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Process for manufacturing an epoxide

The invention relates to a process for manufacturing an epoxide by reaction between an olefin and a peroxide compound in the presence of a zeolite-based catalyst. The invention relates more particularly to a process for manufacturing 1,2-epoxypropane (or propylene oxide) by reaction between propylene and hydrogen peroxide.

It is known practice to manufacture propylene oxide by epoxidation of propylene using hydrogen peroxide in the presence of a catalyst of the type TS-1, as described, for example, in patent application EP 0,230,949. This known process has the drawback of leading, under certain conditions, to low selectivities.

The invention is directed towards overcoming this drawback by providing a process for manufacturing an epoxide which is of high selectivity.

The invention consequently relates to a continuous process for manufacturing an epoxide, according to which an olefin is reacted, in a reactor in the liquid phase, with a peroxide compound in the presence of a zeolite-based catalyst and in the presence of a solvent, and a gaseous compound is introduced continuously into the reactor at a flow rate which is sufficient to entrain at least some of the epoxide produced, which is recovered with the gaseous compound at the point at which it leaves the reactor.

One of the essential characteristics of the invention lies in the introduction of a gaseous compound into the reactor. The reason for this is that it has been observed that the epoxide reacts in the epoxidation reaction medium with the water and the solvent to form by-products which reduce the selectivity of the epoxidation reaction. It has now been found that by introducing a gaseous compound into the reaction medium at a flow rate which is sufficient to allow the epoxide produced to be entrained and to remove it from the reactor at the same time as the gaseous compound, the contact time between the epoxide produced and the

epoxidation reaction medium is reduced. The formation of by-products is thus avoided and the selectivity of the epoxidation is increased.

The function of the gaseous compound is to entrain the epoxide produced out of the reaction medium in order to prevent the epoxide from remaining in contact with the reaction medium for too long, and thus to avoid the formation of by-products. In other words, the gaseous compound allows the epoxide produced to be removed from the reaction medium by stripping.

The gaseous compound used in the process according to the invention can be any compound which is in gaseous form under the epoxidation conditions and which has no negative influence on the epoxidation reaction. It can be chosen from inert gases such as nitrogen.

One advantageous embodiment of the process according to the invention consists in introducing, into the reactor, the olefin in gaseous form and in a large excess such that the gaseous olefin can act, partially or completely, as the gaseous compound, i.e. it can entrain the epoxide produced and remove it from the reactor.

Another specific embodiment of the process according to the invention consists in introducing the gaseous compound into the reactor at a flow rate such that it makes it possible not only to entrain at least some of the epoxide produced, but also to circulate the liquid phase in the reactor, in particular when this reactor is a loop-type reactor.

In the process according to the invention, the gaseous compound is generally introduced into the reactor at a flow rate such that the ratio of the flow rate of the gaseous compound to the flow rate of supply of the peroxide compound is at least 5, in particular at least 8, values of at least 10 being common. The ratio of these flow rates is generally less than or equal to 50, in particular less than or equal to 30, values of less than or equal to 20 being common.

Any type of reactor, in particular a loop-type

reactor, can be used in the process according to the invention. Bubble-siphon loop-type reactors, in which the circulation of the liquid and also optionally of the catalyst is obtained by bubbling a gas into one of the branches, are suitable for use. An example of such a reactor is shown schematically in Figure 1. The gaseous compound (preferably the olefin) is introduced into the bottom of the reaction zone 1 via the pipe 2. The other reagents (peroxide compound, solvent, catalyst, optionally one or more additives) are introduced into the reactor via the pipes 3 and 4. The liquid phase circulates in the reactor in the direction of the arrows. The gaseous compound rises in the reaction zone 1 and thus entrains the epoxide produced therein. A mixture of the gaseous compound and of epoxide produced leaves the reactor via the pipe 5. The liquid phase leaving from the top of the reaction zone 1 is recycled into the bottom of the reaction zone via a heat exchanger 6. The overflow of the liquid phase, which is depleted in propylene oxide by means of stripping, is carried out via the pipe 7. A reactor comprising two concentric zones, the central zone providing the function of zone 1 of the reactor shown schematically in Figure 1, and the peripheral zone providing the function of zone 6 of the reactor shown schematically in Figure 1, can also be used in the process according to the invention.

In the process according to the invention, it may prove advantageous to maintain the pH of the liquid phase during the reaction between the olefin and the peroxide compound at a value of at least 4.8, in particular of at least 5. The pH is advantageously less than or equal to 6.5, in particular less than or equal to 6. Good results are obtained when the pH is from 4.8 to 6.5, preferably from 5 to 6. The pH of the liquid phase during the epoxidation reaction can be controlled by addition of a base. This base can be chosen from water-soluble bases. These can be strong bases. As examples of strong bases, mention may be made of NaOH and KOH. They can also be weak bases. The weak bases can

be inorganic. As examples of weak inorganic bases, mention may be made of NH_4OH, Na_2CO_3, $NaHCO_3$, Na_2HPO_4, K_2CO_3, Li_2CO_3, $KHCO_3$, $LiHCO_3$ and K_2HPO_4. The weak bases can also be organic. Weak organic bases which may be suitable are the alkali metal or alkaline-earth metal salts of carboxylic acids preferably containing from 1 to 10 carbon atoms. Sodium acetate may be mentioned by way of example. Weak bases give good results. Weak organic bases are preferred. Sodium acetate is particularly suitable.

The peroxide compounds which can be used in the process according to the invention are peroxide compounds containing active oxygen which are capable of carrying out an epoxidation. Hydrogen peroxide and peroxide compounds which can produce hydrogen peroxide under the epoxidation reaction conditions are suitable for use. Hydrogen peroxide is preferred.

In the process according to the invention, the peroxide compound is generally used in an amount of at least 1 mol per kg of liquid phase, in particular at least 1.5 mol per kg of liquid phase. The amount of peroxide compound is generally less than 10 mol per kg of reaction medium; it is usually less than or equal to 5 mol per kg of liquid phase, in particular less than or equal to 3 mol per kg of liquid phase.

In the process according to the invention, the peroxide compound is advantageously used in the form of an aqueous solution. In general, the aqueous solution contains at least 10% by weight of peroxide compound, in particular at least 20% by weight. It usually contains not more than 70% by weight of peroxide compound, in particular 50% by weight.

In the process according to the invention, the olefin reacts with the peroxide compound in the presence of the catalyst and the solvent at a temperature which is generally at least 0°C, in particular at least 20°C. The temperature is generally less than 150°C; it is usually less than or equal to 70°C, in particular less than or equal to 40°C.

In the process according to the invention, the reaction between the olefin and the peroxide compound can take place at atmospheric pressure. It can also take place under pressure. Generally, this pressure does not exceed 40 bar. A pressure of 20 bar is suitable in practice.

The catalysts used in the process according to the invention contain a zeolite, i.e. a solid containing silica which has a microporous crystalline structure. The zeolite is advantageously free of aluminium. It prefer-ably contains titanium.

The zeolite which can be used in the process according to the invention can have a crystalline structure of ZSM-5, ZSM-11, MCM-41 type or of beta-zeolite type. Zeolites of ZSM-5 type are suitable for use. Those with an infrared absorption band at about 950-960 cm^{-1} are preferred.

The zeolites which are particularly suitable are the titanium silicalites. Those corresponding to the formula $xTiO_2(1-x)SiO_2$ in which x is from 0.0001 to 0.5, preferably from 0.001 to 0.05, give good performance. Materials of this type, known under the name TS-1 and having a crystalline structure of ZSM-5 type, give particularly favourable results.

The epoxide which can be prepared by the process according to the invention is an organic compound comprising a group corresponding to the general formula:

The epoxide generally contains from 2 to 20 carbon atoms, preferably from 3 to 10 carbon atoms. An epoxide which can be prepared advantageously by the process according to the invention is a 1,2-epoxypropane.

The olefins which are suitable in the process according to the invention contain from 3 to 10 carbon atoms. Propylene is preferred.

Solvents which can be used in the process according to the invention can be aliphatic organic derivatives containing from 1 to 4 carbon atoms. Methanol can be mentioned by way of example.

The initial content of peroxide compounds in the liquid phase is generally between 0.1 and 10 mol/kg. It is preferably between 1.5 and 3 mol/kg.

Examples 1 and 2

Propylene oxide was manufactured in a bubble-siphon reactor as shown schematically in Figure 1, by reaction between propylene and 35% hydrogen peroxide in the presence of methanol and 5.25 g of catalyst TS-1, used in the form of beads 0.5 mm in diameter.

The tests were carried out at a temperature of 35°C, with a continuous supply of hydrogen peroxide at a flow rate of 0.57 mol/h. The amount of methanol used was 16 mol/mol of H_2O_2. In Example 1, 75 l/h (s.t.p) of propylene (i.e. 3.3 mol/h) were injected. In Example 2, 250 l/h (s.t.p) of propylene (i.e. 11.2 mol/h) were injected. At these flow rates, the introduction of propylene into the reactor caused circulation of the liquid reaction medium and of the catalyst in suspension.

In Example 1, a selectivity towards propylene oxide of 83% and a degree of conversion of the H_2O_2, after reaction for 500 hours, of 76% were obtained.

In Example 2, a selectivity towards propylene oxide of 90% and a degree of conversion of the H_2O_2, after reaction for 500 hours, of 79% were obtained.

(The selectivity towards propylene oxide is given by the molar ratio, expressed as a percentage, between the amount of propylene oxide obtained divided by the sum of all of the organic products formed).

Example 3

Propylene oxide was manufactured in a loop reactor similar to the one shown schematically in Fig-

ure 1, by reaction between propylene and 35% hydrogen peroxide in the presence of methanol and of 8.24 g of catalyst TS-1 bound to a honeycomb support.

The tests were carried out at a temperature of 35°C, with a continuous supply of hydrogen peroxide at a flow rate of 0.5 mol/h. The amount of methanol used was 16 mol/mol of H_2O_2. 120 l/h (s.t.p) of propylene and 140 l/h (s.t.p) of nitrogen were injected.

A selectivity towards propylene oxide of 89% and a degree of conversion of the H_2O_2, after reaction for 1 hour, of 60% were obtained.

Example 4

Propylene oxide was manufactured in a bubble-siphon reactor as shown schematically in Figure 1, by reaction between propylene and 40% hydrogen peroxide in the presence of methanol and 5.25 g of catalyst TS-1, used in the form of beads 0.5 mm in diameter.

The tests were carried out at a temperature of 56°C, with a continuous supply of hydrogen peroxide at a flow rate of 0.57 mol/h. The flow rate of propylene is 250 l/h (s.t.p).

In a 1st test, the initial concentration of H_2O_2 in the reaction medium (i.e. in the absence of reaction) is set at 2 mol H_2O_2/kg of liquid phase, which, taking the stripping of the CH_3OH into account, corresponds to a CH_3OH/H_2O_2 ratio in the reaction medium in the absence of reaction equal to 13 mol/mol.

In a 2nd test, the initial concentration of H_2O_2 in the reaction medium (i.e. in the absence of reaction) was brought to 6.5 mol H_2O_2/kg of liquid phase, by simply reducing the flow rate of methanol used relative to the 1st test, from 759 to 375 ml/h. The CH_3OH/H_2O_2 ratio in the reaction medium, in the absence of reaction and taking the stripping of the CH_3OH into account, is close to 2.9 mol/mol under these conditions.

In a 3rd test, the flow rate of methanol used was reduced to 210 ml/h. Taking the stripping of the CH_3OH into account, the initial concentration of H_2O_2 thus goes to 11.4 mol H_2O_2/kg of liquid phase and the

CH_3OH/H_2O_2 ratio in the reaction medium, in the absence of reaction, goes to 1.3 mol/mol.

After testing for 6 h, the degrees of conversion of the H_2O_2 for the 1st, 2nd and 3rd tests are, respectively, 69, 73 and 70%, and the selectivities towards propylene oxide are, respectively, equal to 83, 85 and 89%.

CLAIMS

1. Continuous process for manufacturing an epoxide, according to which an olefin is reacted, in a reactor in the liquid phase, with a peroxide compound in the presence of a zeolite-based catalyst and in the presence of a solvent, and a gaseous compound is introduced continuously into the reactor at a flow rate which is sufficient to entrain some of the epoxide produced, which is recovered with the gaseous compound at the point at which it leaves the reactor.

2. Process according to Claim 1, in which the olefin is introduced into the reactor in gaseous form in a large excess, and in which the olefin acts as the gaseous compound.

3. Process according to Claim 1 or 2, in which the reactor is a loop reactor.

4. Process according to Claim 3, in which the flow rate of the gaseous compound is sufficient to circulate the liquid phase in the loop reactor.

5. Process according to any one of the preceding claims, in which the ratio of the flow rate of the gaseous compound to the flow rate of supply of the peroxide compound is greater than or equal to 5, preferably greater than or equal to 10.

6. Process according to any one of the preceding claims, in which the reactor is of the bubble-siphon loop type.

7. Process according to any one of the preceding claims, in which the pH of the liquid phase is maintained at from 4.8 to 6.5 by addition of a base to the liquid phase.

8. Process according to any one of the preceding claims, in which the peroxide compound is used in an amount of from 1 to 10 mol, preferably from 1.5 to 5 mol, per kg of liquid phase, and in which the peroxide compound is used in the form of an aqueous solution containing from 10 to 70% of peroxide compound, preferably from 20 to 50%.

9. Process according to any one of the preceding

claims, in which the temperature at which the olefin reacts with the peroxide compound in the presence of the catalyst and the solvent is from 0 to 150°C, generally from 0 to 70°C, preferably from 20 to 40°C.

10. Process according to any one of the preceding claims, in which the zeolite is titanium silicalite, preferably of TS-1 type having a crystalline structure of ZSM-5 type.

11. Process according to any one of the preceding claims, in which the epoxide is 1,2-epoxypropane, the olefin is propylene, the peroxide compound is hydrogen peroxide, the solvent is methanol and the gaseous compound is propylene.