



(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
04.08.2004 Bulletin 2004/32

(51) Int Cl.7: **C01B 15/029**, C07B 33/00,
B01J 31/10, B01J 23/44,
B01J 23/42, C07D 301/12,
C07D 303/14

(21) Application number: **03380019.4**

(22) Date of filing: **03.02.2003**

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
HU IE IT LI LU MC NL PT SE SI SK TR
Designated Extension States:
AL LT LV MK RO

(71) Applicant: **REPSOL QUIMICA S.A.**
E-28046 Madrid (ES)

(72) Inventors:
• **Frutos, Pilar de**
28045 Madrid (ES)
• **Padilla, Ana**
28903 Madrid (ES)
• **Riesco, José Manuel**
28047 Madrid (ES)

- **Campos Martin, José Miguel**
28045 Madrid (ES)
- **Brieva, Gema Blanco**
28925 Alcorcon (Madrid) (ES)
- **Serrano, Encarnacion Cano**
28903 Getafe (Madrid) (ES)
- **Capel Sanchez, Maria del Carmen**
28045 Madrid (ES)
- **Garcia Fierro, José Luis**
28002 Madrid (ES)

(74) Representative:
Garcia-Cabrerizo y del Santo, Pedro Maria
Oficina Garcia Cabrerizo, S.L.,
Vitruvio, 23
28006 Madrid (ES)

(54) **Integrated process for selective oxidation of organic compounds**

(57) Oxidized compounds are produced in a continuous integrated process in liquid phase, which comprises: Step I, synthesis of non acidic hydrogen peroxide solutions by direct reaction between hydrogen and oxygen by catalytic reaction utilizing a noble metal catalyst. Step II, this hydrogen peroxide solution is directly

mixed with an organic substrate, a suitable catalyst and optionally a solvent. The integrated process requires no treatment step and is particularly well adapted to the production of propylene oxide.

Description**FIELD OF THE INVENTION**

[0001] The invention refers to an integrated process for selective oxidation of organic compounds, in liquid phase, which comprises a first step for direct synthesis of a non acidic hydrogen peroxide solution and a second step for oxidation an organic substrate with the reaction mixture of the first step.

STATE OF THE ART

[0002] Selective oxidation reactions are a major class of chemical transformations which account for the production of a wide variety of important chemical products, including alcohols, carbonyl compounds, epoxides, hydroxylates, acids, glycols and glycol ethers, lactones, oximes, and oxygenated sulfur and nitrogen compounds such as sulfoxides, sulfones, nitrones, azo compounds, and other N-oxides. Performing these chemical transformations efficiently, economically, and safely requires a suitable oxidizing agent which can be purchased or produced to react with the desired organic chemical feedstock, which is then converted to the oxidized organic chemical product.

[0003] Several significant problems face conventional oxidation processes. Some industrial processes use gas containing oxygen such as air or pure oxygen. But using oxygen combined with organic chemical feedstocks may accidentally achieve gas compositions in the explosive range, thereby posing a serious safety hazard. Such oxidation processes can also be prone to forming explosive gas mixtures. Oxidative processes using oxygen or air also tend to suffer from product selectivity problems related to over-oxidation of the organic chemical feedstock, normally producing undesired carbon oxides (CO, CO₂)

[0004] An attractive alternative to using oxygen or air as the oxidation agent is the use of organic hydroperoxides as oxidizing agents. These hydroperoxide compounds, typically generated by oxidation of suitable intermediates with air or O₂, are reacted with chemical feedstocks to form oxygenated products and organic by-products. The most common processes for producing propylene oxide (PO) use tert-butyl hydroperoxide and ethylbenzene hydroperoxide as hydroperoxides. These processes cause the formation of a higher quantity of co-products of commercial interest with respect to PO. For example, the process via tert-butyl hydroperoxide co-produces 2.5—3.5 kg of tert-butyl alcohol per kg of PO, whereas via ethylbenzene hydroperoxide co-produces 2.2-2.5 kg of styrene per kg of PO. The presence of these co-products can be of little advantage if the request for PO and the respective co-products is not suitably balanced. For example, when the demand for styrene, or methyl tert-butyl ether (MTBE) which could be obtained from tert-butyl alcohol, is high, the economics

of this process are competitive; otherwise these processes are not economic.

[0005] Instead of using organic peroxides, hydrogen peroxide is a known desirable oxidizing agent. The by-product of oxidation reactions using hydrogen peroxide is typically water, a safe compound that can be easily recovered and reused or disposed. The amount of water on a weight basis is much less than the amount of organic by-product when organic hydroperoxides are used, and thereby represents significant savings in process costs. However, past attempts to develop selective chemical oxidation processes based on hydrogen peroxide have encountered significant difficulties. Conventional hydrogen peroxide production utilizes the anthraquinone process, wherein the anthraquinone is first hydrogenated to anthrahydroquinone and then autoxidized to release hydrogen peroxide and the anthraquinone for recycle. Hydrogen peroxide is generated at low concentrations in the solution, and very large flows of anthraquinone and anthrahydroquinone must be handled in order to produce the desired hydrogen peroxide product. Accordingly, such conventionally produced hydrogen peroxide is generally too expensive for commercial use as an oxidizing agent for selective chemical oxidation processes.

[0006] A second method for the production of hydrogen peroxide comprises the use of secondary alcohols such as isopropanol and methylbenzylalcohol (US 2,871,102, EP 378388, EP 1074548) or high-boiling secondary alcohols such as diaryl methanol (US 4,303,632) with oxygen. These known processes, however, substantially suffer from disadvantages deriving from the necessity of operating at high reaction temperatures (generally ranging from 100 to 180°C), the partial oxidation of the ketone which is formed as main co-product, the necessity of using a hydrogen peroxide stabilizer (orthophosphoric acid or sodium pyrophosphate). Furthermore, these processes are complicated by the necessity of separating and recovering the cetone and by products from the reaction mixture after using the hydrogen peroxide solution in a subsequent epoxidation process.

[0007] An important alternative is generating hydrogen peroxide directly by the catalytic reaction of hydrogen and oxygen, which avoids the difficulty of accompanying large flows of a working solution and can reduce the cost of hydrogen peroxide. These processes generally use a catalytic system consisting of a noble metal, particularly metals of the platinum group or their mixtures, in the form of salts or as supported metals, by reacting the two gases in a solvent consisting of an aqueous medium or an aqueous organic medium. The prior art includes a number of catalytic technologies which directly convert hydrogen and oxygen to hydrogen peroxide, but generally utilize a hydrogen/oxygen feed wherein the hydrogen concentration is greater than about 10 mol % (US 4,681,751, US 4,772,458, US 4,832,938, US 5,338,531), which is well above the flam-

mability limit of 4.5 mol % for such mixtures and creates a serious process hazard. At hydrogen feed concentrations below 4.5 mol %, the prior art catalysts are not sufficiently active and selective to generate hydrogen peroxide product at a reasonable rate (WO 99/41190, WO 01/05498 WO 01/05501, US 6,168,775 B1). The prior art technologies need the use in the reaction medium of high concentrations of promoters, for example acid promoters, halogenated products and/or other additives. This makes it necessary to add stabilizers, with onerous purification operations of the H₂O₂ solution before its use in the oxidation reactions.

[0008] Various oxidation processes for organic chemical feedstocks utilizing hydrogen peroxide are known. For example, US 4,701,428 discloses hydroxylation of aromatic compounds and epoxidation of olefins such as propylene with H₂O₂ using a titanium silicalite catalyst. Also, US 4,824,976; US 4,937,216; US 5,166,372; US 5,214,168; US 5,912,367, WO 94/238234 and WO 99/48884 all disclose epoxidation of various olefins including propylene using titanium compounds catalysts.

[0009] EP 978316 describes a process for catalytic oxidation of an organic compound selected from olefins, aromatic hydrocarbons, ammonia and carbonyl compounds, including a first step for direct synthesis of hydrogen peroxide using a metal of group VIII supported on activated carbon functionalized with sulfonic acids, and a second step for oxidation of said organic compound substrate with the reaction mixture from the first step containing hydrogen peroxide to obtain the desired oxidized product. When the olefin is propylene, the best overall yield of propylene oxide, based on hydrogen feed, that can be achieved is 83%. However, higher yields of oxidized organic compounds are much desired.

[0010] US 2001/0016187 describes a process for selective oxidation of organic chemical feedstocks utilizing directly produced hydrogen peroxide intermediate oxidant, including a first step for direct synthesis of hydrogen peroxide using a supported phase-controlled noble metal catalyst, namely a Pd/carbon black catalyst, in a solvent, in the presence of acid promoters and/or stabilizers, such as sulfuric acid, and a second step for oxidation of said organic compound substrate with the reaction mixture from the first step containing hydrogen peroxide to obtain the desired oxidized product. No data concerning oxidation of any organic chemical feedstock is provided.

SUMMARY OF THE INVENTION

[0011] The present invention provides an integrated process for the oxidation of organic compounds comprising the following steps: Step I, production of hydrogen peroxide from hydrogen and oxygen in the presence of a solvent and a catalyst comprising at least a noble or semi-noble metal supported on a halogen free acid resin; and Step II, wherein the hydrogen peroxide solution is directly mixed with an organic substrate, a

suitable catalyst and optionally a solvent to produce the corresponding oxidized compound. The integrated process requires no treatment step and is particularly well adapted to the production of propylene oxide.

BRIEF DESCRIPTION OF THE FIGURE

[0012]

Figure 1 provides an overview of a preferred embodiment of the continuous, integrated process of the invention. The scheme for organic compounds oxidation using hydrogen peroxide generated by direct reaction of oxygen and hydrogen is illustrated in the Figure. In the first step hydrogen and oxygen (as purified oxygen or air) are reacted over the supported noble metal catalyst in the presence of a liquid solvent in a first reactor or in a first chamber of a twin-chambered tank reactor to generate a liquid solution of hydrogen peroxide. The reaction mixture resulting from this first step is combined, in the second step of the process, in a second reactor or in a second chamber of a twin-chambered tank reactor, with an organic compound which undergoes oxidation.

[0013] The reaction mixture from the second step is then fractionated by any of the means that are standard within the art. As a result of the fractionation, unreacted organic compound may be purified and recycled back to the corresponding reactor or chamber. The fractionation process may also provide for isolation of the solvent used in the hydrogen peroxide synthesis. Such fractionation may be employed as a secondary procedure, or as an integral part of the product purification (as illustrated in Figure 1). This solvent isolated in the fractionation procedure may be recycled for further use.

[0014] The figure portrays reagents within boxes, and reactions within ellipses. The arrows indicate ingredients required and/or generated by the individual steps of the procedure. The major reagents and reactions are shown in bold typeface, as are the arrows depicting the major additions (ingredients required) and products (ingredients generated) associated with the individual steps of the process.

DETAILED DESCRIPTION OF THE INVENTION

[0015] The present invention provides an effective process for selective oxidation of organic chemical compounds with directly produced hydrogen peroxide, comprising the following steps:

- (i) preparing a non acidic hydrogen peroxide solution by reacting hydrogen and oxygen in a solvent, in the presence of a first catalyst comprising at least a noble metal or semi-noble metal belonging to groups VII to XI of the periodic table supported on

a halogen-free acid resin;

(ii) recovering the reaction mixture of step (i) containing said non acidic hydrogen peroxide solution; and

(iii) contacting said non acidic hydrogen peroxide solution with an organic chemical compound, in the presence of a second catalyst to render an oxidized product.

[0016] The reaction solution of the first reaction (hydrogen peroxide synthesis) may be used directly as a reagent for the second reaction (oxidation). There is no requirement for purification or enrichment of intermediates, or for the removal of by-products from the production of hydrogen peroxide. The second reaction uses the products of the first reaction to oxidize an organic substrate at moderately elevated temperature and pressure. This oxidation reaction is performed in the presence of suitable catalysts. The oxidized product may be recovered from the reaction medium of the second reaction.

[0017] The expression "non acidic hydrogen peroxide solution", as used in the present description, means that although a catalitical amount of an acid promoter, e.g. HBr, is used in the direct synthesis of hydrogen peroxide from hydrogen and oxygen in a solvent, said compound is added in an amount such that is not sufficient to render acidic the pH of the resultant hydrogen peroxide solution.

[0018] According to the present invention, the coupled hydrogen peroxide generating reaction and oxidation reaction may be performed in a continuous manner, using an appropriate reactor, such as, a twin-chambered tank reactor for example, permitting controlled addition of the hydrogen peroxide containing reaction mixture from the first reaction (in the first chamber) into a second chamber. This second chamber would house the oxidation reaction, with forced mixing of the contents and agitation therein of a suspension of catalyst particles. Reactant solutions may be added in combination or sequentially. For example, either the reaction mixture generating hydrogen peroxide, or the organic chemical compound, for example an olefin, or both of these reagents may be added to the reactor incrementally.

[0019] The oxidation product may be separated from the oxidation reaction mixture by standard methods known in the art, such as liquid-liquid extraction, extraction by distillation or fractional distillation. These operations may be performed on the entire reaction mixture, and may follow removal of said second catalyst. Alternatively, the oxidized product may be separated from part or all of the reaction mixture according to a periodic program, or from a part of the reaction as a component of a continual operation.

[0020] Other components of the oxidation reaction mixture may be isolated by recognized means of frac-

tionation, such as differential distillation, either as part of the process of purifying the product or as a distinct fractionation procedure, preceding or following removal of the oxidized product. The solid catalyst may be separated from the oxidation reaction mixture for regeneration by methods well known in the art, such as filtration. Regeneration of the catalyst is described in greater detail below.

[0021] The integrated process for the industrial oxidation of organic compounds that is provided by the invention solves a similar problem to that addressed, in part, by the integrated procedures disclosed in the prior art as described above. In addition, the present invention incorporates improvements to the component reactions of the integrated process which increase their rate, selectivity and compatibility, resulting in significant enhancement of the process as a whole. Certain of these improvements, such as the use into the peroxide-generating reaction of halogen-free acidic resin supported noble metal catalyst can get non-acidic hydrogen peroxide solutions which can be used directly in the oxidation reaction step without any purification or additive feed benefit the overall efficiency of the integrated process.

[0022] In particular, the distinctions that differentiate the present invention from US Patent Application No. 2001/016187 which also discloses an integrated process for oxidizing organic feedstocks, illustrate significant advantages of the present invention:

i. By improving the activity of the peroxide-generating reaction the present invention permits greater concentrations of hydrogen peroxide to be generated in the first reaction mixture which is then used as oxidant solution for the oxidation reaction. The overall yield and efficiency of the process may therefore be increased, provided that the hydrogen peroxide at these elevated concentrations can be maintained in solution by the selected organic solvent and can be prevented from reacting with other components of the reactions making up the integrated process. The current invention successfully addresses each of these requirements.

ii. High concentrations of acid promoters such as inorganic acids (sulfuric, phosphoric, nitric, ...) or organic acids (per example, sulphonic acids) are not required in the hydrogen peroxide generation reaction, avoiding the production of acidic hydrogen peroxide solutions that are corrosive and require the use of special equipments.

iii. The ability to use the reaction mixture from the first step directly as an ingredient of the second reaction, providing the peroxide for the oxidation, permits great advantages in efficiency and cost-effectiveness, since no intermediate step is required in order to purify or neutralize the peroxide. Hydrogen peroxide synthesis and oxidation steps will be described in a

detailed manner below.

HYDROGEN PEROXIDE SYNTHESIS STEP

[0023] In this step, hydrogen and oxygen (as purified oxygen or air) are reacted continuously over the supported noble metal or semi-noble metal catalyst in the presence of a liquid solvent in a reactor to generate a liquid solution of non acidic, hydrogen peroxide. The reactor may contain a fixed, fluidized or slurried bed of the catalyst. The liquid medium may be water, or a suitable organic solvent such as an alcohol, for example, a C₁-C₁₂ alcohol, a C₁-C₁₂ glycol, or mixtures thereof. Suitable organic solvents can include various alcohols, aromatics, and esters, or any other organic compound that is inert in reaction conditions. Solvents are preferably water-soluble alcohols such as methanol, ethanol, n-propanol, isopropanol, tert-butanol, isobutanol and mixtures thereof. In a particular embodiment, the solvent is selected from the group formed by water, C₁-C₁₂ alcohols, C₁-C₁₂ glycols, and mixtures thereof. The hydrogen concentration in the reactor is maintained below the flammability limit of about 4.5 mol %. The liquid-phase concentration of hydrogen peroxide intermediate product can vary over a useful range of 1-30 wt %. The optimum hydrogen peroxide concentration depend on a variety of factors, including hydrogen cost, separation requirements, and optimal peroxide concentration for best performance of the downstream oxidation reactor. In general, the preferred H₂O₂ concentration will be 1-25 wt %, and more preferably will be 5-20 wt %.

[0024] The catalyst used in the first step is a halogen-free acidic resin-supported noble or semi-noble metal catalyst that selectively produces essentially only the hydrogen peroxide intermediate, as disclosed in our pending European patent application No. 02380057.6. The halogen-free acidic resin supported noble metal catalyst has been experimentally proved to directly produce hydrogen peroxide at very high selectivity. By using this catalyst in a reactor and at reaction conditions of -10°C to 100°C, preferably 10-75°C, at a pressure above atmospheric pressure, typically comprised between 2 and 30 MPa, optionally in the presence of an inert gas, the process first reaction step will produce hydrogen peroxide intermediate at very high selectivity, typically, equal to or higher than 80%.

[0025] The molar ratio hydrogen/oxygen can vary in a broad range and is preferably comprised between 1/1 and 1/100, more preferably between 1/10 and 1/50.

[0026] The support employed in the catalyst used in the process of this invention comprises a resin functionalized with halogen-free acid groups. Preferably, the resins used in the preparation of the catalyst to be used in the first reaction are formed by homopolymerization of monomers or copolymerization of two or more monomers. Examples of resins suitable as a support in the present invention include styrenic, acrylic, methacrylic polymers or styrene-divinylbenzene copolymers. These

resins are preferably functionalized with halogen-free acid groups such as sulphonic, carboxylic, dicarboxylic, etc. (Encyclopedia of Chemical Technology Kirk Othmer 3rd Edition, Vol. 13, p 678-705, Wiley-Interscience, John Wiley and Sons, 1981). Furthermore the resins used in the present invention can have an inorganic part, e. g. the resin is deposited onto an inorganic solid.

[0027] In a particularly preferred embodiment, the halogen-free acid resin is a sulphonated styrene-divinylbenzene copolymer resin.

[0028] The catalyst of the first reaction comprises at least a noble metal or semi-noble metal selected from groups VII to XI of the periodic table supported on the above resin.

[0029] Preferably, said noble or semi-noble metal is selected from the group consisting of palladium, platinum, silver, gold, rhodium, iridium, ruthenium, osmium, and mixtures thereof. Most preferred metal is palladium, optionally in combination with other metal cited.

[0030] The catalyst is preferably prepared by adding a noble metal or semi-noble metal belonging to groups VII to XI of the periodic table, preferably palladium, platinum, silver, gold, rhodium, iridium, ruthenium, osmium, or mixtures of two or more of these metals, to the non-halogenated acid resin. The amount of metal supported can vary in a broad range, but is preferably comprised between 0.001 and 20% with respect to the non-halogenated acid resin, more preferably between 0.1 and 10%.

[0031] The addition of the metal to the support can be performed using any of the known preparation techniques of supported metal catalyst, e.g. impregnation, adsorption, ionic exchange, etc. For the impregnation, it is possible to use any kind of inorganic or organic salt of the metal to be impregnated that is soluble in the solvent used in the addition of the metal. Suitable salts are for example acetate, nitrate, halide, oxalate, etc.

[0032] In a particular embodiment, the first step comprises:

a) feeding to a reactor, containing the catalyst in a fixed bed or dispersed in a liquid medium:

a1) a liquid stream consisting of an alcohol or an alcohol-water mixture, and

a2) a gaseous stream containing hydrogen and oxygen, and optionally an inert gas, wherein the concentration of hydrogen is lower than 4.5% by volume; and

b) removing from the reactor:

b1) a liquid stream substantially consisting of the stream a1 and also the hydrogen peroxide and water produced by the reaction; and

b2) a gaseous stream consisting of the non-re-

acted gases and eventual inert gases.

[0033] When the first reaction is performed in a slurry reactor, the catalyst is preferably removed from the hydrogen peroxide solution stream using the techniques known in the art such as decantation, centrifugation, filtration, etc. In the preferred embodiment of the invention wherein the catalyst is used in fixed bed, obviously, the separation step is not necessary.

[0034] Although not necessary, in some cases it may be desirable to remove a portion of the solvent or water from the first reactor effluent to generate a more concentrated hydrogen peroxide solution.

[0035] The final non acidic hydrogen peroxide solution is passed on to a second catalytic reaction step.

OXIDATION STEP

[0036] The reaction mixture containing hydrogen peroxide from the hydrogen peroxide synthesis reaction is used as the oxidant for the oxidation reaction in which an organic compound undergoes oxidation by the hydrogen peroxide in the presence of a catalyst. The ability to use the reaction mixture from the first step directly as an ingredient of the second reaction, providing the peroxide for the oxidation, permits great advantages in efficiency and cost-effectiveness, since no intermediate step is required in order to purify the peroxide.

[0037] A variety of organic chemical compounds can be used in the overall process of the instant invention in order to produce the desired oxidized organic chemical compounds. Major classes of organic chemical compounds include aromatics, alkanes, carbonyl compounds and olefins, as well as compounds containing mixed functionality and heteroatoms such as sulfur or nitrogen, with the olefin compounds being preferred. The major groups of oxidized organic chemical compounds are alcohols, epoxides, carboxylic acids, hydroxylated aromatics, aldehydes/ketones, glycols, oximes and N-oxides.

[0038] Some important specific and preferred organic chemical compounds and their corresponding oxidized products which may be processed by the two-step selective catalytic oxidation process of this invention utilizing hydrogen peroxide intermediate as the oxidant are listed below:

Propylene	Propylene Oxide
Allyl Alcohol	Glycidol
Allyl Chloride	Epichlorohydrin
Cyclohexene	Cyclohexene Oxide
Cyclohexanone	Cyclohexane Oxime
Benzene	Phenol
Phenol	Hydroquinone and Pyrocatechol

[0039] Olefins are more preferred organic compounds, with propylene being the most preferred feedstock for producing propylene oxide.

[0040] The non acidic hydrogen peroxide solution obtained in the first step and an additional solvent, if it is desirable, are fed, preferably continuously, together with a selected organic chemical feedstock into a catalytic reactor, which may be a fixed bed or slurry-type reactor containing a known oxidation catalyst such as TS-1, TS-2, Ti β , Ti-MCM-41, titanium on amorphous silica, etc., or any known catalyst capable of oxidizing efficiently organic compounds with hydrogen peroxide. For a fixed bed reactor, the preferred catalyst particle size will be 0.5-20 mm, and for a fluidized or slurry reactor the preferred catalyst size will be 50-1,000 microns. The reactor is maintained at about -30°C to 200°C of temperature, preferably at -10°C to 100°C temperature. The oxidation reaction is carried out at a pressure, usually above atmospheric pressure, enough to keep the organic feedstock in the liquid phase. In a particular embodiment, the oxidation reaction is carried out at a pressure between 0.1 and 10 MPa, preferably, between 0.1 and 5 MPa. If the reactor is of the slurry type, the effluent liquid stream removed from the reactor will contain unreacted feedstocks, solvent and catalyst particles, and preferably the catalyst should be recovered by centrifugation, filtration or any adequate means and reused. For fixed bed reactors, no catalyst recovery and recycle is needed. Following any catalyst recovery, the remaining liquid stream is passed to organic feedstock recovery; this unreacted organic compound could be recycled back to the reactor together with make up feedstock supplied. The unreacted organic compound recovery step may be carried out in a single distillation tower or it may include sequential distillation towers operated at progressively lower pressures as desired.

[0041] The remaining stream is passed to product purification, where product is removed for further purification as desired. Solvents and any heavy fractions are passed to a solvent recovery unit. The solvent fed to the organic compound oxidation, if it is necessary, is recycled back to the oxidation reactor. The liquid solvent employed in the hydrogen peroxide solution are recycled back to the first step, while heavy fractions and the net water produced in reactor are withdrawn for other use or disposal.

[0042] Any useful process schemes or sequences for oxidized product purification and recovery are also possible as will be understood by those skilled in this art will be applied to this invention.

[0043] In order to illustrate the nature of the invention more fully, and the manner in which it is to be practiced, the following examples are presented:

EXAMPLES

Example 1

[0044] A catalyst was prepared from a commercial resin functionalized with sulphonic groups (Lewatit® K2641 Bayer AG, non-halogenated macroporous resin, with an exchange capacity of 4.8 eq/l, pore diameter 70 nm, porosity 0.3 ml/g, and a specific surface area BET 35 m²/g). Firstly the resin was washed three times with acetone, using equal volumes of solvent and resin. Next, a resin suspension (4 g) is prepared with 50 ml of methanol. To this suspension, a palladium (II) acetate solution (86 mg) in acetone (20 ml) is added drop by drop. The suspension was dried in a rotative evaporator under vacuum, the temperature of the bath was 45°C. The solid obtained was air-dried at 110°C for 2 hours.

Example 2

[0045] 1.6 g of a catalyst, prepared as described in Example 1, are put inside an autoclave with 150 g of methanol and 24 ppm of HBr. The mixture was pressurized at 9.6 MPa(a) with nitrogen and stabilized at 40°C. Then the reactor was feed with the gas reaction mixture H₂:O₂:N₂ (3.6:46.4:50) with a total flow of 2500 mlN/min and the stirring was started up (1500 rpm) to initiate the reaction. After 2 h of the reaction a hydrogen peroxide concentration of 9.3 wt% was reached. The hydrogen peroxide selectivity was 80%.

Example 3

[0046] A hydrogen peroxide solution, prepared as described in Example 2, was used in the epoxidation of 1-octene without any kind of previous purification. 1-octene (0.1 mol), methanol (55 ml) and a hydrogen peroxide solution was prepared as described in Example 2 (4.4 g) were heated at 333 K (approximately 60°C). Then, 1 g of TS-1 catalyst (prepared as described in J. A. Martens, Ph. Buskens, P. A. Jacobs A. van der Pol, J. H. C. van Hooff C. Ferrini, H. W. Kouwenhoven, P. J. Kooyman and H. van Bekkum, Appl. Catal. A: General, 99, 71 (1993)) was added. The transformation of H₂O₂ obtained was of 93% and the efficiency of H₂O₂ was 90.5%, after 1.5 hours of reaction. From oct-1-ene converted the selectivity to epoxide was 50% and 50% to methylethers.

Example Comparative 1

[0047] A synthetic solution of hydrogen peroxide as taught by Example 2 of US Patent Application No. 2001/016187, 4.2 wt % H₂O₂ and 1% wt H₂SO₄ in water, was employed in the epoxidation of 1-octene using a TS-1 catalyst under the same reaction conditions of above Example 3. A 60% efficiency of H₂O₂ was observed. No epoxide formation was detected. From oct-

1-ene converted the selectivity to methylethers (2-methoxy-octan-1-ol and 1-methoxy-octan-2-ol) was 88% and 2% to 1,2-octanediol. This comparative example teaches that hydrogen peroxide solutions obtained according to US Patent Application No. 2001/016187 are not adequate to epoxidize alkenes without pretreatment of such solutions.

Example 4

[0048] A hydrogen peroxide solution, prepared as described in Example 2, was used in the epoxidation of 1-octene without any kind of previous purification. 0.2 moles of olefin, 11 g of 2-methyl-2-propanol and 1 g of catalyst prepared according to Example 3 of WO 99/48884 were introduced into the reactor. The mixture was heated to 80°C and 6 g of the H₂O₂ solution were added drop by drop for 30 minutes. The transformation of H₂O₂ obtained was of 93% and efficiency of 95%, after one hour of reaction from the beginning of the addition of the hydrogen peroxide. The only product detected from 1-octene was the epoxide.

Example 5

[0049] A hydrogen peroxide solution prepared as described in Example 2 was used in the epoxidation of propylene without any kind of previous purification. This solution was diluted with tert-butanol as solvent (stream a). A stirred continuous tank reactor equipped with a filter to maintain the catalyst inside the reactor, was charged with 13.88 g of powdered catalyst, prepared according to Example 3 of WO 99/48884. The reactor was heated to 70°C, then 319.5 g/h of propylene and 222.2 g/h of stream a were fed continuously to the reactor. After 60 minutes, 96% conversion of H₂O₂ and 95% selectivity towards propylene oxide on the basis of hydrogen peroxide reacted.

Example 6

[0050] 1 g of titanium silicalite (TS-1), the same employed in Example 3, was mixed with 50 g of a mixture consisting in 41 wt % methanol, 31 wt % water, 20 wt % cyclohexanone and 8 wt % ammonia. This mixture was suspended in a reactor and heated at reflux. Then, 3 g of the hydrogen peroxide solution prepared in Example 1 were added continuously during 5 h. The conversion of hydrogen peroxide was 100%, and the selectivity to cyclohexanone oxime was 99%.

Example 7

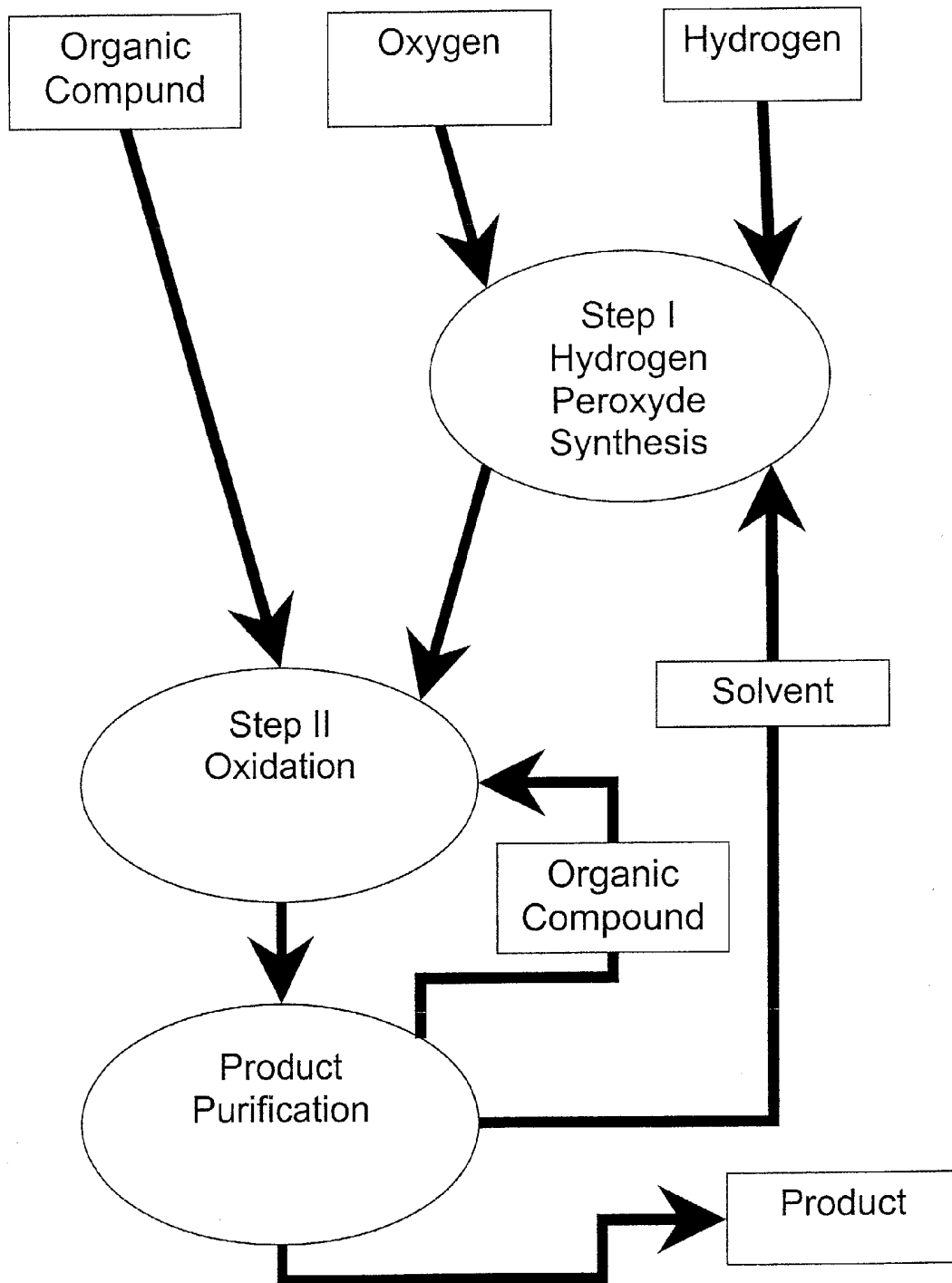
[0051] A hydrogen peroxide solution, prepared as described in Example 2, was used in the epoxidation of allyl alcohol without any kind of previous purification. 22.6 g of alcohol and 1 g of catalyst prepared according to Example 3 of WO 99/48884 were introduced into the

reactor. The mixture was heated to 80°C and 4 g of the H₂O₂ solution were added drop by drop for 30 minutes. The transformation of H₂O₂ obtained was of 100% and the specificity for epoxide of 99.9%, after one hour of reaction, from the beginning of the addition of the hydrogen peroxide.

[0052] Although this invention has been described broadly and also identifies specific preferred embodiments, it will be understood that modifications and variations may be made within the scope of the invention as defined by the following claims.

Claims

1. A process for selective oxidation of organic chemical compounds with directly produced hydrogen peroxide, comprising:
 - (i) preparing a non acidic hydrogen peroxide solution by reacting hydrogen and oxygen in a solvent, in the presence of a first catalyst comprising at least a noble metal or semi-noble metal belonging to groups VII to XI of the periodic table supported on a halogen-free acid resin;
 - (ii) recovering the reaction mixture of step (i) containing said non acidic hydrogen peroxide solution; and
 - (iii) contacting said non acidic hydrogen peroxide solution with an organic chemical compound, in the presence of a second catalyst to render an oxidized product.
2. Process according to claim 1, wherein the hydrogen peroxide from step (i) is directly used as an ingredient of the step (iii).
3. Process according to claim 1, wherein said noble or semi-noble metal is selected from the group formed by palladium, platinum, silver, gold rhodium, iridium, ruthenium, osmium and their mixtures.
4. Process according to claim 1, wherein the quantity of the noble or semi-noble metal, or their mixtures, in said catalyst ranges from 0.001% to 20% in weight with respect to the halogen-free acid resin, and preferably, from 0.1% to 10% in weight with respect to the halogen-free acid resin.
5. Process according to claim 1, wherein said halogen-free acid resin is a sulphonated styrene and divinylbenzene copolymer resin.
6. Process according to claims 1 to 5 wherein the solvent used in step (i) is selected from the group formed by water, C₁-C₁₂ alcohols, C₁-C₁₂ glycols, and their mixtures.
7. Process according to claims 1 to 6, wherein the reaction temperature between hydrogen and oxygen in the presence of a solvent and catalyst ranges from -10°C to 100°C, preferably from 10°C to 75°C.
8. Process according to claims 1 to 7, wherein the reaction between hydrogen and oxygen in the presence of a solvent and a catalyst is carried out at a pressure above atmospheric pressure, preferably between 2 to 30 MPa, optionally in the presence of an inert gas, and with a molar relation between the hydrogen and oxygen in the gas phase ranging from 1/1 to 1/100.
9. Process according to claims 1 to 8, wherein the second catalyst is selected from the group formed by titanium silicalite-1 (TS-1), titanium silicalite-2 (TS-2), titanium supported on amorphous silica, and Ti-MCM-41.
10. Process according to claims 1 to 9, wherein the reaction temperature in step (iii) ranges from -30°C to 200°C, preferably from -10°C to 150°C.
11. Process according to claims 1 to 10, wherein the organic compound oxidation is carried out at a pressure between 0.1 and 10 MPa, preferably, between 0.1 and 5 MPa.
12. Process according to claims 1 to 11, wherein the organic compound oxidation is carried out in the presence of an additional solvent.
13. Process according to claims 1 to 12, wherein the organic compound is an alkene.
14. Process according to claims 1 to 12, wherein the organic compound is selected from propylene, allyl alcohol, allyl chloride, cyclohexene, cyclohexanone, benzene, and phenol.





European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 03 38 0019

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	US 4 007 256 A (SCHOENTHAL GALEON W ET AL) 8 February 1977 (1977-02-08) * the whole document * ---	1-14	C01B15/029 C07B33/00 B01J31/10 B01J23/44
Y	EP 0 978 316 A (ENICHEM SPA) 9 February 2000 (2000-02-09) *claims; examples 6-15; in particular, examples 10, 14 and 15* ---	1-14	B01J23/42 C07D301/12 C07D303/14
Y	US 2001/016187 A1 (ZHOU ET AL.) 23 August 2001 (2001-08-23) *the abstract; the claims and the examples* ---	1-14	
Y	US 6 500 969 B1 (ZHOU BING ET AL) 31 December 2002 (2002-12-31) *the abstract; column 6, lines 22-67; column 7, lines 1-54; column 8, lines 31-36; the examples and the claims* ---	1-14	
Y	GB 1 056 123 A (ICI LTD) 25 January 1967 (1967-01-25) * the whole document * ---	1-8	TECHNICAL FIELDS SEARCHED (Int.Cl.7)
Y	US 3 294 488 A (DUNLOP ARTHUR K ET AL) 27 December 1966 (1966-12-27) * the whole document * ---	1-8	C01B C07B C07D B01J
Y	US 6 346 228 B1 (CHOUDHARY VASANT RAMCHANDRA ET AL) 12 February 2002 (2002-02-12) * the whole document * ---	1-8	
Y	US 5 641 467 A (HUCKINS HAROLD A) 24 June 1997 (1997-06-24) *abstract; column 3, last paragraph; column 8, lines 34-36 and the claims* ---	1-8	
	-/--		
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
MUNICH		24 April 2003	Lorenzo Varela, M.J.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone		T : theory or principle underlying the invention	
Y : particularly relevant if combined with another document of the same category		E : earlier patent document, but published on, or after the filing date	
A : technological background		D : document cited in the application	
O : non-written disclosure		L : document cited for other reasons	
P : intermediate document		& : member of the same patent family, corresponding document	

EPO FORM 1503 03.82 (P/AC01)



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 03 38 0019

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
Y	US 4 681 751 A (GOSSER LAWRENCE W) 21 July 1987 (1987-07-21) *the abstract; column 3, lines 39-68; the examples and the claims* ---	1-8	
Y	US 4 009 252 A (MIYAZAKI HIDETAKA ET AL) 22 February 1977 (1977-02-22) *the abstract; columns 4 and 5; the examples and the claims* ---	1-8	
Y	EP 0 366 419 A (ATOMIC ENERGY OF CANADA LTD) 2 May 1990 (1990-05-02) * the whole document * -----	1-8	
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 24 April 2003	Examiner Lorenzo Varela, M.J.
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

EPO FORM 1503 03.82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 03 38 0019

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

24-04-2003

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4007256 A	08-02-1977	DE 2615625 A1	21-10-1976
		FR 2306937 A1	05-11-1976
		GB 1539962 A	07-02-1979
		JP 51124698 A	30-10-1976
EP 0978316 A	09-02-2000	IT M1981843 A1	07-02-2000
		EP 0978316 A1	09-02-2000
		JP 2000202291 A	25-07-2000
		KR 2000017077 A	25-03-2000
		SG 72974 A1	23-05-2000
		TW 467866 B	11-12-2001
		US 6284213 B1	04-09-2001
US 2001016187 A1	23-08-2001	US 6168775 B1	02-01-2001
		US 6500969 B1	31-12-2002
		US 2002106320 A1	08-08-2002
US 6500969 B1	31-12-2002	US 2001016187 A1	23-08-2001
		US 2002106320 A1	08-08-2002
GB 1056123 A	25-01-1967	NONE	
US 3294488 A	27-12-1966	DE 1106738 B	18-05-1961
		FR 1226512 A	13-07-1960
		GB 844029 A	10-08-1960
US 6346228 B1	12-02-2002	NONE	
US 5641467 A	24-06-1997	AU 710994 B2	07-10-1999
		AU 3324495 A	07-03-1996
		CA 2197655 A1	22-02-1996
		EP 0776316 A1	04-06-1997
		JP 10504008 T	14-04-1998
		WO 9605138 A1	22-02-1996
		US 6042804 A	28-03-2000
US 4681751 A	21-07-1987	AT 25839 T	15-03-1987
		CA 1240481 A1	16-08-1988
		DE 3462598 D1	16-04-1987
		EP 0132294 A1	30-01-1985
		ES 8604467 A1	01-07-1986
		FI 842527 A ,B	23-12-1984
		JP 1023401 B	02-05-1989
		JP 1540661 C	31-01-1990
		JP 60011209 A	21-01-1985
		NO 842509 A ,B,	27-12-1984

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 03 38 0019

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

24-04-2003

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4681751 A		ZA 8404714 A	26-02-1986
US 4009252 A	22-02-1977	JP 1104996 C	16-07-1982
		JP 51004097 A	13-01-1976
		JP 56047121 B	07-11-1981
		AR 203794 A1	15-10-1975
		AU 8243575 A	06-01-1977
		BE 830818 A1	16-10-1975
		BR 7504143 A	29-06-1976
		CA 1057027 A1	26-06-1979
		CS 192546 B2	31-08-1979
		DE 2528601 A1	15-01-1976
		FR 2277030 A1	30-01-1976
		IT 1039416 B	10-12-1979
		NL 7507877 A	06-01-1976
		RO 67269 A1	30-12-1980
EP 0366419 A	02-05-1990	CA 1317740 A1	18-05-1993
		DE 68917255 D1	08-09-1994
		DE 68917255 T2	19-01-1995
		EP 0366419 A1	02-05-1990
		JP 2258610 A	19-10-1990
		US 5082647 A	21-01-1992