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(54) Title: PROCESS FOR PREPARING CATALYST USED IN PRODUCTION OF ACROLEIN AND/OR ACRYLIC ACID AND PROCESS FOR PREPARING ACROLEIN AND/OR ACRYLIC ACID BY DEHYDRATION REACTION OF GLYCERIN

(57) Abstract: A process for preparing a catalyst having a minimized amount of basic sites used in a production of acrolein and acrylic acid by dehydration reaction of glycerin, comprising more than one cycle of contacting a material with a solution of at least one acid precursor or one heteropolyacid or one heteropolyacid salt, drying and calcining the resulting solid mixture. This invention relates also to an improved catalyst used in the dehydration reaction of glycerine and further to a process for preparing acrolein and/or acrylic acid carried out in the presence of the dehydration catalyst.

Description

Title of Invention: PROCESS FOR PREPARING CATALYST USED IN PRODUCTION OF ACROLEIN AND/OR ACRYLIC ACID AND PROCESS FOR PREPARING ACROLEIN AND/OR ACRYLIC ACID BY DEHYDRATION REACTION OF GLYCERIN

Technical Field

[0001] This invention relates to improvement in a process for preparing a catalyst used in dehydration reaction of glycerin to produce unsaturated aldehyde such as acrolein and/or unsaturated carboxylic acid such as acrylic acid.

[0002] This invention relates also to an improved catalyst used in the dehydration reaction of glycerin.

[0003] This invention relates further to a process for preparing acrolein and/or acrylic acid carried out in the presence of the dehydration catalyst.

Background Art

[0004] Glycerin is obtained in large amount as a byproduct when bio-fuel is produced from bio resources that do not depend on fossil resources, and research of new uses of glycerin is under development.

[0005] Acrolein is a key intermediate for the synthesis of methionine, a synthetic protein used as an animal feed supplement, which has emerged as a substitute for fishmeal. Acrolein is also a non-isolated synthetic intermediate of acrylic acid, for which the importance of its applications and its derivatives is known. Acrolein also leads, via reaction with methyl vinyl ether then hydrolysis, to glutaraldehyde, which has many uses in leather tanning, as a biocide in oil well drilling and during the treatment of cutting oils, and as a chemical sterilising agent and disinfectant for hospital equipment.

[0006] Acrolein is 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 oxides. Glycerin, derived from plant oils in the production of biodiesel fuels is one of the routes envisaged as a substitute for propylene, glycerin being able to be subjected to a catalytic dehydration reaction in order to produce acrolein. Such a process makes it possible to thus respond to the concept of green chemistry within a more general context of protecting the environment.

[0007] Numerous catalyst systems have already been the subject of studies for the dehydration reaction of glycerin to acrolein.

[0008] 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 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%.

[0009] In US Patent No. 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.

[0010] US Patent No. 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 degrees centigrade, 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 mordenite, montmorillonite and acidic zeolites; supports, such as oxides or siliceous materials, for example alumina $(A1_20_3)$, titanium oxide $(Ti0_2)$, covered by monobasic, dibasic or tribasic inorganic acids; oxides or mixed oxides such as gamma-alumina, ZnO/Al_20_3 mixed oxide, or heteropoly acids. The use of these catalysts would make it possible to solve the problem of formation of secondary products generated with the iron phosphate type catalysts described in the aforementioned document FR 695,931.

[001 1] According to International Application WO 2006/087084, 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.

[0012] U.S. Patent Specification No. 2009054538 discloses catalyst composition comprising phosphotungstic or phosphomolybdic acid on silica support and the acrolein yields obtained are not over 71% with the catalysts.

[0013] WO 2007/058221 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-modal pore size distribution 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.

[0014] Inventors have proposed also, in WO 2009/136537, WO 2009/128555 and other pending applications, an improved dehydration catalyst comprising mainly a compound in which protons in a heteropolyacid are exchanged at least partially with at least one cation selected from elements belonging to Group 1 to Group 16 of the Periodic Table of Elements.

[0015] In WO 2011/046232, the catalytic dehydration of glycerin is carried out under a pressurized condition and in the presence of a catalyst prepared according to a process comprising the steps of mixing a solution of at least one metal selected from elements belonging to Group 1 to Group 16 of the Periodic Table of Elements or its onium with a solution of heteropolyacid or constituents of heteropolyacid, and of calcinating the resulting solid substance directly or after the resulting solid substance is supported on a carrier.

[0016] As are explained above, known patents teach to select an acidic support for dehydrating glycerin. However, the catalysts recommended in the prior art for producing acrolein from glycerin 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 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, when acrolein is used for producing acrylic acid, the propanaldehyde present may be oxidized to propionic acid that is 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 glycerin.

[0017] The inventors have proposed in WO 2006/087084 an improved process for the manufacture of acrolein by dehydration of glycerol in the presence of acid gas additives. The improved process is based on dehydration of glycerol in the presence of a solid acid catalyst having a Hammett acidity of less than +2, such as sulfated zirconias, phosphated zirconias, tungstated zirconias, silica zirconias, sulfated titanium or tin oxides, phosphated aluminas or silicas, doped iron phosphates, or phospho- or silicotungstic acid salts, implemented in a reaction medium comprising a gas phase comprising from 1 to 3000 ppm of an acid compound within the meaning of the Pearson classification chosen, for example, from SO_3, SO_2 or NO_2, the dehydration reaction being carried out either in the gas phase or in the liquid phase.

[0018] Inventors of this application searched for a solution that can solve the above-mentioned problems and finally found that acrolein can be produced by dehydration reaction of glycerin at higher yield by using an acidic catalyst having a minimized amount of basic sites.

Citation List

Patent Literature

[0019] PTL 1: French Patent FR 695 931
PTL 2: US Patent No. 2,558,520
PTL 3: US Patent No. 5,387,720
PTL 4: WO 2006/087084
PTL 5: U.S. Patent Specification No. 2009054538
PTL 6: WO 2007/058221
PTL 7: WO 2009/136537
PTL 8: WO 2009/128555
PTL 9: WO 2011/046232

Summary of Invention

Technical Problem

[0020] Inventors found an improved process for preparing a catalyst used in dehydration reaction of glycerin, which can improve the yield of products of acrolein and acrylic acid.

[0021] Inventors have discovered that the catalysts of acid type known for the catalysis of the dehydration reaction of glycerin which are solid homogeneous or multiphase materials insoluble in the reaction medium which, although acidic, can also exhibit some undesirable sites probably the cause of the formation of the by-products by reaction mechanisms which are sometimes not easy to predict.

[0022] Previous work shows that a solid is rarely composed either of solely acidic sites or of solely basic sites. Acid solids have most of the time both acidic sites, which are predominant, but also some basic sites. This dichotomy is illustrated in particular in the paper by A. Auroux and A. Gervasini "J. Microcalorimetric Study of the Acidity and Basicity of Metal Oxide Surfaces", Phys. Chem., (1990) 94, 6371-79 where figure 13 shows that one and the same oxide can simultaneously adsorb an acid compound, such as $C0_2$, and a basic compound, such as NH_3. Without wishing to be committed to any one theory, it is believed that the latter compounds contribute to the formation of the byproducts in the reaction of dehydration of glycerin.

[0023] The acidity of the solids can be measured in numerous ways and the Hammett method is only one of them (K. Tanabe et al. in "Studies in Surface Science and Catalysis", Vol. 51, 1989, Chap. 1 and 2).

[0024] The work by C. Marcilly Vol. 1, in Editions Technip (ISBN No. 2-7108-0841-2), furthermore lists various methods for measuring the acidity and the basicity of the solids.

[0025] Inventors found that by neutralizing some basic sites present on the surface of the solid catalyst used in a production of acrolein and acrylic acid by dehydration reaction of glycerin, acrolein and acrylic acid can be produced at higher productivity and for longer time.

[0026] Therefore it is an object of the present invention to provide a process for preparing a catalyst having a minimized amount of basic sites used in a production of acrolein and acrylic acid by dehydration reaction of glycerin.

[0027] Another object of this invention is to provide an improved catalyst obtained by the above process having a minimized amount of basic sites that can produce acrolein and acrylic acid at a higher yield and at a higher productivity.

[0028] Still another object of this invention is to provide an improved process for producing acrolein and acrylic acid by a catalytic dehydration reaction of glycerin.

Solution to Problem

[0029] From the first aspect, the present invention provides a process for preparing a catalyst having a minimized amount of basic sites used in a production of acrolein and acrylic acid by dehydration reaction of glycerin, comprising more than one cycle of contacting a material with a solution of at least one acid precursor or one heteropolyacid or one heteropolyacid salt, drying and calcining the resulting solid mixture.

[0030] The said process is based on multiple neutralization steps of a material that may include basic or amphoteric materials that those of ordinary skill in the art would not select with the previous knowledge, or known acidic materials that present basic sites.

[0031] In the invention, "a minimized amount of basic sites" means that the basic sites decrease at each cycle contacting/drying/calcining of the process of the invention to obtain a catalyst having a minimized amount of basic sites.

[0032] Basic sites may be determined by any known methods of prior art, for example by adsorption of an acid compound such as $C0_2$ or $S0_2$, and by microcalorimetric measurements of the energy of adsorption.

[0033] In one embodiment of the process of the invention, the material which is used as raw material to be contacted with the solution is a basic material or an amphoteric material having a specific surface area greater than 5 m^2/g, preferably greater than 30 m^2/g.

[0034] The basicity may be related to the composition of the material (surface defects such as impurities like alkaline metals), or to the crystal structure of the material.

[0035] Basic materials or amphoteric materials can be for example basic mixed metal oxide, such as zirconium lanthanum oxide, zirconium cerium oxide, zirconium strontium oxide, zirconium ytterbium oxide, metal hydroxides such as zirconium oxide or hydroxyapatite or layered double hydroxides such as hydrotalcite.

[0036] Basic sites may be characterized by $S0_2$ adsorption. Preferred materials are those characterized by adsorption of $S0_2$ higher than 20 micromole $S0_2/g$.

[0037] In another embodiment of the process of the invention, the material which is used as raw material to be contacted with the solution, is an acidic solid having basic sites.

[0038] Acidity of the solid may be characterized by NH_3 adsorption or Hammett acidity. Preferred acidic solids have a Hammett acidity of less than +2, and have basic sites expressed by adsorption of $S0_2$ higher than 20 micromole $S0_2$/g.

[0039] Such acidic materials may be chosen for example among natural or synthetic siliceous materials or acidic zeolites; mineral supports, such as oxides, coated with mono-, di-, tri- or polyacidic inorganic acids; oxides or mixed oxides, or alternatively heteropoly acids.

[0040] The material used in the present invention is not limited specially but the material may be silica, diatomaceous earth, alumina, silica alumina, silica magnesia, zirconia, titania, niobia, magnesia, zeolite, silicon carbide, carbide, ceria, boria, ceria-titania, zirconia-ceria, alumina-titanate and alumina-boria.

[0041] The acidic solids may be advantageously chosen from zeolites, Nafion (registered tradename) composites (based on sulfonic acid of fluorinated polymers), chlorinated aluminas, phosphotungstic and/or silicotungstic acids and acid salts, and various solids of metal oxide type such as tantalum oxide Ta_20_5, niobium oxide Nb_20_5, alumina Al_20_3, titanium oxide $Ti0_2$, zirconia $Zr0_2$, tin oxide $Sn0_2$, silica $Si0_2$ or silico-aluminate $Si0_2$-Al_20_3, impregnated with acidic functions such as boric acid, sulphuric acid, tungstic acid, phosphoric acid, or molybdic acid or a combination thereof. The preferred acidic solids are sulfate zirconias, phosphate zirconias, tungsten zirconias, siliceous zirconias, sulfate titanium or tin oxides, and phosphate aluminas or silicas.

[0042] According to the process of the invention, the material is contacted with a solution in excess or not.

[0043] The word "contacted" means the techniques of impregnation, washing, or treatment like chemical exchange, according to the nature of the solution.

[0044] The solution used in the process of the invention is a solution of at least one acid precursor or one heteropolyacid or one heteropolyacid salt.

[0045] The acid precursor may be a mono-, di-, tri- or polyacidic inorganic acid, for example $HN0_3$, HC1, H_2S0_4, H_2W0_4, boric acid, niobic acid, or a salt of a mono-, di-, tri- or polyacidic inorganic acid, such as for example ammonium oxalatoniobiate.

[0046] The heteropolyacid is represented by the general formula (1):

$H_a(X_1Y_cZ_dO_e)\ nH_20$ (l)

in which

H is hydrogen,

X is P or Si,

Y is more than one element selected from the group comprising W, Mo, Ti, Zr, V, Nb, Ta, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, In, Tl, Sn and Pb,

Z is more than one element selected from the group comprising W, Mo, Ti, Zr, V,

Nb, Ta, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, In, Tl, Sn and Pb, and a, b, c and satisfying following ranges:
a is not less than 0 but less than 9
c is greater than 0 but not greater than 12, and
d is not less than 0 but less than 12
e is a number determined by the oxidation of the elements and n is any positive number.

[0047] Heteropoly acids are preferred, but heteropoly acids in which protons in a heteropolyacid are exchanged at least partially with at least one cation selected from elements belonging to Group 1 to Group 16 of the Periodic Table of Elements or with ammonium may be used, preferably with ammonium.

[0048] The process invention may have following features taken separately or in combination:

(1) the contacting is performed by techniques of pore volume impregnation (incipient wetness) for example by spraying the solution

(2) the contacting is performed by excess solution impregnation,

(3) the contacting is performed by chemical exchange with excess solution.

(4) the multiple contacting procedure is performed with different solutions at each step.

(5) the contacting is performed statically or dynamically

(6) the calcination is carried out under an atmosphere of air, inert gas or a mixture of oxygen and inert gas, or under a reducing gas.

(7) the calcination is carried out at a temperature of 150 to 900 degrees centigrade for 0.5 to 20 hours.

(8) between two and four cycles are performed, preferably three cycles are performed.

[0049] The present invention provides further a catalyst having a minimized amount of basic sites obtained by the above process for production of acrolein and acrylic acid by dehydration reaction of glycerin.

[0050] The minimized amount of basic sites means for example that adsorption of $S0_2$ is lower than 20 micromole $S0_2$ per gram of catalyst..

[0051] The present invention provides further a process for preparing acrolein by catalytic dehydration of glycerin in the presence of the catalyst.

[0052] The present invention provides further a process for preparing acrylic acid in which the resulting acrolein from the above process is further oxidized to produce acrylic acid.

[0053] The above processes may have following features (1) to (7) taken separately or in combination:

(1) The dehydration of glycerin is effected in the presence of oxygen gas with the conditions disclosed for example in WO 06/087083 or WO 06/1 14506.

(2) The dehydration of glycerin 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 glycerin 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.

(3) The dehydration of glycerin is carried out in a plate heat exchanger type reactor or in a fixed bed reactor or in a fluidized bed type reactor or in a circulating fluidized bed or in a moving bed.

(4) The process for preparing acrylic acid has an intermediate step of partial condensation and removal of water and heavy by-products issuing from the dehydration step, as described for example in WO 08/087315.

(5) The resulting acrolein from the catalytic dehydration of glycerin is further oxidized to produce acrylic acid, according to the methods well known to the skilled in the arts.

(6) The process for preparing acrylic acid further comprises the steps of collecting the resultant acrylic acid as a solution by using water or a solvent and then of purifying the resultant solution containing acrylic acid by using for example distillation and/or crystallization.

(7) The present invention provides further a process for preparing acrylonitrile, characterized in that acrolein obtained by the above process for preparing acrolein by catalytic dehydration of glycerin is subjected to ammoxidation, as described for example in WO 08/1 13927.

Advantageous Effect of Invention

[0054] By using the improved catalyst, acrolein and acrylic acid can be produced at higher yield by the dehydration reaction of glycerin.

Description of Embodiments

[0055] In the first preferred embodiment, the glycerin dehydration catalyst according to this invention is prepared by impregnating a basic material at incipient wetness by spraying the material with a solution of a heteropolyacid, then drying the resulting solid under ambient pressure at about 120 degrees centigrade for several hours and calcinating under air at a temperature of 400 to 500 degrees centigrade for several hours. The same operations are repeated at least once again, preferably twice again.

[0056] The heteropolyacid is known and has several structures such as Keggin type, Dawson type and Anderson type and possess generally such high molecular weight as 700 to 8,500. There are dimer complex forms and those dimer complex are included in the present invention.

[0057] In another preferred embodiment, a solution of a heteropolyacid in which protons are exchanged at least partially with at least one cation selected from elements belonging to Group 1 to Group 16 of the Periodic Table of Elements or with ammonium may be used as impregnating solution.

[0058] The elements belonging to Group 1 to Group 16 of the Periodic Table of Elements may be sodium, potassium, rubidium, cesium, magnesium, calcium, strontium, barium, scandium, yttrium, lanthanide, titanium, zirconium, hafnium, chromium, manganese, rhenium, iron, ruthenium, osmium, cobalt, rhodium, iridium, nickel, palladium, platinum, copper, silver, gold, zinc, gallium, indium, thallium, germanium, tin, lead, bismuth and tellurium. The onium salts of heteropolyacid may be amine salts, ammonium salts, phosphonium salts and sulfonium salts, preferably ammonium salts.

[0059] The heteropolyacids used in this invention to prepare a glycerin dehydration catalyst may be for example phosphotungstic acid, metatungstic acid, tungstosilicic acid, phosphomolybdic acid and silicomolybdic acid.

[0060] The constituents of heteropolyacid that can be used in the present invention can be any form that results in the heteropolyacid. The constituents of heteropolyacid may be, for example, a combination of an acid such as phosphoric acid, silicic acid, molybdic acid, tungstic acid, metatungstic acid and borotungustic acid with a salt such as for example ammonium pertungstate, ammonium phosphate and ammonium metasilicate.

[0061] In a variation, the glycerin dehydration catalyst according to this invention may be prepared by mixing a material with an aqueous solution of an inorganic acid or an ammonium salt of an inorganic acid to take away surface basic metals.

[0062] The mixing can be carried out at ambient temperature (about 20 degrees centigrade). Higher temperatures of about 40 degrees centigrade to about 150 degrees centigrade may be used, if desired. This treatment may be continued, preferably with agitation, for about 0.1 to about 5 hours sufficient to permit the chemical exchange. At the end of the mixture step, the excess aqueous solution can be removed from the treated material, for example by filtration.

[0063] The resulting solid substance is then dried and calcinated to obtain the catalyst.

[0064] The material can be granule and powder and may have any shape such as sphere, pellet, cylindrical body, hollow cylinder body and bar with optional molding aid.

[0065] The material has preferably a specific surface area of greater than 80 m^2/g, preferably greater or equal to 100 m^2/g.

[0066] The impregnated amount can be 5% to 50 % by weight of the material.

[0067] Solvent for preparing the impregnating solution is not limited specially and can be any solvent that can make the solution. Water is preferably used as solvent, so that the solution is preferably an aqueous solution.

[0068] The catalyst may have any shape and can be granule, powder or monolith. In case of gas phase reactions, however, it is preferable to mold the catalyst into a shape of monolith, sphere, pellets, cylinder, hollow cylinder, bar or the like optionally with adding a molding aid or the catalyst is shaped into these configurations together with carrier and optional auxiliary agents. A size of molded catalyst is for example 1 to 10 mm for a fixed bed and less than 1 mm for a fluidized bed.

[0069] In case of a fluidized bed reactor for the process for preparing acrolein, it is preferred to have a powder with appropriate average particle size distribution namely between 40 and 300 micrometers, preferably between 60 and 150 micrometers.

[0070] 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 or the fluidized bed is preferable. Regeneration of the catalyst can be effected outside the reactor. When the catalyst is taken out of a reactor system for regeneration, the catalyst is burnt in air or in oxygen-containing gas. In case of liquid phase reaction, usual general reactors for liquid reactions for solid catalysts can be used. Since the difference in boiling point between glycerin (290 degrees centigrade) and acrolein and acrylic acid is big, the reaction is effected preferably at relatively lower temperatures so as to distil out acrolein continuously.

[0071] The reaction temperature for producing acrolein and acrylic acid by dehydration of glycerin in gas phase is effected preferably at a temperature of 200 to 450 degrees centigrade. If the temperature is lower than 200 degrees centigrade, the life of catalyst will be shortened due to polymerization and carbonization of glycerin and of reaction products because the boiling point of glycerin is high. On the contrary, if the temperature exceeds 450 degrees centigrade, the selectivity of acrolein and acrylic acid will be lowered due to increment in parallel reactions and successive reactions. Therefore, more preferable reaction temperature is 250 to 350 degrees centigrade. 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.

[0072] A feed rate of a material gas is preferably 500 to 10,000h^{-1} in term of the space velocity of GHSV (Gas Hourly Space Velocity, defined as the ratio between the gas flow rate in Normal Temperature and Pressure conditions and the volume of catalyst). The selectivity will be lowered if the GHSV becomes lower than 5001V^{1} due to successive reactions. On the contrary, if the GHSV exceeds 10,000h^{-1}, the conversion will be lowered.

[0073] The reaction temperature of the liquid phase reaction is preferably from 150 to 350 degrees centigrade. 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 conditions of 3 atm to 70 atm.

[0074] The material of glycerin is easily available in a form of aqueous solution of glycerin. In the invention, glycerin or glycerol may be used. 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 and acrylic acid and material glycerin. Temperature that is necessary to gasify glycerin is increased.

Examples

[0075] Now, the present invention will be explained in much detail with referring several examples, but this invention should not be limited to those described in following examples. In the following Examples and Comparative Examples, % means mole %.

[0076] Example 1:

Hydroxyapatite powder (nanoXIM HAp402 from Fluidinova, molar ratio Ca/P = 1.67, BET surface area 100 m^2/g) was pressed, crushed and sieved to obtain particle size of 35 to 48 mesh. A sample of the obtained powder (35.0 g) was impregnated at incipient wetness by spraying a solution of phosphotungstic acid (2.58 g as dry basis) and deionized water (31.2 g). The sample was dried at 120 degrees centigrade for 3 hours and calcined under air at 400 degrees centigrade for 3 hours. The solid was then impregnated a second time with the same amount of phosphotungstic acid and deionized water. Drying and calcination were performed in the same manner. The solid was then sieved again to keep particle size of 35 to 48 mesh. This catalyst sample is a hydroxyapatite that has undergone a double impregnation with a cumulated amount of 14.6 g of phosphotungstic acid per 100 g of support.

[0077] The catalyst was tested in a fixed bed reactor operated under ambient pressure. Namely, 5 ml of the resulting catalyst powder was packed in a stainless steel reaction tube (diameter of 16 mm).

[0078] An aqueous solution of glycerin (concentration of 30 % by weight) was fed to an evaporator together with nitrogen at 280 degrees centigrade so that glycerin was evaporated and the resulting gas was passed through the fixed catalyst bed. Feed gas had the following composition in mol %: glycerol : nitrogen : water = 6.2 : 20.5 : 73.3. Total feed gas flow was 20 Nl/h. Gas hourly space velocity (GHSV) was 4,000 h^{-1} (ratio of feed gas flow in Nl/h by catalyst volume in liter).

[0079] Temperature of the reactor was set to 290 degrees centigrade and the reaction gases were eliminated during the first hour of run. Reaction gases were then collected for 1 hour in 2 traps in series filled with deionized water and cooled to 1 degree centigrade. The collected products were analyzed. Temperature was then increased to 350 degrees centigrade and after 2 hours of stabilization, the reaction gases were collected for 1 hour. The collected products were analyzed.

[0080] Quantitative analysis was performed by gas chromatography (HP 6890 Agilent, Alltech EC-1000 column, FID detector, CP4900 Varian, Silicaplot and Molecular Sieve 5Angstroms TCD detectors). Standardization with glycerol and acrolein standards was used to determine the absolute amounts of products and to calculate the conversion (%) of glycerol, and the selectivity (%) and the yield (%) of acrolein.

Conversion (%) of glycerol = (mole number of glycerol reacted / mole number of glycerol supplied) x 100

Selectivity (%) to acrolein = (mole number of acrolein obtained / mole number of glycerol reacted) x 100

Yield (%) of acrolein = (mole number of acrolein obtained / mole number of glycerol fed) x 100

Results are shown in Table 1.

[0081] Example 2:

Hydroxyapatite powder (nanoXIM HAp402 from Fluidinova, molar ratio Ca/P = 1.67, BET surface area 100 m^2/g) was pressed, crushed and sieved to obtain particle size of 35 to 48 mesh. A sample of the obtained powder (35.0 g) was impregnated at incipient wetness by spraying a solution of phosphotungstic acid (2.58 g as dry basis) and deionized water (31.2 g). The sample was dried at 120 degrees centigrade for 3 hours and calcined under air at 400 degrees centigrade for 3 hours. The solid was then impregnated for a second time with the same amount of phosphotungstic acid and deionized water. Drying and calcination were performed in the same manner. The sample was then impregnated for a third time with the same amount of phosphotungstic acid and deionized water. Drying and calcination were performed in the same manner. The sample was sieved again to keep particle size of 35 to 48 mesh. This catalyst sample is a hydroxyapatite that has undergone a triple impregnation with a cumulated amount of 22 g of phosphotungstic acid per 100 g of support.

[0082] Procedure of catalyst test was reproduced as in example 1. Results are shown in table 1.

[0083] Comparative example 3:

Hydroxyapatite powder (nanoXIM HAp402 from Fluidinova, molar ratio Ca/P = 1.67, BET surface area 100 m^2/g) was pressed, crushed and sieved to obtain particle size of 35 to 48 mesh. A sample of the obtained powder (35.0 g) was impregnated at incipient wetness by spraying a solution of phosphotungstic acid (7.68 g as dry basis) and deionized water (31.2 g). The sample was dried at 120 degrees centigrade for 3 hours and calcined under air at 400 degrees centigrade for 3 hours. The solid was sieved again to keep particle size of 35 to 48 mesh. This catalyst sample is a hydroxyapatite that has undergone a single impregnation with an amount of 22 g of phosphotungstic acid per 100 g of support.

Procedure of catalyst test was reproduced as in example 1. Results are shown in table 1.

[0084] Comparative example 4:

Hydroxyapatite powder (nanoXIM HAp402 from Fluidinova, molar ratio Ca/P = 1.67, BET surface area 100 m^2/g) was pressed and crushed and sieved to obtain particle size of 35 to 48 mesh. No impregnation was done.

[0085] Procedure of catalyst test was reproduced as in example 1, except that the catalyst was directly tested at 350 degrees centigrade. Results are shown in table 1.

[0086] Example 5:

A 50 g sample of hydroxyapatite powder (nanoXIM HAp402 from Fluidinova, molar ratio Ca/P = 1.67, BET surface area 100 m^2/g) was impregnated at incipient wetness by spraying a solution of ammonium metatungstate (3.8 g as dry basis) and deionized water (45 g). The sample was dried at 120 degrees centigrade for 3 hours and calcined under air at 400 degrees centigrade for 3 hours. The solid was then impregnated for a second time with the same amount of ammonium metatungstate and deionized water. Drying and calcination were performed in the same manner. The sample was then impregnated for a third time with the same amount of ammonium metatungstate and deionized water. Drying and calcination were performed in the same manner. The sample was then pressed, crushed and sieved to obtain particle size of 35 to 48 mesh. This catalyst sample is a hydroxyapatite that has undergone a triple impregnation with a cumulated amount of 22.8 g of ammonium metatungstate per 100 g of support.

[0087] Procedure of catalyst test was reproduced as in example 1. Results are shown in table 1.

[0088] Example 6:

A 50 g sample of hydroxyapatite powder (nanoXIM HAp402 from Fluidinova, molar ratio Ca/P = 1.67, BET surface area 100 m^2/g) was impregnated at incipient wetness by spraying a solution of ammonium metatungstate (3.8 g as dry basis) and deionized water (45 g). The sample was dried at 120 degrees centigrade for 3 hours and calcined under air at 400 degrees centigrade for 3 hours. The solid was then impregnated for a second time with the same amount of ammonium metatungstate and deionized water. Drying and calcination were performed in the same manner. The sample was then pressed, crushed and sieved to obtain particle size of 35 to 48 mesh. This catalyst sample is a hydroxyapatite that has undergone a double impregnation with a cumulated amount of 15.2 g of ammonium metatungstate per 100 g of support.

[0089] Procedure of catalyst test was reproduced as in example 1. Results are shown in table 1.

[0090] Comparative example 7:

A 50 g sample of hydroxyapatite powder (nanoXIM HAp402 from Fluidinova, molar ratio Ca/P = 1.67, BET surface area 100 m^2/g) was impregnated at incipient wetness by spraying a solution of ammonium metatungstate (7.6 g as dry basis) and deionized water (45 g). The sample was dried at 120 degrees centigrade for 3 hours and calcined under air at 400 degrees centigrade for 3 hours. The solid was then pressed, crushed and sieved to obtain particle size of 35 to 48 mesh. This catalyst sample is a hydroxyapatite that has undergone a single impregnation with an amount of 15.2 g of ammonium metatungstate per 100 g of support.

[0091] Procedure of catalyst test was reproduced as in example 1, except that the catalyst was directly tested at 350 degrees centigrade. Results are shown in table 1.

[0092] Example 8:

An 80 g sample of hydroxyapatite powder (nanoXIM HAp402 from Fluidinova, molar ratio Ca/P = 1.67, BET surface area 100 m^2/g) was poured into 350 ml of 1 N nitric acid. After 1 hour stirring, the suspension was filtered on a fritted funnel and the liquid phase eliminated. Treatment of recovered solid with the same amount of nitric acid followed by filtration was performed a second and a third time. The solid was then rinsed with deionized water and dried at 120 degrees centigrade for 3 hours and was calcined under air at 400 degrees centigrade for 3 hours. About 25 g of recovered solid was then impregnated at incipient wetness by spraying a solution of ammonium metatungstate (4.0 g as dry basis) and 18.3 g of deionized water. The sample was dried at 120 degrees centigrade for 3 hours and calcined under air at 400 degrees centigrade for 3 hours. The solid was then pressed, crushed and sieved to obtain particle size of 35 to 48 mesh. This catalyst sample is a hydroxyapatite that has undergone 3 treatments with nitric acid and one with an amount of 16 g of ammonium metatungstate per 100 g of support.

[0093] Procedure of catalyst test was reproduced as in example 1. Results are shown in table 1.

[0094] Another catalyst test was performed in the same conditions as in example 1 except that the catalyst was directly tested at 330 degrees centigrade. In those conditions, glycerol yield was 81%, acrolein yield was 47% and acrolein selectivity was 58%.

[0095]

[Table 1]

Example	1	2	Comp 3	Comp 4	5	6	Comp 7	8
Support	HAP	HAP	HAP	HAP	HAP	HAP	HAP	HAP
Material of impregnation	PW	PW	PW	-	W	W	W	H^+ then W
Number of treatments	2	3	1	0	3	2	1	3+1
Cumulative g of impregnation material per 100 g of support	14.6	22	22	0	22.8	15.2	15.2	16
Glycerol conversion at 290°C (%)	27	36	6		45	42		34
Acrolein yield at 290°C (%)	9	13	1		19	14		14
Acrolein selectivity at 290°C (%)	34	36	19		43	39		40
Glycerol conversion at 350°C (%)	100	100	61	88	100	100	100	100
Acrolein yield at 350°C (%)	56	59	26	18	48	39	33	60
Acrolein selectivity at 350°C (%)	56	59	42	20	48	39	33	60
Acetol yield at 350°C (%)	17	17	13	26	8	10	13	13
Acetol selectivity at 350°C (%)	17	17	22	29	8	10	13	13
Carbon balance at 350°C	87	87	88	85	81	81	71	84

HAP is used for hydroxyapatite, PW is used for phosphotungstic acid, and W is used for ammonium metatungstate.

[0096] Example 9:

Zirconium lanthanum oxide (Z1201 from Daiichi Kigenso Kagaku Kogyo, 90.9% $Zr0_2$ + 9.1% La_20_3) was pressed, crushed and sieved to obtain particle size of 35 to 48 mesh. A sample of the obtained powder (15 g) was impregnated at incipient wetness by spraying a solution of ammonium metatungstate (1.8 g as dry basis) and 18.5 g of deionized water. The sample was dried at 120 degrees centigrade for 3 hours and calcined under air at 700 degrees centigrade for 3 hours. The solid was then impregnated for a second time with the same amount of ammonium metatungstate and deionized water. Drying and calcination were performed in the same manner. A third step of impregnation drying and calcination was performed in the same manner. The sample was then sieved again to keep particle size of 35 to 48 mesh. This catalyst sample is a zirconium lanthanum oxide that has undergone a triple impregnation with cumulated amount of 12 g of ammonium metatungstate per 100 g of support.

[0097] Procedure of catalyst test was reproduced as in example 1. Results are shown in table 2.

[0098] Comparative example 10:

Zirconium lanthanum oxide (Z1201 from Daiichi Kigenso Kagaku Kogyo, 90.9%

ZrO_2 + 9.1% La_2O_3) was pressed, crushed and sieved to obtain particle size of 35 to 48 mesh. A sample of the obtained powder (15 g) was impregnated at incipient wetness by spraying a solution of ammonium metatungstate (0.60 g as dry basis) and 18.5 g of deionized water. The sample was dried at 120 degrees centigrade for 3 hours and calcined under air at 700 degrees centigrade for 3 hours. The solid was sieved again to keep particle size of 35 to 48 mesh. This catalyst sample is a zirconium lanthanum oxide that has undergone a single impregnation with an amount of 12 g of ammonium metatungstate per 100 g of support.

[0099] Procedure of catalyst test was reproduced as in example 1. Results are shown in table 2.

[0100] Example 11:

Hydrotalcite pellets (22451 160 from Norpro Saint Gobain - surface area 80 m^2/g) were crushed and sieved to obtain particle size of 35 to 48 mesh. A 50 g sample was impregnated at incipient wetness by spraying a solution of ammonium metatungstate (6.4 g as dry basis) and 25.5 g of deionized water. The sample was dried at 120 degrees centigrade for 3 hours and calcined under air at 700 degrees centigrade for 3 hours. The solid was then impregnated for a second time with the same amount of ammonium metatungstate and deionized water. Drying and calcination were performed in the same manner. The sample was then impregnated for a third time with the same amount of ammonium metatungstate and deionized water. Drying and calcination were performed in the same manner. The sample was sieved again to keep particle size of 35 to 48 mesh. This catalyst sample is an hydrotalcite that have undergone a triple impregnation with a cumulated amount of 19 g of ammonium metatungstate per 100 g of support.

[0101] Procedure of catalyst test was reproduced as in example 1, except that the catalyst was directly tested at 350 degrees centigrade. Results are shown in table 2.

[0102] Example 12:

Hydrotalcite pellets (22451 160 from Norpro Saint Gobain - surface area 80 m^2/g) were crushed and sieved to obtain particle size of 35 to 48 mesh. A 50 g sample was impregnated at incipient wetness by spraying a solution of ammonium metatungstate (6.4 g as dry basis) and 25.5 g of deionized water. The sample was dried at 120 degrees centigrade for 3 hours and calcined under air at 700 degrees centigrade for 3 hours. The solid was then impregnated a second time with the same amount of ammonium metatungstate and deionized water. Drying and calcination were performed in the same manner. The sample was sieved again to keep particle size of 35 to 48 mesh. This catalyst sample is an hydrotalcite that have undergone a double impregnation with a cumulated amount of 13 g of ammonium metatungstate per 100 g of support.

[0103] Procedure of catalyst test was reproduced as in example 1. Results are shown in table 2.

[0104] Comparative example 13:

Hydrotalcite pellets (22451 160 from Norpro Saint Gobain - surface area 80 m^2/g) were crushed and sieved to obtain particle size of 35 to 48 mesh. No impregnation was done.

[0105] Procedure of catalyst test was reproduced as in example 1, except that the catalyst was directly tested at 350 degrees centigrade. Results are shown in table 2.

[0106] [Table 2]

Example	9	Comp 10	11	12	Comp 13
Support	ZrLa	ZrLa	MgAl	MgAl	MgAl
Material of impregnation	W	W	W	W	-
Number of treatments	3	1	3	2	0
Cumulative g of impregnation material per 100 g of support	12	12	19	13	0
Glycerol conversion at 290°C (%)	50	47		17	
Acrolein yield at 290°C (%)	26	24		1	
Acrolein selectivity at 290°C (%)	50	50		4	
Glycerol conversion at 350°C (%)	100	100	59	37	26
Acrolein yield at 350°C (%)	48	42	15	7	4
Acrolein selectivity at 350°C (%)	48	42	24	18	17
Acetol yield at 350°C (%)	5	2	9	5	7
Acetol selectivity at 350°C (%)	5	2	16	13	26
Carbon balance at 350°C	83	80	81	85	96

ZrLa is used for zirconium lanthanum oxide, MgAl is used for hydrotalcite, and W is used for ammonium metatungstate.

[0107] Example 14:

A solid acid of zirconium hydroxide was prepared according to a process disclosed in JP-A 1-2000-247641. Namely, 1350g of water was added to 150g of zirconium oxychloride (Wako Junyaku: $ZrOCl_2$ $8H_20$) to prepare an aqueous solution of 10wt% of zirconium oxychloride, then, into which an aqueous 25wt% ammonia solution was added in drop wise until pH becomes 10.1. The resulting white precipitate was filtered and washed to obtain a precursor of zirconium hydroxide. This precursor was dried at 120 degrees centigrade for overnight to obtain zirconium hydroxide ($Zr(OH)_4$).

[0108] 50 g of the resulting zirconium hydroxide was dispersed in water and the resulting solution was added with 4.7g of ammonium metatungustic acid (Nippon Inorganic Colour & Chemical Co., Ltd. $(NH_4)_6(H_2W_{12}0_{40})6H_20$) and stirred for 2 hours. The resulting white slurry was filtered, washed and then calcinated in a muffle furnace at 500 degrees centigrade in air for 5 hours to obtain a powder of $W0_3/Zr0_2$ (tungsten oxide = 10wt%).

[0109] An aqueous solution of 85% phosphoric acid was added into 2.2g of pure water and stirred to prepare 56 ml of an aqueous solution of phosphoric acid. The resulting phosphoric acid aqueous solution was added to 50 g of the $W0_3/Zr0_2$ and stirred at ambient temperature for 2 hours. The resulting slurry was dried under reduced pressure by a rotary evaporator at 60 degrees centigrade. Powder obtained was further dried under ambient pressure at 120 degrees centigrade for 10 hours and then was calcinated in a muffle furnace at 500 degrees centigrade in air for 3 hours.

[01 10] The resulting catalyst was tested in a pass-through type fixed bed reactor operated under ambient pressure. Namely, the powder of catalyst was compacted by a press, crushed and passed through a sieve to obtain particles of 9 to 12 meshes. 10 cc of the resulting catalyst particles were packed in a stainless steel reaction tube (diameter of 20 mm). An aqueous solution of glycerin (concentration of 50 % by weight) was fed to an evaporator heated to 300 degrees centigrade so that glycerin was evaporated and the resulting gas was passed directly to the fixed catalyst bed together with air and nitrogen. Temperature of the reactor packed with the catalyst was set to 290 degrees centigrade. Feed gas had the following composition in mol %: glycerol : oxygen : nitrogen : water = 4.7 : 2.8 : 69.5 : 24.0. Gas hourly space velocity (GHSV) was 2,020 h^{-1}.

[0111] Reaction gases were collected in a condenser and quantitative-analyzed by gas chromatography (7890A Agilent, DB-WAX column). Each product was corrected by the gas chromatograph in factor to determine the absolute amounts of glycerin fed, glycerin remained and each product to calculate the conversion (%) of material (glycerin conversion), the selectivity (%)of objective substance (acrolein selectivity)and the yield (%) of objective substance (acrolein yield).

[0112] Conversion (%) of material = (mole number of material reacted / mole number of material supplied) xlOO

Selectivity (%) to objective substance = (mole number of objective substance obtained / mole number of material reacted) x 100

Yield (%) of acrolein = (mole number of objective substance obtained / mole number of material fed) x 100

[01 13] The conversion (%) of glycerin and the yields (%) of acrolein and of other byproducts were compared by using the quantitative analysis.

[0114] Comparative Example 15:

For comparison with an acid-treatment with phosphoric acid, $W0_3/Zr0_2$ was evaluated without the acid-treatment. That is to say, $W0_3/Zr0_2$ used in Example 14 (tungsten oxide = 10 wt %) was used and evaluated under the same reaction conditions as Example 14 to compare with the result of acid-treated $W0_3/Zr0_2$. Results are shown in table 3.

[0115] [Table 3]

	Example 14	Comp. 15
Support	$Zr0_2$	$Zr0_2$
Material of impregnation	W Then H^+	W
Number of treatments	1+ 1	1
Cumulative g of impregnation material per 100 g of support	11	11
Glycerol conversion at 290°C (%)	99. 8	99.7
Acrolein yield at 290°C (%)	77.9	70.2
Acrolein selectivity at 290°C (%)	78.0	70.4
CO_X yield at 290°C (%)	7.9	14.6
CO_X selectivity at 290°C (%)	8.0	14.6
Carbon balance at 290°C	99.6	99.2

Claims

[Claim 1] A process for preparing a catalyst having a minimized amount of basic sites used in a production of acrolein and acrylic acid by dehydration reaction of glycerin, comprising more than one cycle of contacting a material with a solution of at least one acid precursor or one heteropolyacid or one heteropolyacid salt, drying and calcining the resulting solid mixture.

[Claim 2] The process of claim 1 in which the material is a basic material or an amphoteric material having a specific surface area greater than 5 m^2/g, preferably greater than 30 m^2/g.

[Claim 3] The process of claim 1 or 2 in which the material is a basic mixed metal oxide, a metal hydroxide or a layered double hydroxide.

[Claim 4] The process of claim 1 in which the material is an acidic solid having basic sites

[Claim 5] The process of any one of claims 1 to 4, in which the acid precursor is a mono-, di-, tri- or polyacidic inorganic acid, or its salt.

[Claim 6] The process of any one of claims 1 to 4, in which the heteropolyacid is represented by the general formula (1):

$H_a(X_1Y_cZ_dO_e)\ nH_20$ (l)

in which

H is hydrogen,

X is P or Si,

Y is more than one element selected from the group comprising W, Mo, Ti, Zr, V, Nb, Ta, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, In, Tl, Sn and Pb,

Z is more than one element selected from the group comprising W, Mo, Ti, Zr, V, Nb, Ta, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, In, Tl, Sn and Pb,

and a, b, c and satisfying following ranges:

a is not less than 0 but less than 9

c is greater than 0 but not greater than 12, and

d is not less than 0 but less than 12

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

[Claim 7] The process of any one of claims 1 to 6 in which the contacting is performed by techniques of pore volume impregnation or excess solution impregnation, or washing, or chemical exchange with excess solution.

[Claim 8] The process of any one of claims 1 to 7 in which the multiple contacting procedure is performed with different solutions at each step.

[Claim 9] The process of any one of claims 1 to 8 in which the calcination is carried out under an atmosphere of air, inert gas or a mixture of oxygen and inert gas, or under a reduced gas.

[Claim 10] The process of any one of claims 1 to 9 in which the calcination is carried out at a temperature of 150 to 900 degrees centigrade for 0.5 to 20 hours.

[Claim 11] A catalyst having a minimized amount of basic sites used in a production of acrolein and acrylic acid by dehydration reaction of glycerine, obtained by the process according to any one of claims 1 to 10.

[Claim 12] A process for preparing acrolein by catalytic dehydration of glycerin carried out in the presence of a catalyst according to claim 11.

[Claim 13] The process of claim 12 in which the dehydration of glycerin is effected in the presence of oxygen gas.

[Claim 14] The process of claim 12 or 13 in which the dehydration of glycerin is effected in the presence of a gas containing propylene.

[Claim 15] The process of any one of claims 12 to 14 carried out in a plate heat exchanger type reactor or in a fixed bed reactor or in a fluidized bed type reactor or in a circulating fluidized bed or in a moving bed.

[Claim 16] The process of any one of claims 12 to 15, in which the resulting acrolein is further oxidized to produce acrylic acid.

[Claim 17] The process of claim 16 having an intermediate step of partial condensation and removal of water and heavy by-products issuing from the dehydration step.

[Claim 18] A process for preparing acrylonitrile, characterized in that acrolein obtained by the process of any one of claims 12 to 15 is subjected to ammoxidation.

[Claim 19] A process for preparing acrylic acid comprising a first step of catalytic dehydration of glycerin by the process of any one of claims 12 to 15 and a second step of gas phase oxidation of the gaseous reaction product containing acrolein formed by the dehydration reaction, then collecting the resultant acrylic acid as a solution by using water or a solvent and purifying the resultant solution containing acrylic acid by using for example distillation and/or crystallization.

INTERNATIONAL SEARCH REPORT

International application No
PCT/JP2011/004040

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J23/00 B01J23/30 B01J27/16 B01J27/188 B01J37/02
B01J35/10 C07C45/52 C07C47/22
ADD.

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)
B01J 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)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2011/033689 A1 (NIPPON KAYAKU KK [JP]; ARKEMA FRANCE [FR]; MAGATANI YASUHIRO [JP]; OKU) 24 March 2011 (2011-03-24) abstract page 4, lines 7-37 page 11, line 2 - page 12, line 5 example 2 claims 1,2,8,11,17-22 -----	1-19
X	US 2010/204502 A1 (DUBOIS JEAN-LUC [FR]) 12 August 2010 (2010-08-12) abstract paragraphs [0050], [0051], [0053] - [0056], [0066], [0067], [0070], [0073], [0075] - [0077], [0082] - [0085] example 7 ----- -/--	1-19

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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Date of the actual completion of the international search 5 March 2012	Date of mailing of the international search report 14/03/2012
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 Fischbach, Malaika

INTERNATIONAL SEARCH REPORT

International application No
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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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X	US 3 432 558 A (RYLAND LLOYD B) 11 March 1969 (1969-03-11) abstract column 3, lines 13-28,43-68 column 4, lines 35-70 examples 5,10 -----	1-11
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INTERNATIONAL SEARCH REPORT

Information on patent family members

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