrained in a vapor stream. With such a device, demisted vapor condenses on tubes without contamination by heavy-products. Such equipments are for example commercialized by Koch-Glitsch. They include Knitted meshes, Vanes, Fiberbeds and Cyclones. Preferred devices are Knitted Mesh and Fiberbeds.

The process according to this invention can be used advantageously in following second step of ammoxidation of acrolein glycerol to acrylonitrile, so that the resulting acrolein prepared by present invention is utilized effectively.

Now, the present invention will be explained in detail with referring illustrative examples but this invention should not be limited to those described in following examples. In the following Examples and Comparative Examples, % means mole %.

Example 1 (reference)

Preparation of NbOx

7.4529 g of niobium hydrogen oxalate ($\text{Nb}(\text{HC}_2\text{O}_4)_5 \cdot n\text{H}_2\text{O}$) was dispersed in 25 ml of distilled water and was subjected to ultrasonic wave vibration for 10 minutes. The resulting dispersion was introduced in an autoclave and was subjected to hydrothermal synthesis at 175°C for three days.

5 The resulting slurry was vacuum filtered, washed with distilled water and then dried at 80°C for one night to obtain a catalyst powder of NbOx .

Fig. 1 shows X-ray diffraction pattern of a catalyst obtained. Fig. 1 shows two peaks at $2\theta = 22.6$, $2\theta = 46.1$ and one peak at $2\theta < 2^\circ$.

Reactivity of the catalyst

10 The reactivity of the catalyst obtained was evaluated in a fixed bed through which reactants pass operated at ambient pressure. The catalyst powder was shaped in a press and passed through a sieve to obtain particles having particle sizes of 9 to 12 meshes. 10 cc of the particles were packed in a reaction tube made of SUS (diameter of 20 mm) to form a catalyst bed.

15 An aqueous solution of glycerin (concentration of 30 % by weight) was fed to an evaporator heated at 320°C at a flow rate of 21 g/hr by a pump so that glycerin was gasified. The resulting gasified glycerin was passed through the fixed catalyst bed together with air. The fixed catalyst bed was heated at a temperature of 280°C . Feed gas had following composition in mol %:

20 glycerin : nitrogen: oxygen : water = 6.8 : 9.1 : 2.4 : 82.

GHSV (calculated as the ratio of the normalized flow rate and the catalyst volume) was 2240 h^{-1} .

25 Products were condensed in a condenser and quantitative-analyzed by a gas chromatograph (GC-4000, GL Science, DB-WAX column). 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 (the conversion of glycerin) and the yield of objective substance (the yield of acrolein) from an amount of glycerin fed, an amount of glycerin remained and amounts of the products by following equations:

30 The conversion (%) of material = (a mole number of material reacted / a mole number of material supplied) $\times 100$

$$\begin{aligned} \text{The yield (\%)} &= \left(\frac{\text{a mole number of objective substance obtained}}{\text{a mole number of material fed}} \right) \\ &\times 100 \end{aligned}$$

Results are summarized in Table 1.

5

Example 2 : Preparation of WNbOx

1.1376 g of niobium oxide ($\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$) was dispersed in 25 ml of distilled water and was subjected to ultrasonic wave vibration for 10 minutes to prepare a dispersion of niobium oxide. In a separated flask, 0.7660 g of ammonium metatungstate ($(\text{NH}_4)_6 [\text{H}_2\text{W}_{12}\text{O}_{40}] n\text{H}_2\text{O}$ ($n = \text{about } 30$, a product of Nippon Inorganic Colour & Chemical)) was dissolved in 20 ml of distilled water. The resulting aqueous solution of ammonium metatungstate was added into the dispersion of niobium oxide slowly. The resulting mixture was introduced in an autoclave and was subjected to hydrothermal synthesis at 175°C for three days.

15 The resulting slurry was vacuum filtered, washed with distilled water and then dried at 80°C for one night to obtain a catalyst powder of WNbOx.

This catalyst shows X-ray diffraction pattern of Fig. 1 which has two peaks at $2\theta = 22.6$, $2\theta = 46.1$ and one peak at $2\theta < 2^\circ$, the latter is similar to the pattern of the catalyst of example 1.

20 The reactivity of the catalyst obtained was evaluated by the same method as Example 1 but with the following conditions:

. The fixed catalyst bed was heated at a temperature of 280°C . Feed gas had following composition in mol %:

glycerin : nitrogen: oxygen : water = 6.4 : 13.7 : 3.6 : 76.

25 GHSV (calculated as the ratio of the normalized flow rate and the catalyst volume) was 2400 h^{-1} .

The results are summarized in Table 1.

Example 3 : Preparation of Cs-exchanged WNbOx

30 The catalyst of WNbOx obtained in Example 2 was ion-exchanged with Cs.

0.2612 g of CsCl was added to 25 ml of distilled water. Into the resulting

aqueous solution of CsCl, 1.0 g of WNbOx obtained in Example 2 was added and stirred at ambient temperature for 24 hours. Then, the resulting slurry was vacuum-filtered, washed with distilled water and then dried at 80°C for one night to obtain a Cs-exchanged WNbOx.

5 The reactivity of the catalyst obtained was evaluated by the same method as Example 1 but with the following conditions:

. The fixed catalyst bed was heated at a temperature of 300°C. Feed gas had following composition in mol %:

glycerin : nitrogen: oxygen : water = 6.6 : 11.1 : 3.0 : 79. GHSV
10 (calculated as the ratio of the normalized flow rate and the catalyst volume) was 2300 h⁻¹.

The results are summarized in Table 1.

Example 4 : Calcination of WNbOx

15 The WNbOx powder obtained in Example 2 was calcinated in a horizontal type electric furnace at 500°C in air for 3 hours to obtain a fired catalyst. The reactivity of the catalyst obtained was evaluated by the same method as Example 1 but with the following conditions

. The fixed catalyst bed was heated at a temperature of 280°C. Feed gas
20 had following composition in mol %:

glycerin : nitrogen: oxygen : water = 7.0 : 7.6 : 2.0 : 83. GHSV
(calculated as the ratio of the normalized flow rate and the catalyst volume) was 2190 h⁻¹.

The results are summarized in Table 1.

25

Comparative Example 1

Commercially available niobium oxide (Nb₂O₅ · nH₂O, SOEKAWA Chemical Co., Ltd.) was calcinated in air in a Muffle furnace at 500°C in air for 3 hours to obtain a NbOx catalyst.

30 X-ray diffraction pattern of this catalyst is shown in Fig. 1 in which strong peaks are observed at 2θ = 22.8, 28.7, 36.9 and 46.4° which are typical peaks of niobium penta oxide.

The reactivity of the catalyst obtained was evaluated by the same method as Example 1 and the results are summarized in Table 1.

Comparative Example 2

5 Commercially available niobium hydrogen oxalate ($\text{Nb}(\text{HC}_2\text{O}_4)_5 \cdot n\text{H}_2\text{O}$, SOEKAWA Chemical Co., Ltd.) was calcinated in air in a Muffle furnace at 500°C in air for 3 hours to obtain a NbOx catalyst.

The resulting catalyst is amorphous and shows no X-ray diffraction pattern as is shown in Fig. 1.

10 The reactivity of the catalyst obtained was evaluated by the same method as Example 1 and the results are summarized in Table 1.

Table 1

	Glycerin conversion after 12 hrs on stream (%)	Acrolein yield after 12 hrs on stream (%)
Example 1 (reference)	100	28
2	100	75
3	100	71
4	100	67
Comparative 1	26.5	16.2
2	41.3	21.9

Examples 5 – 6 : Preparation of SiWNbOx

15 a) *preparation of a solution of Niobium.*

640 g of distilled water then 51.2 g of niobic acid from CBMM (i.e. 0.304 moles of niobium) are introduced into a 5 l beaker. Then 103.2 g (0.816 moles) of dehydrated oxalic acid is added. The molar ratio oxalic acid/niobium is therefore 2.69. The slurry obtained previously is heated at 60 °C for 2 hours, being covered
20 so as to avoid evaporation and with stirring. Thus a white suspension is obtained and left to cool to 30 °C under stirring, which takes about 2 hours. After decantation, the small white deposit representing less than 5 % of introduced

niobium is eliminated.

b) preparation of a solution of W.

2120 g of distilled water, 100 g of ammonium paratungstate (3132 g/mole) i.e. 0.383 moles of tungsten), are introduced in a 5 liters beaker. The solution is
5 heated at 60 °C for 1 hr and 20 minutes, being covered to avoid evaporation and with stirring. In this way a clear solution is obtained.

c) Introduction of silica.

393.6 g of Ludox AS40 silica (containing 40 wt % of silica) is introduced under stirring in the previous tungsten solution. The latter retains its limpidity. Then the
10 previously prepared niobium solution is added. A gel is quickly formed within a few minutes. This solution is then dried by atomization. The atomizer used is a laboratory atomizer (ATSELAB from Sodeva). The atomization takes place in a nitrogen atmosphere. The nitrogen flow rate is 45 Nm³/h, the flow rate of slurry is 500 g/h, the inlet temperature of the gas is comprised between 155 °C and
15 170 °C, the outlet temperature is comprised between 92 and 100 °C. Then the product recovered which has a particle size less than 40 microns, is placed in an oven overnight at 130 °C, on a Teflon coated plate.

d) Precalcination and calcination.

The precalcination was carried out under air and the calcination was carried out
20 under nitrogen, in stainless steel capacities. An internal thermometer well allows precise monitoring of the temperature. First 50 g of precursor obtained previously was precalcined for 4 hours at 300 °C under air flow of 50 ml/min/g of precursor. The solid obtained is called CATALYST A.

25 g of the solid obtained at the previous step (CATALYST A) is then calcined
25 for 2 hrs at 600 °C under a nitrogen flow of 15 ml/min/g of solid. A new solid CATALYST B is then obtained.

Reactivity of CATALYST A AND CATALYST B

The catalysts A and B were evaluated in a fixed bed reactor operated under ambient pressure in a fixed bed. Namely, the resulting catalyst powder is
30 compacted and then crushed. Crushed particles are passed through sieves to obtain particles having a particle size of 9 to 12 mesh. 10 cc of the catalyst granules or particles is packed in a SUS reaction tube (diameter of 10 mm).

An aqueous solution of glycerin (a concentration of 20 % by weight) is fed to an evaporator at a flow rate of 21 g/hr by a pump so that glycerin is gasified at 300°C. The resulting gasified glycerin is passed through the fixed catalyst bed together with air. The fixed catalyst bed is heated at a temperature of 260°C to 350°C. Feed gas has a following composition in mol %: glycerin: oxygen: nitrogen: water = 4.2 : 2.2 : 8.1 : 85.5. GHSV is 2,500 h⁻¹.

Products are condensed in a condenser and quantitative-analyzed by a gas chromatograph. Proportions of products are corrected in factors from the results of the gas chromatograph to determine absolute amounts of products to calculate the conversion (%) of material (the conversion of glycerin), the selectivity of target substance (the selectivity of acrolein) and the yield of target substance (the yield of acrolein) from an amount of glycerin fed, an amount of glycerin remaining and amounts of the products by following equations:

The conversion (%) of material = 100 * (a mole number of material reacted / a mole number of material supplied)

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

The yield (%) objective substance = 100 * (a mole number of objective substance obtained / a mole number of material fed)

Results are shown in Table 2.

Table 2

	CATALYST	Reaction temperature, °C	Acrolein yield, %
Exemple 5	A	310	65
6	B	300	70

25 Example 7

This example was made to show that acrolein having a lower propanaldehyde content can be produced by the process according to the present invention.

In the example, a tubular reactor consisting of a tube 85 cm long and with an inside diameter of 6 mm is used to perform the glycerol dehydration reaction in the gas phase at atmospheric pressure. This reactor is placed in a heated chamber maintained at the reaction temperature, which is 300°C. The catalyst B is ground and pelletized to obtain particles of 0.5 to 1.0 mm. 2 ml of catalyst B are loaded into the reactor to form a 'bottom' catalytic bed. Then 10 ml of tungsten zirconia (90.7% ZrO₂ - 9.3% WO₃) from Daiichi Kigenso (supplier reference H1417) are loaded on top of the Catalyst B layer. This loading is maintained at the reaction temperature for 5 to 10 minutes before introducing the reagents. The reactor is fed with an aqueous solution containing 20% by weight of glycerol at a mean feed flow rate of 12 ml/h. The aqueous glycerol solution is vaporized in a heated chamber, and then passes over the catalyst. The calculated contact time is about 2 sec (ratio of catalyst volume to flowrate at normalized temperature and pressure). The duration of a catalyst test is about 7 hours, which corresponds to about 80 ml of aqueous glycerol solution passed over the catalyst. After reaction, the products are condensed in a trap refrigerated with crushed ice. Samples of the effluents are collected periodically. For each sample collection, the flow is interrupted and a gentle flow of nitrogen is passed through the reactor to purge it. The trap at the reactor outlet is then replaced, the nitrogen flow is stopped and the reactor is returned under a flow of reagent. The test is continued until appreciable deactivation of the catalyst is noted.

For each experiment, the total mass of products entering and leaving is measured, which allowed a mass balance to be determined. Similarly, the products formed are analysed by chromatography. Two types of analysis were performed:

- an analysis by chromatography on a filled column (FFAP column 2 m*1/8") on a Carlo Erba chromatograph equipped with a TCD detector. The quantitative analysis is performed with an external standard (2-butanone);
- an analysis by chromatography on a capillary column (FFAP column 50 m*0.25 mm) on an HP6890 chromatograph equipped with a FID detector with the same samples stored at -15°C.

The first method is particularly suitable for rapid analysis of the products,

and especially the yield of acrolein. The second method is used to have a more precise analysis of all the reaction by-products. Moreover, analyses by GC-MS or by chromatography after silylation are performed to confirm these results.

The products thus quantified are the unreacted glycerol, the acrolein
5 formed and the by-products such as propanaldehyde,.

In the example, the glycerol conversion, the acrolein and propanaldehyde yields are defined as follows:

- glycerol conversion (%) = $100 \times \frac{\text{number of moles of glycerol remaining}}{\text{number of moles of glycerol introduced}}$;
- 10 - acrolein yield (%) = $\frac{\text{number of moles of acrolein produced}}{\text{number of moles of glycerol introduced}}$;
- propanaldehyde yield (%) = $\frac{\text{number of moles of propanaldehyde produced}}{\text{number of moles of glycerol introduced}}$.

All the results are expressed as molar percentages relative to the glycerol
15 introduced.

Table 3

Cumulative glycerol introduced (g)	8	16	24
Glycerol conversion, %	100	100	92
Acrolein yield, %	65	68	63
Propanaldehyde yield, %	0.5	0.08	0.10

Example 8

The previous example 7 is reproduced without the bottom layer of catalyst B
20 Results are shown in Table 4.

Table 4

Cumulative glycerol introduced (g)	8	16	24
Glycerol conversion, %	100	100	92
Acrolein yield, %	68	72	65
Propanaldehyde yield, %	3.1	2.1	1.6

The process according to this invention in which glycerin is catalytic dehydrated to prepare acrolein and acrylic acid is very advantageous for industrial uses, because acrolein and acrylic acid can be produced at higher yield and in higher efficiency.

5

Claims

1. Process for preparing acrolein by dehydration of glycerin in the presence of molecular oxygen in an amount chosen so as to be outside the flammability range at any point in the plant characterized in that said dehydration is carried out in the presence of a catalyst comprising as a main component, a mixed oxide containing niobium oxide NbO_x and at least one element taken from the group of tungsten, molybdenum and chromium.
2. Process according to claim 1 characterized in that the X-ray diffraction pattern (Cu-K α , λ = 1.5428 nm) of said niobium oxide (NbO_x) has two peaks at $2\theta = 22.6 \pm 0.4$, $2\theta = 46.1 \pm 0.4$.
3. Process according to claim 1 or 2 characterized in that the mixed oxide is represented by the following general formula:

$$A_a (B_b NbO_x) \cdot nH_2O$$
 in which A is at least one member selected from elements belonging to Group 1 to Group 16 of the Periodic Table of Elements and ammonium, B is at least one element selected from W, Mo and Cr, Nb is niobium, $a \geq 0$, $b > 0$, x is a number determined by oxidation numbers of the elements and n is a any positive number.
4. Process according to any one of claims 1 to 3 characterized in that said catalyst is prepared by hydrothermal synthesis.
5. Process according to claim 4 characterized in that said catalyst is prepared by oxidizing a niobium containing compound which will be changed to an oxide when heated by hydrothermal synthesis technique.
6. Process according to any one of claims 1 to 3 characterized in that said catalyst is prepared by coprecipitation synthesis technique.

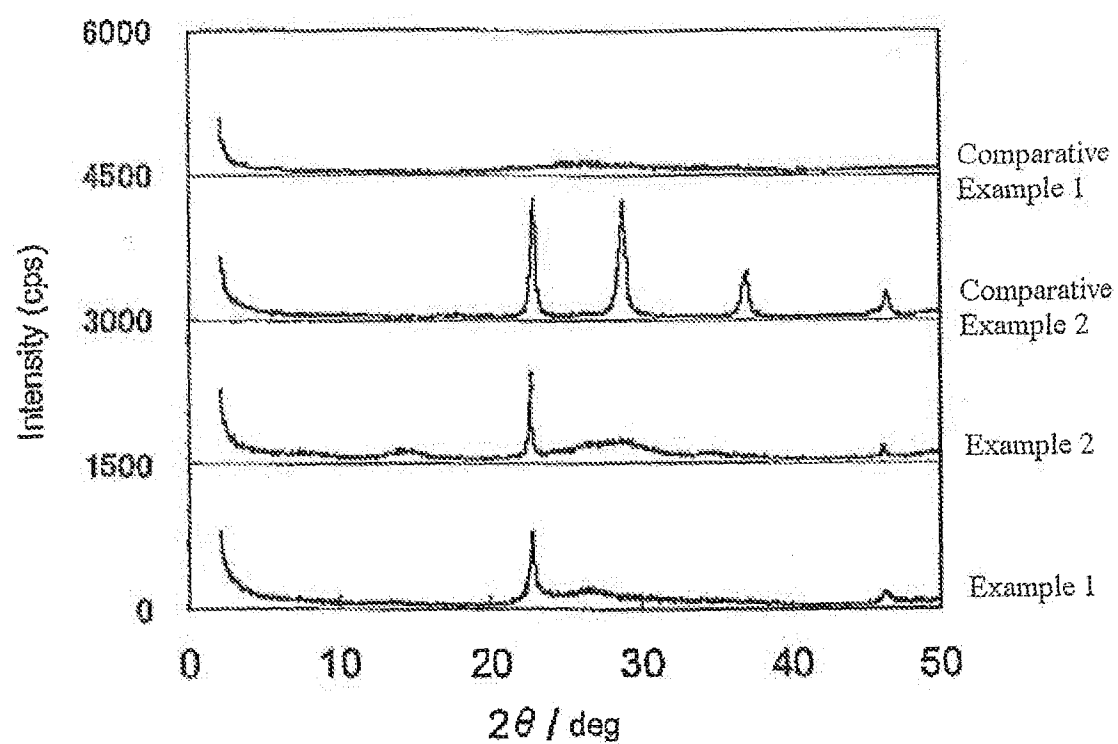
7. Process according to any one of claims 1 to 6 characterized in that said catalyst comprises one salt of elements belonging to Group 1 to Group 16 of the Periodic Table of Elements and ammonium, or is exchanged partially with at least one element belonging to Group 1 to Group 16 of the Periodic Table of Elements and ammonium.
8. Process according to claim 7 characterized in that the element belonging to Group 1 to 16 of the Periodic Table of Elements is preferably selected from the group comprising alkali metals such as cesium, potassium or rubidium, alkaline earth metals, rare earths, V, Ti, Ta, Mn, Fe, Co, Ni, Cu, Zn, Ga, In, Tl, Sn and Pb
9. Process according to any one of claims 1 to 8 characterized in that a mixture containing at least glycerin, water, oxygen or an oxygen-containing gas, and where appropriate an inert gas and/or recycle gases is passed, in the gas phase, over the said catalyst that is maintained at a reaction temperature between 180 and 500°C.
10. Process according to claim 9 characterized in that a first active catalyst bed or a first reactor enabling the dehydration of glycerin is placed upstream of the said catalyst comprising niobium oxide (NbO_x).
11. Process for preparing acrylic acid from glycerin comprising a first step of the dehydration reaction of glycerin to acrolein according to any one of claims 1 to 10 and a step of oxidizing acrolein to acrylic acid.
12. Process according to Claim 11 characterized in that use is made of an intermediate step of partial condensation of water and of the heavy by-products derived from the dehydration step.
13. Process for preparing acrylonitrile from glycerin comprising a first step of

preparing acrolein according to the process from any one of claims 1 to 10 and a step of ammoxidizing acrolein to acrylonitrile.

14. Process for preparing acrylamide from glycerin comprising a first step of
5 preparing acrolein according to the process from any one of claims 1 to 10 and a step of amidification of acrolein to acrylamide.

15. Use of acrolein obtained according to the process of any one of claims 1 to
10 10 to prepare glutaraldehyde, pyridine, methionine, or acrolein polymers or copolymers.

Fig. 1



INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2010/002181

A. CLASSIFICATION OF SUBJECT MATTER INV. C07C45/52 C07C47/22 ADD. C07C57/055 C07C253/26 C07C231/00		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) C07C		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EP0-Internal, CHEM ABS Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2005/044874 A1 (CHEMEQ LTD [AU]; TILBROOK MATTHEW [AU]) 19 May 2005 (2005-05-19) abstract	15
Y	CHAI ET AL: "Sustainable production of acrolein: Gas-phase dehydration of glycerol over Nb2O5 catalyst", JOURNAL OF CATALYSIS, ACADEMIC PRESS, DULUTH, MN, US, vol. 250, no. 2, 14 August 2007 (2007-08-14), pages 342-349, XP022200532, ISSN: 0021-9517, DOI: DOI:10.1016/J.JCAT.2007.06.016 abstract last paragraph; page 344, column 2	1-14
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☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family		
Date of the actual completion of the international search 5 April 2011		Date of mailing of the international search report 13/05/2011
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Delanghe, Patrick

INTERNATIONAL SEARCH REPORT

International application No

PCT/IB2010/002181

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Information on patent family members

International application No

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