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IN THE MATTER OF a Singapore Application corresponding to PCT Application PCT/EP97/02815

I, Stephen DRANE BSc PhD BDÜ,
c/o Europa House, Marsham Way, Gerrards Cross, Buckinghamshire, England, do solemnly and sincerely declare that I am conversant with the English and German languages and am a competent translator thereof, and that to the best of my knowledge and belief the following is a true and correct translation of the PCT Application filed under No. PCT/EP97/02815.

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S. DRANE
For and on behalf of RWS Group plc

The preparation of epoxides from olefins and hydrogen peroxide or hydroperoxides

The present invention relates to an improved process for preparing epoxides from olefins and hydrogen peroxide or hydroperoxides using an oxidation catalyst based on titanium or vanadium silicates with a zeolite structure.

Processes for preparing epoxides from olefins and aqueous hydrogen peroxide using titanium silicates as epoxidation catalysts are disclosed in EP-A 100 119 (1) and by M.G. Clerici et al., J. Catal. 129, (1991) 159-167 (2).

According to (1), the epoxidation of ethylene, propene, allyl chloride, 2-butene, 1-octene, 1-tridecene, mesityl oxide, isoprene, cyclooctene and cyclohexene using dilute aqueous hydrogen peroxide in the presence of a titanium silicalite is carried out in an autoclave. The hydrogen peroxide concentration in the reaction mixture can in this case be reduced to 10% by weight.

(2) discloses that it is in fact possible to reduce the hydrogen peroxide concentration in such epoxidations to 1%. The sources of hydrogen peroxide employed for the titanium silicalite-catalyzed epoxidations described in (2) of propene to propylene oxide are 30 - 35% strength aqueous H_2O_2 solutions.

However, prior art epoxidation processes of these types have disadvantages. The use of concentrated hydrogen peroxide solutions (with about 10 - 70% by weight of H_2O_2) may result in considerable safety problems in carrying out the reaction because of the possibility of spontaneous decomposition of the hydrogen peroxide or of its byproducts (eg. hydroperoxides), especially in the presence of certain organic solvents. The elimination of such safety problems results in considerably greater expense and higher process costs. Even without said safety aspect, the process costs are still high because moderately to highly concentrated hydrogen peroxide solutions are relatively costly.

It is an object of the present invention to provide a simple, efficient and, in particular, economic process for epoxidizing olefins which does not have the disadvantages of the prior art.

We have found that this object is achieved by a process for preparing epoxides from olefins and hydrogen peroxide or hydroperoxides in liquid phase using an oxidation catalyst based

on titanium or vanadium silicalites with a zeolite structure, wherein the concentration of hydrogen peroxide or of the hydroperoxides in the reaction mixture is in the range from 0.05 to less than 1% by weight, in particular from 0.1 to 0.8% by weight, especially from 0.2 to 0.6% by weight, during the reaction.

Hydroperoxides which can be employed are all organic hydroperoxides which are conventionally used as oxidizing agents for such epoxidations and have the formula R-O-O-H where R is, as a rule, an organic radical having 1 to 30 carbon atoms. Of particular interest in this connection are cumene and diisopropylbenzene hydroperoxides.

In a preferred embodiment, the sources of hydrogen peroxide employed for the epoxidation according to the invention are aqueous hydrogen peroxide solutions, in particular technical (ie. not purified) hydrogen peroxide solutions, containing from 0.1 to 10% by weight, in particular 0.15 to 5% by weight, especially 0.2 to 2% by weight, of hydrogen peroxide.

Particularly suitable technical sources of hydrogen peroxide are extraction solutions which contain hydrogen peroxide and derive from an anthraquinone working solution for preparing hydrogen peroxide.

Further very suitable technical sources of hydrogen peroxide are streams or residues, eg. vapors or bottom products, which contain hydrogen peroxide and derive from a hydrogen peroxide distillation, these streams or residues usually not having undergone further concentration of their H_2O_2 content.

Also particularly suitable as technical sources of hydrogen peroxide are extraction solutions which contain hydrogen peroxide and derive from fermenter broths or from enzyme-containing mixtures, ie. from sources which are naturally occurring or obtainable biotechnologically.

The employed oxidation catalysts based on titanium or vanadium silicates with a zeolite structure are known in the art. As is well known, zeolites are crystalline aluminosilicates with ordered channel and cage structures whose pore openings are in the micropore range smaller than 0.9 nm. The network of such zeolites is composed of SiO_4 and AlO_4 tetrahedra which are linked by common oxygen bridges. A review of the known structures is to

be found, for example, in W.M. Meier and D.H. Olson, "Atlas of Zeolite Structure Types", Butterworth, 2nd Ed., London 1987.

Other known zeolites contain no aluminum and have in the silicate lattice titanium as Ti(IV) partly replacing Si(IV). These titanium zeolites, especially those with a crystal structure of the MFI type, and possible ways of preparing them are described, for example, in EP-A 311 983 or EP-A 405 978. Apart from silicon and titanium, such materials may also contain elements such as aluminum, zirconium, tin, iron, cobalt, nickel, gallium, boron or small amounts of fluorine.

The titanium in the zeolite oxidation catalyst described may be partly or completely replaced by vanadium. The molar ratio of titanium and/or vanadium to the total of silicon plus titanium and/or vanadium is, as a rule, in the range from 0.01:1 to 0.1:1.

Titanium zeolites with an MFI structure are known to be identifiable from a particular pattern on determination of their X-ray diffraction diagrams and, in addition, from a skeletal vibration band in the infrared region (IR) at about 960 cm^{-1}, and thus differ from alkali metal titanates or crystalline and amorphous TiO_2 phases.

Said titanium and vanadium zeolites are typically prepared by reacting an aqueous mixture of an SiO_2 source, and of a titanium or vanadium source such as titanium dioxide or an appropriate vanadium oxide and of a nitrogen-containing organic base ("template compound"), eg. tetrapropylammonium hydroxide, with or without added alkali metal compounds, in a pressure vessel at elevated temperature for several hours or some days, resulting in the crystalline product. The latter is filtered off, washed, dried and combusted at high temperature to remove the organic nitrogen base. In the resulting powder, the titanium or vanadium is present at least partly inside the zeolite framework with four-, five- or six-fold coordination in varying proportions. To improve the catalytic characteristics it is also possible to carry out a subsequent treatment by washing several times with a solution of hydrogen peroxide in sulfuric acid, after which the titanium or vanadium zeolite powder must be again dried and combusted; this can be followed by a treatment with alkali metal compounds in order to convert the zeolite from the H form into the cation form.

Preferred titanium or vanadium zeolites are those with a pentasil structure, especially the types with X-ray assignment to a BEA, MOR, TON, MTW, FER, MFI, MEL or MFI/MEL mixed structure. Zeolites

of this type are described, for example, in W.M. Meier and D.H. Olson, "Atlas of Zeolite Structure Types", Butterworths, 2nd Ed., London 1987. Also conceivable for the present invention are titanium-containing zeolites with the structure of ZSM-48, ZSM-12, ferrierite or β-zeolite and of mordenite.

The process according to the invention for preparing epoxides can in principle be carried out using all conventional reaction procedures and in all conventional types of reactor, for example in a suspension procedure or in a fixed bed arrangement. Continuous or batchwise operation is possible.

The epoxidation according to the invention in liquid phase is expediently carried out in water alone or in a mixture of water and water-miscible organic solvents. Particularly suitable organic solvents are alcohols such as methanol, ethanol, isopropanol, tert-butanol or mixtures thereof. If a mixture of such organic solvents with water is used, their content in the complete mixture is usually from 5 to 95% by volume, in particular 30 to 85% by volume.

The epoxidation according to the invention is, as a rule, carried out at from -20 to 70°C, in particular -5 to 50°C, under from 1 to 10 bar.

The olefin which is employed can be any organic compound which contains at least one ethylenically unsaturated [sic] double bond. It may be aliphatic, aromatic or cycloaliphatic in nature and may have a linear or branched structure. The olefin preferably contains from 2 to 30 carbon atoms. More than one ethylenically unsaturated [sic] double bond may be present, for example in dienes or trienes. The olefin may additionally contain functional groups such as halogen atoms, carboxyl groups, carboxylic ester functionalities, hydroxyl groups, ether bridges, sulfide bridges, carbonyl functionalities, cyano groups, nitro groups or amino groups.

Typical examples of such olefins are ethylene, propene, 1-butene, cis- and trans-2-butene, 1,3-butadiene, pentenes, isoprene, hexenes, octenes, nonenes, decenes, undecenes, dodecenes, cyclopentene, cyclohexene, dicyclopentadiene, methylenecyclopropane, vinylcyclohexane, vinylcyclohexene, allyl chloride, acrylic acid, methacrylic acid, crotonic acid, vinylacetic acid, allyl alcohol, alkyl acrylates, alkyl methacrylates, oleic acid, linoleic acid, linolenic acid, esters and glycerides of such unsaturated fatty acids, styrene, α-methylstyrene, divinylbenzene, indene and stilbene. The process

according to the invention can also be used to epoxidize mixtures of said olefins.

The process according to the invention is particularly suitable for epoxidizing propene to propylene oxide.

Olefins can be successfully epoxidized in accordance with the present invention using titanium or vanadium silicalites at far below the hydrogen peroxide concentration known in the art. Because of the low hydrogen peroxide concentration in the system, safety problems no longer occur. In addition, hydrogen peroxide solutions can be employed without interfering stabilizers which are necessary at high concentrations. In addition, the process according to the invention has the advantage that low-cost technical sources of hydrogen peroxide can be used as starting material; the impurities present in such sources surprisingly do not interfere with the epoxidation according to the invention.

The following examples are intended to illustrate the process according to the invention without implying a restriction.

Example 1

455 g of tetraethyl orthosilicate were introduced into a four-neck flask (2 l capacity) and, while stirring (250 rpm, paddle stirrer), 15 g of tetraisopropyl orthotitanate were added from a dropping funnel over the course of 30 min. A clear colorless mixture formed. Finally, 800 g of a 20% by weight tetrapropylammonium hydroxide solution (alkali content < 10 ppm) were added, and the mixture was stirred for one hour. The alcohol mixture (about 450 g) formed in the hydrolysis was removed by distillation at 90 - 100°C. The volume was made up with 1.5 l of deionized water, and the sol, which had become slightly opaque, was transferred into a stainless steel stirred autoclave with a capacity of 2.5 l.

The temperature of the closed autoclave (anchor stirrer, 200 rpm) was raised to 175° at a rate of 3°/min. The reaction was complete after 92 hours. The cooled reaction mixture (white suspension) was centrifuged and the residue was washed with water several times until neutral. The resulting solid was dried at 110°C for 24 hours (weight 149 g).

The template still present in the zeolite was finally removed by combustion in air at 550°C for 5 hours (loss on calcination: 14% by weight).

The pure white product had, according to wet chemical analysis, a Ti content of 1.5% by weight and a residual alkali content below 100 ppm. The yield based on SiO_2 was 97%. The crystallites had a size of 0.05 to 0.25 µm, and the product showed a typical IR band at about 960 cm^{-1}.

Example 2

45 ml of methanol and 0.5 g of titanium silicate powder from Example 1 were introduced into a 250 ml glass autoclave, and the suspension was stirred with a magnetic stirrer. The closed glass autoclave was then cooled to -30°C, and 20.7 g of propene were injected. The glass autoclave was then warmed to 0°C, and 23 g of 0.5% by weight hydrogen peroxide solution were metered in. The reaction mixture was stirred under autogenous pressure at 0°C for 5 h. The catalyst was then removed by centrifugation, and the propylene oxide content was determined by gas chromatography. The propylene oxide content was 0.3% by weight.

Example 3

45 ml of methanol and 0.5 g of titanium silicalite from Example 1 were introduced into a 250 ml glass autoclave, and the suspension was stirred with a magnetic stirrer. The closed glass autoclave was then cooled to -30°C, and 20.2 g of propene were injected. The glass autoclave was then warmed to 0°C, and 23 g of 0.5% by weight hydrogen peroxide solution were metered in. The reaction mixture was stirred under autogenous pressure at 0°C for 30 minutes. The catalyst was then removed by centrifugation, and the propylene oxide content was determined by gas chromatography. The propylene oxide content was 0.18% by weight.

We claim:

1. A process for preparing epoxides from olefins and hydrogen peroxide or hydroperoxides in liquid phase using an oxidation catalyst based on titanium or vanadium silicates with a zeolite structure, wherein the concentration of hydrogen peroxide or of the hydroperoxides in the reaction mixture is in the range from 0.05 to less than 1% by weight during the reaction.

2. A process as claimed in claim 1, wherein the sources of hydrogen peroxide employed for the epoxidation are aqueous hydrogen peroxide solutions containing from 0.1 to 10% by weight of hydrogen peroxide.

3. A process as claimed in claim 2, wherein the sources of hydrogen peroxide employed are extraction solutions which contain hydrogen peroxide and derive from an anthraquinone working solution for preparing hydrogen peroxide.

4. A process as claimed in claim 2, wherein the sources of hydrogen peroxide employed are streams or residues which contain hydrogen peroxide and derive from a hydrogen peroxide distillation.

5. A process as claimed in claim 2, wherein the sources of hydrogen peroxide employed are extraction solutions which contain hydrogen peroxide and derive from fermenter broths or from enzyme-containing mixtures.

6. A process for preparing propylene oxide from propene and hydrogen peroxide or hydroperoxides as claimed in any of claims 1 to 5.