Process for the preparation of epoxides from olefins

Description

The invention relates to a process for the preparation of epoxides by epoxidation of olefinic compounds with hydrogen peroxide in the presence of a titanium silicalite as a catalyst.

Prior art

It is known from EP-B 0 100 118 that olefins can be epoxidized with hydrogen peroxide and converted to glycol ethers in situ in the presence of alcohols if a titanium-containing zeolite, generally called a titanium silicalite, is employed as a catalyst. In respect of the preparation of epoxides, the acid properties of this catalyst are a disadvantage, because some of the epoxide formed already reacts further during the reaction by acid-catalysed ring-opening to give the diol or, in the presence of an alcohol as the solvent, to give diol ethers.

It is known from EP 0 230 949 that the epoxide ring-opening reaction can be partly suppressed if the catalyst is neutralized with a neutralizing agent before and/or during the epoxidation reaction. Strong bases, such as NaOH and KOH, and weak bases, such as ammonia, alkali metal carbonates, alkali metal bicarbonates and alkali metal carboxylates, are mentioned as neutralizing agents in the patent specification. This document indeed imparts a doctrine for the treatment of the catalyst with a base before the epoxidation, but it gives no suggestion as to how the catalyst is to be neutralized during the epoxidation.

M.G. Clerici, P. Ingallina describe in J. Catal. 140 (1993) 71-83 the process of the generic type and the influence of acids, bases and salts on the catalytic activity of the titanium silicalite catalyst. According to this, it is known that the effect of a neutralizing agent on the catalytic properties depends greatly on the amount of neutralizing agent. While the use of a small amount of the neutralizing agent leads to an increase in the selectivity, if the amount is too large there is an inhibition of the catalytic activity for the epoxidation, up to complete blocking of the activity of the catalyst. It is furthermore known that acids present in the reaction medium can increase the rate of reaction. It is known from H. Gao, G. Lu, J. Suo, S. Li, Appl. Catal. A 138 (1996) 27-38 that this adverse effect of the neutralizing agent already occurs at low concentrations, and that concentrations of NaOH or KOH of less than 600 ppm can already lead to a severe loss in catalytic activity.

The known process for the epoxidation of olefins with hydrogen peroxide and a titanium silicalite catalyst with the addition of basic substances has the disadvantage that to date no possibility is known of determining beforehand in an individual case the amount of neutralizing agent required for the desired effect of improving the selectivity and at the same time not reducing or only moderately reducing the rate of reaction. For carrying out the reaction in practice, this has the disadvantage that if a neutralizing agent is used, a small change in the quality of the starting substances and/or the properties of the catalyst can already lead to a marked and unforeseeable change in the activity of the catalyst during the epoxidation. The abovementioned documents give no suggestion as to how the amount of base to be added to the system can be controlled within narrow limits.

The object of the present invention is to provide a process of the generic type with which the disadvantages described for the process which is already known can be overcome. It should be possible to realize the process by discontinuous and, in particular, continuous operation. The invention should also allow the process to be carried out such that with the highest possible increase in selectivity, the conversion changes in a manner which can be determined beforehand.

Subject matter of the invention

It has been found, surprisingly, that the object can be achieved in that the addition of the base used to an epoxidation reactor is carried out with monitoring of the pH and the amount of base is chosen such that for the hydrogen peroxide employed or the mixture of hydrogen peroxide with one or more solvents employed, a constant pH determined beforehand by one or more test experiments results.

The invention thus provides a process for the preparation of an epoxide, comprising epoxidation of an olefinic compound with hydrogen peroxide in the presence of a titanium silicalite catalyst, wherein a solution containing hydrogen peroxide and the olefinic compound are introduced as starting substances periodically or continuously into an epoxidation reactor and a base is additionally employed in the process, which is characterized in that the base is introduced into the epoxidation reactor directly or as a mixture with one or more of the starting substances, with pH control, the pH control is carried out in the reaction mixture or in the mixture(s) with a starting substance comprising the base, and a pH in the range from 4 to 9.5 is established and substantially kept constant. Since the pH in the reaction mixture decisively influences the selectivity and the conversion, the optimum pH is determined beforehand by one or more epoxidation test

experiments carried out at different pH values using the same starting substances, with subsequent determination of the selectivity and the conversion.

By choice of a suitable, constant pH, the epoxide selectivity in the epoxidation of olefins with hydrogen peroxide with a titanium silicalite catalyst can be improved in a reproducible manner, while at the same time the activity of the catalyst decreases only little and in a reproducible manner. If a constant pH is established, variations in the quality of the starting substance or in the composition of the catalyst have less effect on the course of the reaction than if a constant amount of the neutralizing agent is added.

According to a preferred embodiment, the base is added to an aqueous or aqueous-organic hydrogen peroxide solution and the optimum pH, determined from preliminary experiments, for example a pH-dependent test series, is established and kept constant in the solution obtained in this way; in the case of the aqueous hydrogen peroxide solution the optimum pH is in the range from 4 to 6.5, and in the case of an organic-aqueous hydrogen peroxide solution with at least 50 wt.% of an organic water-soluble solvent it is in the range from 5 to 9.5, the pH being based on measurement by means of a glass electrode. A single-stick measurement chain of a glass electrode with an integrated Ag/AgCl comparison electrode is preferably used.

The process according to the invention is suitable for the epoxidation of aliphatic, cycloaliphatic and aliphatic-aromatic olefinic compounds. Olefins having 3 to 8 carbon atoms are preferably employed, particularly preferably propene and 1-butene. The olefinic compound can contain one or more functional groups, such as e.g. hydroxyl, halogen, alkoxy or carbalkoxy. Allyl chloride and allyl alcohol can be readily epoxidized in the process according to the invention.

The hydrogen peroxide is employed in the process according to the invention in the form of an aqueous solution with a hydrogen peroxide content of 1 to 90 wt.%, preferably 10 to 70 wt.%, and particularly preferably 30 to 50 wt.%. The hydrogen peroxide can be employed in the form of the commercially obtainable stabilized solutions. Non-stabilized aqueous hydrogen peroxide solutions such as are obtained in the anthraquinone process for the preparation of hydrogen peroxide are also suitable. As an alternative to this, hydrogen peroxide can also be employed as an organic-aqueous solution or organic solution. Preferably, a pH-controlled aqueous or aqueous-organic hydrogen peroxide solution to which a base has been added is added to the epoxidation reactor.

Crystalline titanium-containing zeolites of the composition $(TiO_2)x(SiO_2)1-x$, where x is from 0.001 to 0.05, and an MFI or MEL crystal structure, known as titanium silicalite-1 and titanium silicalite-2, are suitable in particular as the catalyst. The titanium silicalite catalyst can be employed as a powder or as a shaped catalyst in the form of granules, extrudates or shaped bodies. For shaping, the catalyst can comprise 1 to 99 % of a binder or support material, all binders and support materials which do not react with hydrogen peroxide or the epoxide under the reaction conditions used for the epoxidation being suitable. Granules according to EP-A 0 893 158 or extrudates with a diameter of 1 to 5 mm are preferably employed.

Suitable solvents are all the solvents which are not oxidized or are oxidized to only a small extent by hydrogen peroxide under the reaction conditions chosen and dissolve in water to the extent of more than 10 wt.%. Solvents which are of unlimited miscibility with water are preferred. Suitable solvents are alcohols, such as e.g. methanol, ethanol or tert-butanol; glycols, such as e.g. ethylene

glycol, 1,2-propanediol or 1,3-propanediol; cyclic ethers, such as e.g. tetrahydrofuran, dioxane or propylene oxide; glycol ethers, such as e.g. ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monobutyl ether or the propylene glycol monomethyl ethers, and ketones, such as e.g. acetone or 2-butanone. Methanol is preferably added as the solvent.

Bases which can be employed for the process according to the invention are all the substances by the addition of which the pH can be raised to the required value. Suitable bases are alkali metal hydroxides, ammonia, alkali metal carbonates, ammonium carbonate, alkali metal bicarbonates, ammonium bicarbonate and alkali metal and ammonium salts of carboxylic acids. Alkali metal and ammonium salts of polybasic mineral acids, such as e.g. phosphoric acid and pyrophosphoric acid, are also suitable. Aqueous solutions of the base are preferably employed, particularly preferably aqueous solutions of NaOH, LiOH or ammonia. According to another alternative, the base used to establish the pH is a buffer mixture, such as borax/HCl, borax/NaOH or NaH_2PO_4/NaOH.

All the physical parameters and measurement methods which give a measurement value which depends on the pH in a reproducible manner and varies with the pH are suitable for establishing the pH. A potentiometric measurement with a glass electrode which has a pH-dependent potential is preferably employed. Commercially available pH meters with which the potential is displayed directly on a scale in pH units and electrodes which give a stable and reproducible potential in the aqueous hydrogen peroxide solutions or mixtures thereof with the solvent are suitable. Due to the content of hydrogen peroxide and optionally solvent, a concentration potential additionally occurs at the glass electrode, in addition to the pH-dependent potential. The pH measured with a commercially available pH instrument

therefore deviates from the actual pH, i.e. the common logarithm of the hydrogen ion concentration, by a constant amount, the amount depending in a reproducible manner on the mixing ratio of water, hydrogen peroxide and optionally solvent. For aqueous hydrogen peroxide solutions, this deviation of the pH measurement with a glass electrode compared with the actual pH is known from J. R. Kolczynski, E. M. Roth, E. S. Shanley, J. Am. Chem. Soc. 79 (1957) 531-533.

The pH to be established to achieve the advantage according to the invention depends on the composition of the mixture of hydrogen peroxide, water and optionally solvent and can be determined, as the examples demonstrate, in a simple manner by a series of experiments in which the pH is varied. In the case of a pH measurement with a glass electrode, the effect according to the invention on addition of the base to an aqueous hydrogen peroxide solution with a content of between 30 and 50 wt.% is as a rule achieved when the pH is raised by 1 to 4 pH units and the pH displayed by the meter after addition of the base is between 4 and 6.5. In the same way, the effect according to the invention on addition of the base to a mixture of aqueous hydrogen peroxide and methanol is as a rule achieved when the pH is raised by 1 to 6 pH units and the pH displayed by the meter after addition of the base is between 5 and 9.5.

The process according to the invention for the epoxidation of olefins is carried out at a temperature of -10 to 100 °C, preferably at 20 to 70 °C. The olefin is preferably employed in excess with respect to the hydrogen peroxide, in order to achieve a substantial hydrogen peroxide conversion, the molar ratio of olefin to hydrogen peroxide being equal to/greater than 1, and preferably being in the range from 1.1 to 10. If an organic solvent is added, the amount of solvent is preferably chosen such that only a

liquid phase is present in the reaction mixture. The solvent is preferably added in a weight ratio of 1 to 20 relative to the amount of hydrogen peroxide employed.

The amount of catalyst employed can be varied within wide limits and is preferably chosen such that under the reaction conditions applied, a hydrogen peroxide conversion of about 90 %, preferably more than 95 %, is achieved within 1 min to 5 h.

If an olefin with a boiling point under normal pressure below the reaction temperature chosen is reacted, the reaction is preferably carried out under pressure and under an atmosphere which substantially comprises the vaporous olefin; an olefin partial pressure in the range from 0.1 to 1 MPa is suitable. The pressure here is particularly preferably chosen between 50 and 100 % of the saturation vapour pressure of the olefin at the reaction temperature.

In one embodiment of the invention, the catalyst is suspended in the reaction mixture during the epoxidation reaction. In this case the pH of the hydrogen peroxide or the mixture of hydrogen peroxide and solvent can optionally be established either before or after the addition of the catalyst. If the epoxidation reaction is carried out in a thoroughly mixed reactor, e.g. a stirred tank or a loop reactor, the pH measurement can optionally also take place in the reactor and the base for establishing the pH can be added directly to the reaction mixture.

In another preferred embodiment of the invention, the catalyst is employed in the form of a heap or packing in a tubular reactor and the mixture of hydrogen peroxide, olefin and optionally solvent is passed over this packing. In the case of olefins which are gaseous under the reaction conditions, gaseous olefin and optionally additionally an inert gas are preferably fed in, the gaseous olefin or olefin-gas mixture preferably being passed in

countercurrent to the liquid mixture. The gaseous olefin or olefin-gas mixture in this case is preferably passed through the reactor from the bottom upwards, so that it is dispersed in the form of bubbles in the solution flowing in countercurrent. The amount of the gas stream is chosen here such that unreacted, gaseous olefin or, in the case of complete conversion, the inert gas is removed at the end of the reactor and the molecular oxygen formed in the reactor by decomposition of hydrogen peroxide is discharged from the reactor with this gas stream.

If the catalyst is employed in the form of a heap or packing, it can moreover be conditioned before the start of the epoxidation reaction, by bringing water, optionally mixed with a solvent and/or hydrogen peroxide, to a constant pH by addition of a base and passing it over the catalyst.

The abovementioned bubble procedure is suitable both for the epoxidation according to the invention under pH control and for other processes of the generic type, for example those in which the catalyst is neutralized or in which selectivity-reducing acid functions of the catalyst are neutralized by chemical reaction.

The process according to the invention renders a continuous operating procedure possible, without the selectivity and yield (H_2O_2 conversion) being adversely influenced by quality variations in the starting substances. Due to the separate metering in according to the invention of a base under pH control during the epoxidation, treatment of the catalyst before or during the epoxidation is unnecessary.

Examples

Titanium silicalite granules prepared by the process described in EP 0 893 158, example 3 are used as the catalyst for all the examples. The propylene oxide selectivities (PO selectivity) stated were calculated as the ratio of the concentration of propylene oxide to the sum of the concentrations of the products propylene oxide, 1-methoxypropanol, 2-methoxypropanol and 1,2-propanediol.

Example 1 (comparison example)

300 g methanol are initially introduced into a thermostatically controlled laboratory autoclave with gassing stirrers at 60 °C under a propylene atmosphere and are saturated with propylene under an excess pressure of 5 bar. A mixture of 518 g 50.7 wt.% hydrogen peroxide (distilled), 2586 g methanol, 125 g MTBE (tert-butyl methyl ether), 253 g water and 10 g titanium silicalite is then metered in at a rate of 290 g/h, while stirring. At the same time, reaction mixture is removed via a valve in an amount such that the weight of the contents of the reactor remained [sic] constant. During the metering, propylene is topped up via a pressure regulator in order to keep the pressure in the reactor constant. At regular intervals, the hydrogen peroxide content in the reaction mixture removed is determined by redox titration and the content of propylene oxide, 1-methoxy-2-propanol, 2-methoxy-1-propanol and 1,2-propanediol is determined by GC. After 4 h a stationary operating state is reached. Table 1 shows the hydrogen peroxide conversion and the propylene oxide selectivity in the stationary operating state.

For the hydrogen peroxide employed, a pH of 2.8 was measured with a single-stick measurement chain of glass electrode and integrated Ag/AgCl comparison electrode. Corrected by the concentration potential for 50.7 wt.% hydrogen peroxide, an actual pH of 4.6 results.

Examples 2 to 5

Example 1 is repeated, with the difference that the hydrogen peroxide employed is brought to the pH shown in table 1 by addition of 1 N sodium hydroxide solution, the pH being measured with a single-stick measurement chain of glass electrode and integrated Ag/AgCl comparison electrode. After 4.5 h a stationary operating state with the hydrogen peroxide conversion and the propylene oxide selectivity from table 1 is reached.

Table 1

Example	pH of the H_2O_2	H_2O_2 conversion	PO selectivity
1	2.8	71.0 %	54.9 %
2	4.0	71.4 %	60.7 %
3	4.5	69.5 %	77.1 %
4	4.75	65.3 %	85.2 %
5	5.0	35.3 %	94.2 %

Example 6 (comparison example)

Example 1 is repeated with the difference that sodium nitrate is added to the hydrogen peroxide employed in an amount such that it has the same sodium concentration as the hydrogen peroxide employed in example 4 brought to pH 4.75 with sodium hydroxide solution. After 4.5 h a stationary operating state with a hydrogen peroxide conversion of 69.6 % and a propylene oxide selectivity of 68.0 % is reached.

Example 7 (comparison example)

Example 1 is repeated, with the difference that a different titanium silicalite catalyst is used, the reaction temperature is 65°C and a mixture of 708 g 43.1 wt.% hydrogen peroxide (crude product from the anthraquinone process), 1743 g methanol, 51 g MTBE and 35 g titanium silicalite is metered in at a rate of 200 g/h. After 4.5 h a stationary operating state is reached. Table 2 shows the hydrogen peroxide conversion and the propylene oxide selectivity in the stationary operating state.

Examples 8 to 11

Example 7 is repeated, with the difference that the hydrogen peroxide employed is brought to the pH shown in table 2 by addition of 25 wt.% aqueous ammonia, the pH being measured with a single-stick measurement chain of glass electrode and integrated Ag/AgCl comparison electrode. After 4 to 5.5 h a stationary operating state with the hydrogen peroxide conversion and the propylene oxide selectivity from table 2 is reached.

Table 2

Example	pH of the H_2O_2	H_2O_2 conversion	PO selectivity
7	2.42	58.5 %	66.8 %
8	5.15	53.2 %	88.5 %
9	5.35	50.5 %	92.1 %
10	5.55	41.2 %	92.2 %
11	5.75	27.1 %	92.7 %

Examples 12 to 15

Example 7 is repeated, with the difference that the mixture of hydrogen peroxide, methanol and MTBE employed is brought to the pH shown in table 3 by addition of 25 wt.% aqueous ammonia before the addition of the catalyst, the pH being measured with a single-stick measurement chain of glass electrode and integrated Ag/AgCl comparison electrode. After 4 to 5.5 h a stationary operating state with the hydrogen peroxide conversion and the propylene oxide selectivity from table 3 is reached.

Table 3

Example	pH of the H_2O_2/ MeOH mixture	H_2O_2 conversion	PO selectivity
7	4.39	58.5 %	66.8 %
12	5.46	58.3 %	78.4 %
13	6.81	58.9 %	80.6 %
14	7.22	57.1 %	81.7 %
15	7.69	56.3 %	86.7 %
8	8.12	53.2 %	88.5 %
10	8.23	41.2 %	92.2 %
11	8.66	27.1 %	92.7 %

Examples 16 to 19

65.7 g titanium silicalite catalyst in the form of extrudates of 2 mm diameter are initially introduced into a thermostatically controlled tubular reactor. A mixture of 278 g 42.9 wt.% hydrogen peroxide, 6672 g methanol and 51 g MTBE is brought to the pH shown in table 4 with 25 wt.% aqueous ammonia and then saturated with propene under an increased pressure of 3 bar at 45°C. This mixture is then passed over the catalyst at 39°C at a rate of 900 g/h. At regular intervals, the hydrogen peroxide content in the

emerging reaction mixture is determined by redox titration and the content of propylene oxide, 1-methoxy-2-propanol, 2-methoxy-1-propanol and 1,2-propanediol is determined by GC. After operation for 8 h the hydrogen peroxide conversion and propylene oxide selectivity shown in table 4 are reached.

Table 4

Example	pH of the H_2O_2/ MeOH mixture	H_2O_2 conversion	PO selectivity
16	5.5	94.9 %	62.3 %
17	8.5	74.3 %	78.6 %
18	8.7	65.9 %	86.6 %
19	8.9	56.1 %	92.4 %

Example 20 (comparison example)

68.0 g titanium silicalite catalyst in the form of extrudates of 2 mm diameter are initially introduced into a thermostatically controlled tubular reactor. A mixture of 1334 g 42.9 wt.% hydrogen peroxide, 6600 g methanol and 67 g MTBE is fed in at the lower end of the reactor at 50ºC at a rate of 600 g/h. At the same time, 200 g/h gaseous propene are added at the lower end of the reactor. The liquid reaction mixture and unreacted, gaseous propene in an amount such that an increased pressure of 15 bar is maintained is [sic] removed at the upper end of the reactor. At regular intervals, the hydrogen peroxide content of the reaction mixture removed is determined by redox titration and the content of propylene oxide, 1-methoxy-2-propanol, 2-methoxy-1-propanol and 1,2-propanediol is determined by GC. After operation for 8 h the hydrogen peroxide conversion and propylene oxide selectivity shown in table 5 is reached.

Examples 21 to 23

Example 20 is repeated, with the difference that the mixture of hydrogen peroxide, methanol and MTBE employed is brought to the pH shown in table 5 by addition of 25 wt.% aqueous ammonia, the pH being measured with a single-stick measurement chain of glass electrode and integrated Ag/AgCl comparison electrode. After operation for 8 h, the hydrogen peroxide conversion and propylene oxide selectivity shown in table 5 are reached.

Table 5

Example	pH of the H_2O_2/ MeOH mixture	H_2O_2 conversion	PO selectivity
20	4.8	96.9 %	81.7 %
21	8.0	96.5 %	87.2 %
22	8.5	93.5 %	94.8 %
23	9.0	90.0 %	94.6 %

Patent claims

1. Process for the preparation of an epoxide, comprising epoxidation of an olefinic compound with hydrogen peroxide in the presence of a titanium silicalite catalyst,
wherein a solution containing hydrogen peroxide and the olefinic compound are introduced as starting substances periodically or continuously into an epoxidation reactor and a base is additionally employed in the process,
characterized in that
the base is introduced into the epoxidation reactor directly or as a mixture with one or more of the starting substances, with pH control, the pH control is carried out in the reaction mixture or in the mixture(s) with a starting substance comprising the base, and a pH in the range from 4 to 9.5 is established and substantially kept constant.

2. Process according to claim 1,
characterized in that
the base is added to an aqueous or aqueous-organic hydrogen peroxide solution and the pH is established and kept constant in the solution obtained in this way, in the case of the aqueous hydrogen peroxide solution the pH being in the range from 4 to 6.5, and in the case of an organic-aqueous hydrogen peroxide solution with at least 50 wt.% of an organic water-soluble solvent the pH being in the range from 5 to 9.5, the pH being based on measurement by means of a glass electrode.

3. Process according to claim 1 or 2,
characterized in that
the epoxidation is carried out in the presence of an organic solvent from the series consisting of lower alcohols or/and ethers, the weight ratio of hydrogen

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peroxide to organic solvent being in the range from 1 : 1 to 1 : 20.

4. Process according to one of claims 1 to 3, characterized in that a base from the series consisting of alkali metal hydroxides, alkali metal carbonates, alkali metal bicarbonates, alkali metal phosphates, alkali metal carboxylates and ammonia is used to establish the pH, the base being employed per se or as an aqueous solution.

5. Process according to one of claims 1 to 4, characterized in that the epoxidation is carried out in a fixed bed reactor filled with titanium silicalite catalyst, the olefinic compound and an aqueous or aqueous-organic hydrogen peroxide solution to which a base has been added beforehand for the purpose of establishing and maintaining the pH being passed in co- or countercurrent through the reactor.

6. Process according to one of claims 1 to 5, characterized in that propene is epoxidized at a molar ratio of propene to hydrogen peroxide in the range from equal to/greater than 1 to 10, the epoxidation being carried out in the presence of methanol at a temperature in the range from 20 to 70 °C under a propene pressure in the range from 0.1 to 1.0 MPa.

7. Process according to claim 5 or 6, characterized in that an olefinic compound which is gaseous under the reaction conditions is epoxidized by operating the fixed bed reactor as a bubble column, the olefinic compound being dispersed in the solution flowing in countercurrent.

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