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(54) Abstract Title: **Reaction of epoxidation product with water, alcohol, carbon dioxide or amine to form corresponding 1,2-diol, 1,2-diol ether, 1,2-carbonate or alcohol amine**

(57) An olefin oxide is reacted, in one or more process microchannels (210, in a section 340) of a microchannel reactor, with water, an alcohol, carbon dioxide or an amine to form the corresponding 1,2-diol, 1,2-diol ether, 1,2-carbonate or an alcohol amine, optionally in the presence of an catalyst.

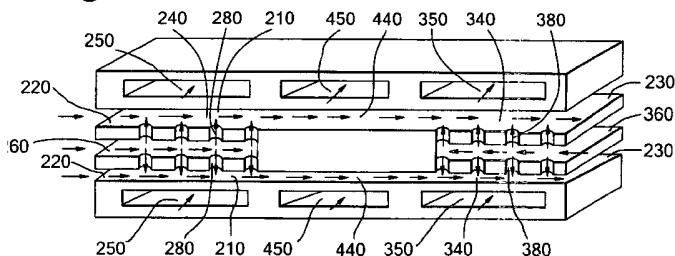
The olefin oxide is optionally obtained by reacting a feed comprising an olefin and oxygen in the presence of an epoxidation catalyst contained in one or more process microchannels in a section (240) upstream of the previous reaction section (340) within the microchannel reactor. The reaction mixture may optionally be quenched by reducing the temperature (preferably to no more than 200 °C) using a heat exchange fluid (in channels 450, in intermediate section 440) downstream of the epoxidation catalyst.

A microchannel reactor suitable for such a process comprises:

one or more process microchannels (210), each comprising:
an upstream end (220);
a downstream end (230);
a first section (240) which is adapted:
to contain an epoxidation catalyst,
to receive a feed comprising an olefin and oxygen,
and to allow conversion of at least a portion of the feed into an olefin
oxide; and
a second section (340)
positioned downstream of the first section and
adapted to receive the olefin, and water, an alcohol, carbon dioxide or
an amine,
and to allow conversion of the olefin oxide.

The reactor may also comprise one or more heat exchange channels (250) to exchange heat with the first section, one or more heat exchange channels (350) to exchange heat with the second section, and one or more heat exchange channels (450) to exchange heat with an intermediate section (440).

Fig.2



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Fig.2

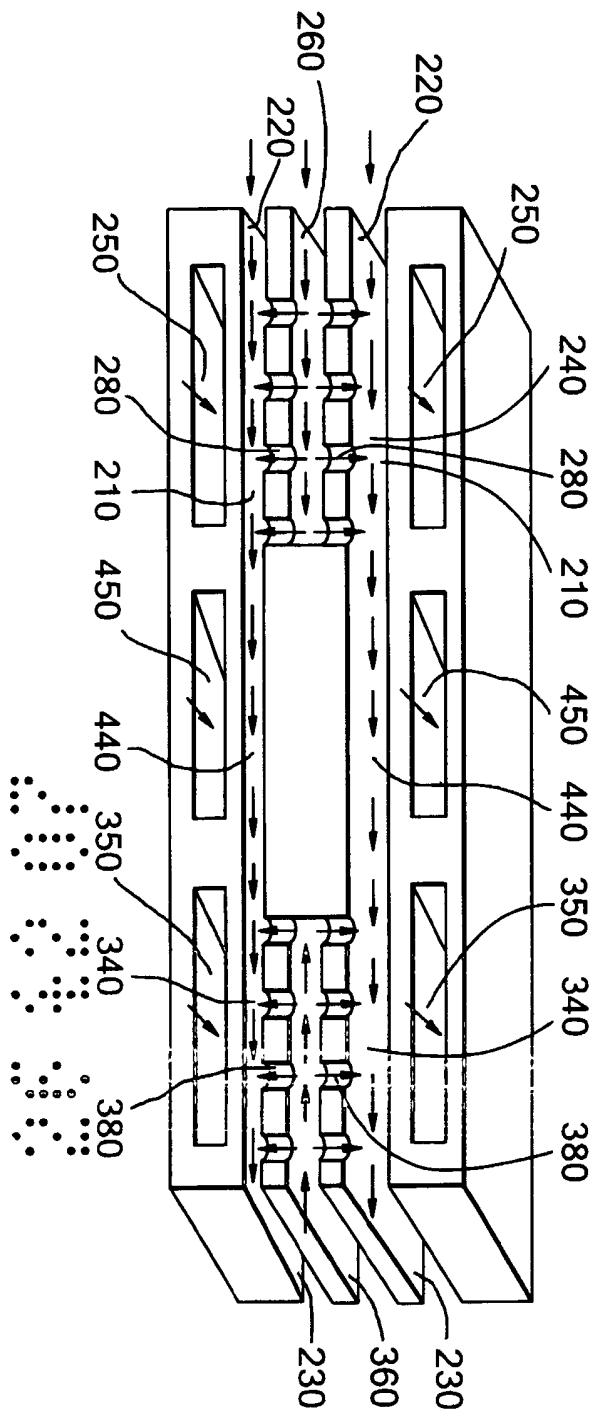
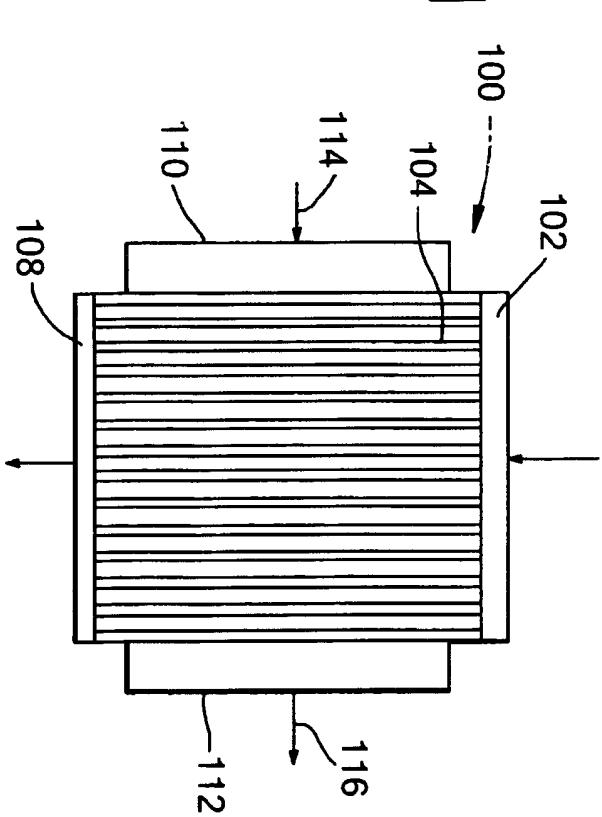


Fig.1



A PROCESS FOR THE PREPARATION OF A CHEMICAL DERIVABLE FROM
AN OLEFIN OXIDE, AND A REACTOR SUITABLE FOR SUCH A PROCESS

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Field of the Invention

The invention relates to a process for the preparation of a chemical derivable from an olefin oxide. In particular, such a chemical may be a 1,2-diol, a 1,2-diol ether, a 1,2-carbonate or an alkanol amine. The invention also relates to a reactor which is suitable for use in such a process.

10 Background of the Invention

Ethylene oxide and other olefin oxides are important industrial chemicals used as a feedstock for making such chemicals as ethylene glycol, propylene glycol, ethylene glycol ethers, ethylene carbonate, ethanol amines and detergents. One 15 method for manufacturing an olefin oxide is by olefin epoxidation, that is the catalyzed partial oxidation of the olefin with oxygen yielding the olefin oxide. The olefin oxide so manufactured may be reacted with water, an alcohol, carbon dioxide, or an amine to produce a 1,2-diol, a 1,2-diol ether, a 1,2-carbonate or an alkanol amine. Such production of a 1,2-diol, a 1,2-diol ether, a 1,2-carbonate or an alkanol 20 amine is generally carried out separately from the manufacture of the olefin oxide, in any case the two processes are normally carried out in separate reactors.

In olefin epoxidation, a feed containing the olefin and oxygen is passed over a bed of catalyst contained within a reaction zone that is maintained at certain reaction conditions. A commercial epoxidation reactor is generally in the form of a shell-and-25 tube heat exchanger, in which a plurality of substantially parallel elongated, relatively narrow tubes are filled with shaped catalyst particles to form a packed bed, and in which the shell contains a coolant. Irrespective of the type of epoxidation catalyst used, in commercial operation the internal tube diameter is frequently in the range of from 20 to 40 mm, and the number of tubes per reactor may range in the thousands, 30 for example up to 12,000.

Olefin epoxidation is generally carried out with a relatively low olefin conversion and oxygen conversion. Recycle of unconverted olefin and oxygen is normally applied in order to enhance the economics of the process. Generally the feed additionally comprises a large quantity of so-called ballast gas to facilitate 35 operation outside the explosion limits. Ballast gas includes saturated hydrocarbons, in

particular methane and ethane. As a consequence, recycling generally involves the handling of large quantities of process streams, which includes the unconverted olefin, unconverted oxygen and the ballast gas. The processing of the recycle stream as normally applied in an olefin epoxidation plant is also fairly complex, as it involves 5 olefin oxide recovery, carbon dioxide removal, water removal and re-pressurizing. The use of ballast gas not only contributes to the cost of processing, it also reduces the epoxidation reaction rate.

The epoxidation catalyst generally contains the catalytically active species, typically a Group 11 metal (in particular silver) and promoter components, on a 10 shaped carrier material. Shaped carrier materials are generally carefully selected to meet requirements of, for example, strength and resistance against abrasion, surface area and porosity. The shaped carrier materials are generally manufactured by sintering selected inorganic materials to the extent that they have the desired properties.

15 During the epoxidation, the catalyst is subject to a performance decline, which represents itself by a loss in activity of the catalyst and selectivity in the formation the desired olefin oxide. In response to the loss of activity, the epoxidation reaction temperature may be increased such that the production rate of the olefin oxide is maintained. The operation of commercial reactors is normally limited with respect to 20 the reaction temperature and when the applicable temperature limit has been reached, the production of the olefin oxide has to be interrupted for an exchange of the existing charge of epoxidation catalyst for a fresh charge.

It would be of great value if improved epoxidation processes and improved epoxidation reactors would become available.

25 Summary of the Invention

The present invention provides such improved epoxidation processes and improved epoxidation reactors. Embodiments of the present invention make use of a reactor which comprises a plurality of microchannels ("process microchannels" hereinafter). The process microchannels may be adapted such that the epoxidation 30 and optionally other processes can take place in the microchannels and that they are in a heat exchange relation with channels adapted to contain a heat exchange fluid ("heat exchange channels" hereinafter). A reactor comprising process microchannels is referred to herein by using the term "microchannel reactor". As used herein, the term "Group 11" refers to Group 11 of the Periodic Table of the Elements.

In an embodiment, the invention provides a process for the preparation of a 1,2-diol, a 1,2-diol ether, a 1,2-carbonate or an alkanol amine, which process comprises

- reacting a feed comprising an olefin and oxygen in the presence of an epoxidation catalyst contained in a first section of one or more process microchannels of a
- 5 microchannel reactor to form an olefin oxide, and
- converting the olefin oxide with water, an alcohol, carbon dioxide or an amine to form the 1,2-diol, 1,2-diol ether, 1,2-carbonate or alkanol amine in a second section of the one or more process microchannels positioned downstream of the first section.

In another embodiment, the invention provides a process for the preparation of a 10 1,2-diol, a 1,2-diol ether, a 1,2-carbonate or an alkanol amine, which process comprises reacting in one or more process microchannels of a microchannel reactor an olefin oxide with water, an alcohol, carbon dioxide or an amine to form the 1,2-diol, 1,2-diol ether, 1,2-carbonate or alkanol amine.

In another embodiment, the invention provides a reactor suitable for the 15 preparation of a 1,2-diol, a 1,2-diol ether, a 1,2-carbonate or an alkanol amine, which reactor is a microchannel reactor comprising one or more process microchannels comprising

- an upstream end,
- a downstream end,
- 20 - a first section which is adapted to contain an epoxidation catalyst, to receive a feed comprising an olefin and oxygen, and to cause conversion of at least a portion of the feed to form an olefin oxide in the presence of the epoxidation catalyst, and
- a second section positioned downstream of the first section which is adapted to receive the olefin oxide; to receive water, an alcohol, carbon dioxide or an amine; and to cause 25 conversion of the olefin oxide to form the 1,2-diol, 1,2-diol ether, 1,2-carbonate or alkanol amine.

Description of the Drawings

FIG. 1 shows a schematic of a microchannel reactor and its main constituents.

FIG. 2 shows a schematic of a typical example of a repeating unit which 30 comprises process microchannels and heat exchange channels and its operation when in use in the practice of the invention. A microchannel reactor of this invention may comprise a plurality of such repeating units.

Detailed Description of the Invention

The use of a microchannel reactor in accordance with this invention leads to one or more of the following advantages:

- the epoxidation catalyst does not necessarily involve the use a shaped carrier, which can 5 eliminate the need for a step for producing a shaped carrier.
- quenching of the olefin oxide inside the process microchannel enables operation under conditions which may be within explosion limits when such conditions would be applied in a conventional shell-and-tube heat exchanger reactor. Such conditions may be achieved by contacting an oxygen rich feed component with an olefin rich feed 10 component within the process microchannels, which oxygen rich feed component and olefin rich feed component are normally outside the explosion limits. Quenching inside the process microchannels also decreases the formation of byproducts, such as aldehydes and carboxylic acids.
- the epoxidation within the process microchannels can advantageously be carried out at 15 conditions of high total concentration of the olefin, oxygen and the olefin oxide, which can lead to a higher epoxidation rate and/or lower epoxidation reaction temperature. Lowering the epoxidation reaction temperature can lead to improved selectivity and improved catalyst life. Employing conditions of high total concentration of the olefin, oxygen and the olefin oxide can also eliminate the need of using a ballast gas, which 20 provides more efficient processing and reduction of the costs of recycling.
- the epoxidation carried out in process microchannels may be operated at a high conversion level of oxygen or the olefin oxide. In particular when the process is carried out at a high olefin conversion level, it is advantageous to operate the epoxidation process in once-through operation, which implies that no recycle stream is applied. In addition, it 25 is advantageous that in such case air may be fed to the process microchannels, instead of oxygen separated from air, which can eliminate the need for an air separation unit.
- carrying out the olefin epoxidation inside the process microchannels enables conversion of the formed olefin oxide inside the same process microchannels to 1,2-diol, 1,2-diol ether, 1,2-carbonate or alkanol amine. This can eliminate the need for additional reactors 30 for such further conversion. It can also eliminate the need for an olefin oxide recovering unit and/or a carbon dioxide removal unit, and it can reduce the need for heat exchanging equipment. Hence, it can reduce the complexity of the additional processing conventionally applied in a manufacturing plant, for example for product recovery. Conversion of the olefin oxide inside the process microchannels also decreases the

formation of byproducts, such as aldehydes and carboxylic acids.

- carrying out the conversion of an olefin oxide into a 1,2-diol, a 1,2-diol ether, a 1,2-carbonate or an alkanol amine inside the process microchannels of a microchannel reactor has the advantageous effect that there is no need to have the reactants present in the

5 reactor in a relatively high dilution. When such reactions are carried out in conventional equipment, a relatively high degree of dilution is frequently applied, for example by having a relatively large excess of, for example, water, alcohol or amine present as diluent. The relatively large amount of diluent, added to the reaction mixture as a relatively cold component, acts as a heat sink. Acting as a heat sink means preventing a

10 large increase of the temperature by having the capability to absorb the heat of reaction. The use of a relatively large amount of diluent is a disadvantage, in that it increases the reaction times and/or reactor volumes and it creates relatively large recycle streams, which all influence the process economics in a unfavorable manner. By the application of a microchannel reactor, a high degree of dilution may be avoided. However, in the

15 presence of less diluent, in particular less excess of water, alcohol or amine, the selectivity to the desired product will become less.

Microchannel reactors suitable for use in this invention and their operation have been described in WO-A-2004/099113, WO-A-01/12312, WO-01/54812, US-A-6440895, US-A-6284217, US-A-6451864, US-A-6491880, US-A-6666909, US-6811829, US-A-6851171, US-A-6494614, US-A-6228434 and US-A-6192596, which are incorporated herein by reference. Methods by which the microchannel reactor may be manufactured, loaded with catalyst and operated, as described in these references, may generally be applicable in the practice of the present invention.

With reference to FIG. 1, microchannel reactor 100 may be comprised of a process header 102, a plurality of process microchannels 104, and a process footer 108. The process header 102 provides a passageway for fluid to flow into the process microchannels 104. The process footer 108 provides a passageway for fluid to flow from the process microchannels 104.

The number of process microchannels contained in a microchannel reactor may be very large. For example, the number may be up to 10^5 , or even up to 10^6 or up to 2×10^6 . Normally, the number of process microchannels may be at least 10 or at least 100, or even at least 1000.

The process microchannels are typically arranged in parallel, for example they may form an array of planar microchannels. The process microchannels may have at

least one internal dimension of height or width of up to 15 mm, for example from 0.05 to 10 mm, in particular from 0.1 to 5 mm, more in particular from 0.5 to 2 mm. The other internal dimension of height or width may be, for example, from 0.1 to 100 cm, in particular from 0.2 to 75 cm, more in particular from 0.3 to 50 cm. The length of

5 the process microchannels may be, for example, from 1 to 500 cm, in particular from 2 to 300 cm, more in particular from 3 to 200 cm, or from 5 to 100 cm.

The microchannel reactor 100 additionally comprises heat exchange channels (not shown in FIG. 1) which are in heat exchange contact with the process microchannels 104. The heat exchange channels may also be microchannels. The

10 microchannel reactor is adapted such that heat exchange fluid can flow from heat exchange header 110 through the heat exchange channels to heat exchange footer 112. The heat exchange channels may be aligned to provide a flow in a co-current, counter-current or, preferably, cross-current direction, relative to a flow in the process microchannels 104. The cross-current direction is as indicated by arrows 114 and

15 116.

The heat exchange channels may have at least one internal dimension of height or width of up to 15 mm, for example from 0.05 to 10 mm, in particular from 0.1 to 5 mm, more in particular from 0.5 to 2 mm. The other internal dimension of height or width may be, for example, from 0.1 to 100 cm, in particular from 0.2 to

20 75 cm, more in particular from 0.3 to 50 cm. The length of the heat exchange channels may be, for example, from 1 to 500 cm, in particular from 2 to 300 cm, more in particular from 3 to 200 cm, or from 5 to 100 cm.

The separation between a process microchannel 104 and the next adjacent heat exchange channel may be in the range of from 0.05 mm to 5 mm, in particular from

25 0.2 to 2 mm.

In some embodiments of this invention, there is provided for first heat exchange channels and second heat exchange channels, or first heat exchange channels, second heat exchange channels and third heat exchange channels, or even up to fifth heat exchange channels, or even further heat exchange channels. Thus, in

30 such cases, there is a plurality of sets of heat exchange channels, and accordingly there may be a plurality of heat exchange headers 110 and heat exchange footers 112, whereby the sets of heat exchange channels may be adapted to receive heat exchange fluid from a heat exchange header 110 and to deliver heat exchange fluid into a heat exchange footer 112.

The process header 102, process footer 108, heat exchange header 110, heat exchange footer 112, process microchannels 104 and heat exchange channels may independently be made of any construction material which provides sufficient strength, dimensional stability and heat transfer characteristics to permit operation of the processes in accordance with this invention. Suitable construction materials include, for example, steel (for example stainless steel and carbon steel), monel, titanium, copper, glass and polymer compositions. The kind of heat exchange fluid is not material to the present invention and the heat exchange fluid may be selected from a large variety. Suitable heat exchange fluids include steam, water, air and oils. In embodiments of the invention which include a plurality of sets of heat exchange channels, such sets of heat exchange channels may operate with different heat exchange fluids or with heat exchange fluids having different temperatures.

A microchannel reactor according to the invention may comprise a plurality of repeating units comprising one or more process microchannels and one or more heat exchange channels. Reference is now made to FIG. 2, which shows a typical repeating unit and its operation.

Process microchannels 210 have an upstream end 220 and a downstream end 230 and may comprise of a first section 240 which may contain a catalyst (not drawn), for example an epoxidation catalyst. First section 240 may be in heat exchange contact with first heat exchange channel 250, allowing heat exchange between first section 240 of process microchannel 210 and first heat exchange channel 250. The repeating unit may comprise first feed channel 260 which ends into first section 240 through one or more first orifices 280. Typically one or more first orifices 280 may be positioned downstream relative to another first orifice 280. During operation, feed comprising the olefin and oxygen may enter into first section 240 of process microchannel 210 through an opening in upstream end 220 and/or through first feed channel 260 and one or more first orifices 280.

Process microchannels 210 may comprise a second section 340 which may or may not be adapted to contain a catalyst, in particular a catalyst which is suitable for the conversion of olefin oxide to 1,2-diol, 1,2-diol ether, 1,2-carbonate or alkanol amine. Second section 340 may or may not contain a catalyst, as described herein. Second section 340 is positioned downstream of first section 240. Second section 340 may be in heat exchange contact with second heat exchange channel 350, allowing heat exchange between second section 340 of process microchannel 210 and second

heat exchange channel 350. The repeating unit may comprise second feed channel 360 which ends into second section 340 through one or more second orifices 380. During operation, feed may enter into second section 340 from upstream in process microchannel 210 and through second feed channel 360 and one or more second orifices 380. Typically one or more second orifices 380 may be positioned downstream relative to another second orifice 380. Second section 340 is adapted for accommodating conversion of olefin oxide to 1,2-diol, 1,2-diol ether, 1,2-carbonate or alkanol amine. Feed entering during operation through second feed channel 360 and one or more second orifices 380 may comprise water, the alcohol, carbon dioxide or the amine. Also, catalyst may be fed through second feed channel 360 and one or more second orifices 380. If desirable, a separate set of second feed channel (not drawn) with one or more second orifices (not drawn) may be present in order to accommodate separate feeding of feed and catalyst.

The first and second feed channels 260 or 360 in combination with first and second orifices 280 or 380, whereby one or more first or second orifices 280 or 380 are positioned downstream to another first or second orifice 280 or 380, respectively, allow for replenishment of a reactant. Replenishment of a reactant is a feature in some embodiments of this invention.

Process microchannels 210 may comprise an intermediate section 440, which is positioned downstream of first section 240 and upstream of second section 340. Intermediate section 440 may be in heat exchange contact with third heat exchange channel 450, allowing heat exchange between intermediate section 440 of process microchannel 210 and third heat exchange channel 450. In some embodiments intermediate section 440 is adapted to quench olefin oxide obtained in and received from first section 240 by heat exchange with a heat exchange fluid in third heat exchange channel 450. Quenching may be achieved in stages by the presence of a plurality of third heat exchange channels 450, for example two or three or four. Such a plurality of third heat exchange channels 450 may be adapted to contain heat exchange fluids having different temperatures, in particular such that in downstream direction of intermediate section 440 heat exchange takes place with a third heat exchange channel 450 containing a heat exchange fluid having a lower temperature.

The feed channels may be microchannels. They may have at least one internal dimension of height or width of up to 15 mm, for example from 0.05 to 10 mm, in particular from 0.1 to 5 mm, more in particular from 0.5 to 2 mm. The other internal

dimension of height or width may be, for example, from 0.1 to 100 cm, in particular from 0.2 to 75 cm, more in particular from 0.3 to 50 cm. The length of the feed channels may be, for example, from 1 to 250 cm, in particular from 2 to 150 cm, and more particularly from 3 to 100 cm, or from 5 to 50 cm.

5 The length of the sections of the process microchannels may be selected independently of each other, in accordance with, for example, the heat exchange capacity needed or the quantity of catalyst which may be contained in the section. The lengths of the sections are preferably at least 1 cm, or at least 2 cm, or at least 5 cm. The lengths of the sections are preferably at most 250 cm, or at most 150 cm, 10 or at most 100 cm, or at most 50 cm. Other dimensions of the sections are dictated by the corresponding dimensions of process microchannel 210.

The microchannel reactor of this invention may be manufactured using known techniques, for example conventional machining, laser cutting, molding, stamping and etching and combinations thereof. The microchannel reactor of this invention may be 15 manufactured by forming sheets with features removed which allow passages. A stack of such sheets may be assembled to form an integrated device, by using known techniques, for example diffusion bonding, laser welding, cold welding, diffusion brazing, and combinations thereof. The microchannel reactor of this invention comprises appropriate headers, footers, valves, conduit lines, and other features to 20 control input of reactants, output of product, and flow of heat exchange fluids. These are not shown in the drawings, but they can be readily provided by those skilled in the art. Also, there may be further heat exchange equipment (not shown in the drawings) for temperature control of feed, in particular for heating feed or feed components, before it enters the process microchannels, or for temperature control of product, in 25 particular for quenching product, after it has left the process microchannels. Such further heat exchange equipment may be integral with the microchannel reactor, but more typically it will be separate equipment. These are not shown in the drawings, but they can be readily provided by those skilled in the art. Heat integration may be applied, for example by using reaction heat of the epoxidation process for heating 30 feed components, or for other heating purposes.

Typically, the epoxidation catalysts are solid catalysts under the conditions of the epoxidation reaction. Such epoxidation catalyst, and any other solid catalysts as appropriate, may be installed by any known technique in the designated section of the process microchannels. The catalysts may form a packed bed in the designated

section of the process microchannel and/or they may form a coating on at least a portion of the wall of the designated section of the process microchannels. The skilled person will understand that the coating will be positioned on the interior wall of the process microchannels. Alternatively or additionally, one or more of the

5 catalysts may be in the form of a coating on inserts which may be placed in the designated section of the process microchannels. Coatings may be prepared by any deposition method, such as wash coating or vapor deposition. In some embodiments, the epoxidation catalyst may not be a solid catalyst under the conditions of the epoxidation, in which case the epoxidation catalyst may be fed to the designated

10 section of the process microchannels together with one or more components of the epoxidation feed and may pass through the process microchannels along with the epoxidation reaction mixture.

The epoxidation catalyst which may be used in this invention is typically a catalyst which comprises one or more Group 11 metals. The Group 11 metals may be selected from the group consisting of silver and gold. Preferably, the Group 11 metal comprises silver. In particular, the Group 11 metal comprises silver in a quantity of at least 90 %w, more in particular at least 95 %w, for example at least 99 %w, or at least 99.5 %w, calculated as the weight of silver metal relative to the total weight of the Group 11 metal, as metal. Typically, the epoxidation catalyst additionally comprises one or more promoter components. More typically, the epoxidation catalyst comprises the Group 11 metal, one or more promoter components and additionally one or more components comprising one or more further elements. In some embodiments, the epoxidation catalyst may comprise a carrier material on which the Group 11 metal, any promoter components and any components comprising one or more further elements may be deposited. Suitable promoter components and suitable components comprising one or more further elements and suitable carrier materials may be as described hereinafter.

In an embodiment, a method of installing an epoxidation catalyst in one or more process microchannels of a microchannel reactor comprises introducing into the one or more process microchannels a dispersion of the epoxidation catalyst dispersed in an essentially non-aqueous diluent, and removing the diluent.

The essentially non-aqueous diluent may be a liquid, or it may be in a gaseous form. As used herein, for liquid diluents, “essentially non-aqueous” means that the water content of the diluent is at most 20 %w, in particular at most 10 %w, more in particular at

most 5 %w, for example at most 2 %w, or even at most 1 %w, or at most 0.5 %w, relative to the weight of the diluent. In particular, for gaseous diluents, "essentially non-aqueous" means that the diluent as present in the process microchannels is above the dew point.

The substantial or complete absence of liquid water in the diluent enables the catalyst to

5 better maintain its integrity during installation, in terms of one or more of its morphology, composition and properties, than when an aqueous diluent is applied. Suitable essentially non-aqueous liquid diluents include organic diluents, for example hydrocarbons, halogenated hydrocarbons, alcohols; ketones, ethers, and esters. Suitable alcohols include, for example methanol and ethanol. The quantity of catalyst which may be

10 present in the liquid diluent may be in the range of from 1 to 50 %w, in particular from 2 to 30 %w, relative to the weight of the total of the catalyst and the liquid diluent.

Suitable essentially non-aqueous gaseous phase diluents include, for example, air, nitrogen, argon and carbon dioxide. The quantity of catalyst which may be present in the gaseous phase diluent may be in the range of from 10 to 500 g/l, in particular from 22 to

15 300 g/l, calculated as the weight of catalyst relative to the volume of the gaseous phase diluent.

The epoxidation catalyst present in the dispersion may be obtained by crushing a conventional, shaped catalyst and optionally followed by sieving. The particle size of the catalyst present in the dispersion is typically such that d_{50} is in the range of from 0.1 to

20 100 μm , in particular from 0.5 to 50 μm . As used herein, the average particle size, referred to herein as " d_{50} ", is as measured by a Horiba LA900 particle size analyzer and represents a particle diameter at which there are equal spherical equivalent volumes of particles larger and particles smaller than the stated average particle size. The method of measurement includes dispersing the particles by ultrasonic treatment, thus breaking up

25 secondary particles into primary particles. This sonification treatment is continued until no further change in the d_{50} value is noticed, which typically requires 5 minute sonification when using the Horiba LA900 particle size analyzer. Preferably, the epoxidation catalyst comprises particles having dimensions such that they pass a sieve with openings sized at at most 50 %, in particular at most 30 % of the smallest dimension

30 of the process microchannel.

Conventional, shaped epoxidation catalysts typically comprise Group 11 metal, one or more promoter components and optionally one or more components comprising a further element dispersed on a shaped carrier material. Suitable carrier materials, suitable

promoter components, suitable components comprising a further element and suitable catalyst compositions in respect of the quantities of Group 11 metal, promoter components and components comprising a further element may be as described hereinafter.

5 Alternatively, and preferably, the epoxidation catalyst present in the dispersion is prepared as described herein.

The dispersion of the catalyst may be introduced such that a packed catalyst bed is formed in the designated section of one or more of the process microchannels, or alternatively such that at least a portion of the walls of the said sections is covered with 10 the catalyst. In the former case, prior to introducing the dispersion of the catalyst, a support device, for example a sieve or a graded particulate material, may have been placed in the downstream portion of the designated section of the one or more of the process microchannels, to support the catalyst and to prevent it from moving further downstream. In the latter case, the catalyst may be deposited on the walls of the process 15 microchannels prior to or after assembling the process microchannels, or the catalyst may be present on inserts placed in the designated section of the process microchannels.

The total quantity of Group 11 metal present in the first section of the process microchannels is not material to the invention, and may be selected within wide ranges. Typically, the total quantity of Group 11 metal may be in the range of from 20 10 to 500 kg/m³, more typically from 50 to 400 kg/m³, in particular from 100 to 300 kg/m³ reactor volume, wherein reactor volume is the total volume defined by the cross sectional area and the total length of the portions of the process microchannels which is occupied by the epoxidation catalyst, by presence of a packed bed and/or by the presence of the epoxidation catalyst on the wall. For the avoidance of doubt, the 25 reactor volume so defined does not include portions of the process microchannel which do not comprise epoxidation catalyst. In embodiments of the invention wherein the feed comprises the olefin and oxygen in a total quantity of at least 50 mole-%, the total quantity of Group 11 metal may be in the range of from 5 to 250 kg/m³, more typically from 20 to 200 kg/m³, in particular from 50 to 150 kg/m³ 30 reactor volume, as defined hereinbefore.

In an embodiment, the invention provides a method of preparing a particulate epoxidation catalyst, which method comprises depositing Group 11 metal and one or more promoter components on a particulate carrier material having a pore size

distribution such that pores with diameters in the range of from 0.2 to 10 μm represent at least 70 % of the total pore volume.

The carrier materials for use in this invention may be natural or artificial inorganic materials and they may include refractory materials, silicon carbide, clays, 5 zeolites, charcoal and alkaline earth metal carbonates, for example calcium carbonate. Preferred are refractory materials, such as alumina, magnesia, zirconia and silica. The most preferred material is α -alumina. Typically, the carrier material comprises at least 85 %w, more typically at least 90 %w, in particular at least 95 %w α -alumina, frequently up to 99.9 %w α -alumina, relative to the weight of the carrier. Other 10 components of the α -alumina may comprise, for example, silica, alkali metal components, for example sodium and/or potassium components, and/or alkaline earth metal components, for example calcium and/or magnesium components.

The surface area of the carrier material may suitably be at least 0.1 m^2/g , preferably at least 0.3 m^2/g , more preferably at least 0.5 m^2/g , and in particular at least 15 0.6 m^2/g , relative to the weight of the carrier; and the surface area may suitably be at most 10 m^2/g , preferably at most 5 m^2/g , and in particular at most 3 m^2/g , relative to the weight of the carrier. "Surface area" as used herein is understood to relate to the surface area as determined by the B.E.T. (Brunauer, Emmett and Teller) method as described in Journal of the American Chemical Society 60 (1938) pp. 309-316. High 20 surface area carrier materials, in particular when they are an α -alumina optionally comprising in addition silica, alkali metal and/or alkaline earth metal components, provide improved performance and stability of operation.

The water absorption of the carrier material is typically in the range of from 0.2 to 0.8 g/g, preferably in the range of from 0.3 to 0.7 g/g. A higher water absorption may be 25 in favor in view of a more efficient deposition of Group 11 metal, promoter components and components comprising one or more elements. As used herein, water absorption is as measured in accordance with ASTM C20, and water absorption is expressed as the weight of the water that can be absorbed into the pores of the carrier, relative to the weight of the carrier.

30 The particulate carrier material may have a pore size distribution such that pores with diameters in the range of from 0.2 to 10 μm represent at least 70 % of the total pore volume. Such relatively narrow pore size distribution can contribute to one or more of the activity, selectivity and longevity of the catalyst. Longevity may be in respect of

5 maintaining the catalyst activity and/or maintaining the selectivity. As used herein, the pore size distribution and the pore volumes are as measured by mercury intrusion to a pressure of 3.0×10^8 Pa using a Micromeritics Autopore 9200 model (130° contact angle, mercury with a surface tension of 0.473 N/m, and correction for mercury compression applied).

10 Preferably, the pore size distribution is such that the pores with diameters in the range of from 0.2 to 10 μm represent more than 75 %, in particular more than 80 %, more preferably more than 85 %, most preferably more than 90 % of the total pore volume. Frequently, the pore size distribution is such that the pores with diameters in the range of from 0.2 to 10 μm represent less than 99.9 %, more frequently less than 99 % of the total pore volume.

15 Preferably, the pore size distribution is such that the pores with diameters in the range of from 0.3 to 10 μm represent more than 75 %, in particular more than 80 %, more preferably more than 85 %, most preferably more than 90 %, in particular up to 100 %, of the pore volume contained in the pores with diameters in the range of from 0.2 to 10 μm .

20 Typically, the pore size distribution is such that pores with diameters less than 0.2 μm represent less than 10 %, in particular less than 5 %, of the total pore volume. Frequently, the pores with diameters less than 0.2 μm represent more than 0.1 %, more frequently more than 0.5 % of the total pore volume.

25 Typically, the pore size distribution is such that pores with diameters greater than 10 μm represent less than 20 %, in particular less than 10 %, more in particular less than 5 %, of the total pore volume. Frequently, the pores with diameters greater than 10 μm represent more than 0.1 %, in particular more than 0.5 % of the total pore volume.

30 The epoxidation catalyst which comprises one or more Group 11 metals dispersed on a carrier material exhibits appreciable catalytic activity when the Group 11 metal content is at least 10 g/kg, relative to the weight of the catalyst. Preferably, the catalyst comprises Group 11 metal in a quantity of from 50 to 500 g/kg, more preferably from 100 to 400 g/kg.

The promoter component may comprise one or more elements selected from rhenium, tungsten, molybdenum, chromium, and mixtures thereof. Preferably the promoter component comprises, as one of its elements, rhenium.

The promoter component may typically be present in the epoxidation catalyst in a quantity of at least 0.05 mmole/kg, more typically at least 0.5 mmole/kg, and preferably at least 1 mmole/kg, calculated as the total quantity of the element (that is rhenium, tungsten, molybdenum and/or chromium) relative to the weight of Group 11 metal. The promoter component may be present in a quantity of at most 250 mmole/kg, preferably at most 50 mmole/kg, more preferably at most 25 mmole/kg, calculated as the total quantity of the element relative to the weight of Group 11 metal. The form in which the promoter component may be deposited is not material to the invention. For example, the promoter component may suitably be provided as an oxide or as an oxyanion, for example, as a rhenate, perrhenate, or tungstate, in salt or acid form.

When the epoxidation catalyst comprises a rhenium containing promoter component, rhenium may typically be present in a quantity of at least 0.5 mmole/kg, more typically at least 2.5 mmole/kg, and preferably at least 5 mmole/kg, in particular at least 7.5 mmole/kg, calculated as the quantity of the element relative to the weight of Group 11 metal. Rhenium is typically present in a quantity of at most 25 mmole/kg, preferably at most 15 mmole/kg, more preferably at most 10 mmole/kg, in particular at most 7.5 mmole/kg, on the same basis.

Further, when the epoxidation catalyst comprises a rhenium containing promoter component, the catalyst may preferably comprise a rhenium copromoter, as a further component deposited on the carrier. Suitably, the rhenium copromoter may be selected from components comprising an element selected from tungsten, chromium, molybdenum, sulfur, phosphorus, boron, and mixtures thereof. Preferably, the rhenium copromoter is selected from components comprising tungsten, chromium, molybdenum, sulfur, and mixtures thereof. It is particularly preferred that the rhenium copromoter comprises, as an element, tungsten.

The rhenium copromoter may typically be present in a total quantity of at least 0.05 mmole/kg, more typically at least 0.5 mmole/kg, and preferably at least 2.5 mmole/kg, calculated as the element (i.e. the total of tungsten, chromium, molybdenum, sulfur, phosphorus and/or boron), relative to the weight of Group 11 metal. The rhenium copromoter may be present in a total quantity of at most 200 mmole/kg, preferably at most 50 mmole/kg, more preferably at most 25 mmole/kg, on the same basis. The form in which the rhenium copromoter may be deposited is not material to the invention. For example, it may suitably be provided

as an oxide or as an oxyanion, for example, as a sulfate, borate or molybdate, in salt or acid form.

The epoxidation catalyst preferably comprises Group 11 metal, the promoter component, and a component comprising a further element. Eligible further elements 5 may be selected from the group of nitrogen, fluorine, alkali metals, alkaline earth metals, titanium, hafnium, zirconium, vanadium, thallium, thorium, tantalum, niobium, gallium and germanium and mixtures thereof. Preferably the alkali metals are selected from lithium, potassium, rubidium and cesium. Most preferably the alkali metal is lithium, potassium and/or cesium. Preferably the alkaline earth metals 10 are selected from calcium and barium. Typically, the further element is present in the epoxidation catalyst in a total quantity of from 0.05 to 2500 mmole/kg, more typically from 0.25 to 500 mmole/kg, calculated as the element on the weight of Group 11 metal. The further elements may be provided in any form. For example, salts of an alkali metal or an alkaline earth metal are suitable.

15 As used herein, the quantity of alkali metal present in the epoxidation catalyst is deemed to be the quantity insofar as it can be extracted from the epoxidation catalyst with de-ionized water at 100 °C. The extraction method involves extracting a 10-gram sample of the catalyst three times by heating it in 20 ml portions of de-ionized water for 5 minutes at 100 °C and determining in the combined extracts the 20 relevant metals by using a known method, for example atomic absorption spectroscopy.

As used herein, the quantity of alkaline earth metal present in the epoxidation catalyst is deemed to the quantity insofar as it can be extracted from the epoxidation catalyst with 10 %w nitric acid in de-ionized water at 100 °C. The extraction method 25 involves extracting a 10-gram sample of the catalyst by boiling it with a 100 ml portion of 10 %w nitric acid for 30 minutes (1 atm., i.e. 101.3 kPa) and determining in the combined extracts the relevant metals by using a known method, for example atomic absorption spectroscopy. Reference is made to US-A-5801259, which is incorporated herein by reference.

30 Methods for depositing Group 11 metal, the one or more promoter components and the one or more component comprising a further element on a carrier material are known in the art and such methods may be applied in the practice of this invention. Reference may be made to US-A-5380697, US-A-5739075, EP-A-266015, and US-B-6368998, which are incorporated herein by reference. Suitably, the

methods include impregnating the particulate carrier materials with a liquid mixture comprising cationic Group 11 metal-amine complex and a reducing agent.

The invention relates to processes for the epoxidation of an olefin comprising reacting a feed comprising the olefin and oxygen in the presence an epoxidation catalyst, as described hereinbefore, contained in one or more process microchannels of a microchannel reactor.

The olefin for use in the present invention may be an aromatic olefin, for example styrene, or a di-olefin, whether conjugated or not, for example 1,9-decadiene or 1,3-butadiene. A mixture of olefins may be used. Typically, the olefin is a monoolefin, for example 2-butene or isobutene. Preferably, the olefin is a mono- α -olefin, for example 1-butene or propylene. The most preferred olefin is ethylene.

The feed for the epoxidation process of this invention comprises the olefin and oxygen. As used herein, the feed to a process is understood to represent the total of reactants and other components which is fed to the section of the process 15 microchannels in which the process in question takes place. Some of the feed components may be fed to the epoxidation process through an opening in upstream end 220 of process microchannels 210. Some of the feed components may be fed through first feed channel 260 and one or more first orifices 280. For example, an olefin rich feed component may be fed through the opening in the upstream end of the 20 process microchannels and an oxygen rich feed component may be fed through the first feed channel and the one or more first orifices. Alternatively, the oxygen rich feed component may be fed through the opening in the upstream end of the process microchannels and the olefin rich feed component may be fed through the first feed channel and the one or more first orifices. Certain feed components may be fed 25 through the opening in the upstream end of the process microchannels and through the first feed channel and the one or more first orifices. For example, the olefin may be fed partly through the opening in the upstream end of the process microchannels and partly through the first feed channel and the one or more first orifices. As another example, oxygen may be fed partly through the opening in the upstream end of the 30 process microchannels and partly through the first feed channel and the one or more first orifices.

In an embodiment, an oxygen rich feed component may be contacted within the process microchannels with an olefin rich feed component. The oxygen rich feed

component is typically relatively lean in the olefin. The oxygen rich feed component may comprise oxygen typically in a quantity of at least 5 mole-%, in particular at least 10 mole-%, more in particular at least 15 mole-%, relative to the total oxygen rich feed component, and typically in a quantity of at most 100 mole-%, or at most 5 99.9 mole-%, or at most 99.8 mole-%, relative to the total oxygen rich feed component. The oxygen rich feed component may comprise the olefin typically in a quantity of at most 5 mole-%, in particular at most 1 mole-%, relative to the total oxygen rich feed component. Such oxygen rich feed component may normally be outside the explosion limits. The olefin rich feed component is typically relatively 10 lean in oxygen. The olefin rich feed component may comprise the olefin typically in a quantity of at least 20 mole-%, in particular at least 25 mole-%, more in particular at least 30 mole-%, relative to the total olefin rich feed component, and typically in a quantity of at most 100 mole-%, or at most 99.99 mole-%, or at most 99.98 mole-%, relative to the total olefin rich feed component. The olefin rich feed component may 15 comprise oxygen typically in a quantity of at most 15 mole-%, in particular at most 10 mole-%, more in particular at most 5 mole-%, relative to the total olefin rich feed component. Such olefin rich feed component may normally be outside the explosion limits.

In the case that there is a plurality of first orifices 280, one or more first 20 orifices 280 positioned downstream of another first orifice 280, converted reactant may be substantially replenished. For example, replenishing converted oxygen may effect that the concentration of oxygen in the feed can be maintained substantially constant along the length of the epoxidation catalyst, which may favor substantially complete conversion of the olefin. Alternatively, the concentration of the olefin may 25 be kept substantially constant by replenishing converted olefin, which may favor substantially complete conversion of oxygen.

Further, in an aspect of the invention, by feeding the olefin rich feed component and the oxygen rich feed component through different channels and mixing the feed components in the process microchannels effects, feed compositions 30 can be accomplished within the process microchannels, while outside the process microchannels such feed compositions could lead to an explosion.

An organic halide may be present in the feed as a reaction modifier for increasing the selectivity, suppressing the undesirable oxidation of the olefin or the olefin oxide to carbon dioxide and water, relative to the desired formation of the

olefin oxide. The organic halide may be fed as a liquid or as a vapor. The organic halide may be fed separately or together with other feed components through an opening in upstream end 220 of the process microchannels 210 or through first feed channel 260 and one or more first orifices 280. An aspect of feeding the organic

5 halide through a plurality first orifices is that there may be an increase in the level of the quantity of the organic halide along the length of the epoxidation catalyst, by which the activity and/or selectivity of the epoxidation catalyst can be manipulated in accordance with the teachings of EP-A-352850, which is incorporated herein by reference. For example, when using a rhenium containing epoxidation catalyst, the

10 activity of the epoxidation catalyst can be enhanced along the length of the epoxidation catalyst. This could allow for better utilization of the epoxidation catalyst in regions where oxygen or the olefin is depleted relative to the regions where oxygen and the olefin are fed.

Organic halides are in particular organic bromides, and more in particular 15 organic chlorides. Preferred organic halides are chlorohydrocarbons or bromohydrocarbons. More preferably they are selected from the group of methyl chloride, ethyl chloride, ethylene dichloride, ethylene dibromide, vinyl chloride or a mixture thereof. Most preferred are ethyl chloride and ethylene dichloride.

In addition to an organic halide, an organic or inorganic nitrogen compound 20 may be employed as reaction modifier, but this is generally less preferred. It is considered that under the operating conditions of the epoxidation process the nitrogen containing reaction modifiers are precursors of nitrates or nitrites (cf. e.g. EP-A-3642 and US-A-4822900, which are incorporated herein by reference). Organic nitrogen compounds and inorganic nitrogen compounds may be employed. Suitable organic 25 nitrogen compounds are nitro compounds, nitroso compounds, amines, nitrates and nitrites, for example nitromethane, 1-nitropropane or 2-nitropropane. Suitable inorganic nitrogen compounds are, for example, nitrogen oxides, hydrazine, hydroxylamine or ammonia. Suitable nitrogen oxides are of the general formula NO_x wherein x is in the range of from 1 to 2, and include for example NO, N_2O_3 and N_2O_4 .

30 The organic halides and the organic or inorganic nitrogen compounds are generally effective as reaction modifier when used in low total concentration, for example up to 0.01 mole-%, relative to the total feed. It is preferred that the organic halide is present at a concentration of at most 50×10^{-4} mole-%, in particular at most

20×10^{-4} mole-%, more in particular at most 15×10^{-4} mole-%, relative to the total feed, and preferably at least 0.2×10^{-4} mole-%, in particular at least 0.5×10^{-4} mole-%, more in particular at least 1×10^{-4} mole-%, relative to the total feed.

In addition to the olefin, oxygen and the organic halide, the feed may

5 additionally comprise one or more further components, for example saturated hydrocarbons, as ballast gas, inert gases and carbon dioxide. The one or more further components may be fed separately or together with other feed components through an opening in upstream end 220 of the process microchannels 210 or through first feed channel 260 and one or more first orifices 280.

10 The olefin concentration in the feed may be selected within a wide range. Typically, the olefin concentration in the feed will be at most 80 mole-%, relative to the total feed. Preferably, it will be in the range of from 0.5 to 70 mole-%, in particular from 1 to 60 mole-%, on the same basis.

15 The oxygen concentration in the feed may be selected within a wide range. Typically, the concentration of oxygen applied will be within the range of from 1 to 15 mole-%, more typically from 2 to 12 mole-% of the total feed.

The saturated hydrocarbons comprise, for example, methane and ethane. Unless stated herein otherwise, saturated hydrocarbons may be present in a quantity of up to 80 mole-%, in particular up to 75 mole-%, relative to the total feed, and

20 frequently they are present in a quantity of at least 30 mole-%, more frequently at least 40 mole-%, on the same basis.

Carbon dioxide may be present in the feed as it is formed as a result of undesirable oxidation of the olefin and/or the olefin oxide, and it may accordingly be present in feed components present in a recycle stream. Carbon dioxide generally has

25 an adverse effect on the catalyst activity. Advantageously, the quantity of carbon dioxide is, for example, below 2 mole-%, preferably below 1 mole-%, or in the range of from 0.2 to 1 mole-%, relative to the total feed.

The inert gases include, for example nitrogen or argon. Unless stated herein otherwise, the inert gases may be present in the feed in a concentration of from 30 to

30 90 mole-%, typically from 40 to 80 mole-%.

The epoxidation process of this invention may be air-based or oxygen-based, see "Kirk-Othmer Encyclopedia of Chemical Technology", 3rd edition, Volume 9, 1980, pp. 445-447. In the air-based process air or air enriched with oxygen is

employed as the source of the oxidizing agent while in the oxygen-based processes high-purity (at least 95 mole-%) oxygen is employed as the source of the oxidizing agent. Presently most epoxidation plants are oxygen-based and this is preferred in the practice of certain embodiment of this invention. It is an advantage of other 5 embodiments of this invention that air may be fed to the process as the source of the oxidizing agent.

The epoxidation process may be carried out using reaction temperatures selected from a wide range. Preferably the reaction temperature is in the range of from 150 to 340 °C, more preferably in the range of from 180 to 325 °C. Typically, 10 the heat transfer liquid present in the first heat exchange channels may have a temperature which is typically 0.5 to 10 °C lower than the reaction temperature.

As disclosed herein before, during use, the epoxidation catalysts may be subject to a performance decline. In order to reduce effects of an activity decline, the reaction temperature may be increased gradually or in a plurality of steps, for example 15 in steps of from 0.1 to 20 °C, in particular 0.2 to 10 °C, more in particular 0.5 to 5 °C. The total increase in the reaction temperature may be in the range of from 10 to 140 °C, more typically from 20 to 100 °C. The reaction temperature may be increased typically from a level in the range of from 150 to 300 °C, more typically from 200 to 280 °C, when a fresh epoxidation catalyst or rejuvenated epoxidation 20 catalyst is used, to a level in the range of from 230 to 340 °C, more typically from 240 to 325°C, when the epoxidation catalyst has decreased in activity.

The epoxidation process is preferably carried out at a pressure, as measured at upstream 220 end of the process microchannels 210, in the range of from 1000 to 3500 kPa.

25 The olefin oxide leaving the section of the process microchannels containing the epoxidation catalyst is comprised in a reaction mixture which may further comprise unreacted olefin, unreacted oxygen, and other reaction products such as carbon dioxide. Typically, the content of olefin oxide in the reaction product is in general in the range of from 1 to 25 mole-%, more typically from 2 to 20 mole-%, in 30 particular from 2 to 5 mole-%.

In an embodiment, the epoxidation process comprises reacting a feed comprising the olefin and oxygen in a total quantity of at least 50 mole-%, relative to the total feed. In this embodiment, the olefin and oxygen may be present in the feed in a total quantity of

at least 80 mole-%, in particular at least 90 mole-%, more in particular at least 95 mole-%, relative to the total feed, and typically up to 99.5 mole-%, in particular up to 99 mole-%, relative to the total feed. The molar ratio of olefin to oxygen may be in the range of from 3 to 100, in particular from 4 to 50, more in particular from 5 to 20. The saturated 5 hydrocarbons and the inert gases may be substantially absent. As used herein, in this context “substantially absent” means that the quantity of saturated hydrocarbons in the feed is at most 10 mole-%, in particular at most 5 mole-%, more in particular at most 2 mole-%, relative to the total feed, and that the quantity of inert gases in the feed is at most 10 mole-%, in particular at most 5 mole-%, more in particular at most 2 mole-%, 10 relative to the total feed. In this particular embodiment, process conditions may be applied such that the quantity of olefin oxide in the epoxidation reaction mixture is in the range of from 4 to 15 mole-%, in particular from 5 to 12 mole-%, for example from 6 to 10 mole-%. Preferably, the epoxidation reaction mixture, including the olefin oxide, is quenched, as described herein.

15 In an embodiment, the epoxidation process comprises applying conditions for reacting the feed such that the conversion of the olefin or the conversion of oxygen is at least 90 mole-%. The conversion of the olefin may be at least 90 mole-% and the conversion of oxygen may be at least 90 mole-%. In particular, in this embodiment, the feed may comprise the olefin and oxygen in a quantity of at most 50 mole-%, relative to 20 the total feed, and the feed may additionally comprise saturated hydrocarbons, as ballast gas, and inert gas. Typically, process conditions are applied such that the conversion of the olefin or the conversion of oxygen is at least 95 mole-%, in particular at least 98 mole-%, more in particular at least 99 mole-%. As used herein, the conversion is the quantity of a reactant converted relative to the quantity of the reactant in the feed, expressed in 25 mole-%. Preferably, the conversion of the olefin is at least 95 mole-%, in particular at least 98 mole-%, more in particular at least 99 mole-% and oxygen may be at least partly replenished. The presence of an excess of oxygen in the feed, relative to the olefin, assists in achieving a high conversion of the olefin. For example, the molar ratio of oxygen over the olefin in the feed may be at least 1.01, typically at least 1.05, in particular at least 1.1, 30 more in particular at least 1.2; and for example at most 5, in particular at most 3, more in particular at most 2. In this embodiment, a relatively high selectivity in the conversion of the olefin into the olefin oxide is achieved. As used herein, the selectivity is the quantity of olefin oxide formed, relative to the quantity of olefin converted, expressed in mole-%. Moreover, such high conversion of the olefin enables that the process may be carried out

economically in a once-through mode, which means that no recycle of unconverted reactants is applied, and that air may be fed to the epoxidation process, which means effectively that the need of an air separation unit is eliminated.

In the practice of this invention, the reaction product, including the olefin oxide, may be quenched, typically, by heat exchange with a heat exchange fluid. The quenching may be conducted in first intermediate section 440 of process microchannels 210 by heat exchange with heat exchange fluid present in one or more third heat exchange channels 450. Typically, the temperature of the reaction product, including the olefin oxide, may be decreased to a temperature of at most 250 °C, more 5 typically at most 225 °C, preferably in the range of from 20 to 200 °C, more preferably 50 to 190 °C, in particular from 80 to 180 °C. The quenching may result in a reduction in temperature in the range of from 50 to 200 °C, in particular from 70 to 160 °C. 10 Quenching enables increasing the total quantity of the olefin oxide and oxygen in the feed of the epoxidation process, and eliminating the ballast gas or reducing the 15 quantity of ballast gas in the feed of the epoxidation process. Also, a result of quenching is that the olefin oxide produced is a cleaner product, comprising less aldehyde and carboxylic acid impurities.

A portion of the epoxidation reaction mixture, including the olefin oxide, may be partly withdrawn from the process microchannel and the microchannel reactor and 20 be processed in the conventional manner, using conventional methods and conventional equipment. However, this does not represent a preferred embodiment of the inventive process. In accordance with the invention, the process comprises converting the olefin oxide with water, an alcohol, carbon dioxide or an amine to form the 1,2-diol, 1,2-diol ether, 1,2-carbonate or alkanol amine in a second section of the one or 25 more process microchannels positioned downstream of the first section.

The conversion of the olefin oxide with water, an alcohol, carbon dioxide or an amine in the second section of the one or more process microchannels may be a thermal conversion, or a conversion which is catalyzed by using a suitable catalyst. Suitable catalysts are, for example, acid catalysts and basic catalysts. Acidic catalysts 30 are, for example, strongly acid ion exchange resins, such as, for example, those comprising sulfonic acid groups on a styrene/divinylbenzene copolymer matrix. Other suitable acid catalysts are, for example, silicas and oxides of metals selected from Groups 3-6 of the Periodic Table of the Elements, for example, zirconium oxide and titanium oxide. Basic catalysts are, for example, strong basic ion exchange resins

such as, for example, those comprising quaternary phosphonium or quaternary ammonium groups on a styrene/divinylbenzene copolymer matrix. Such catalysts are known in the art, for example from EP-A-156449, US-A-4982021, US-A-5488184, US-A-6153801 and US-A-6124508, which are incorporated herein by reference, 5 and/or they are commercially available. Suitable catalysts may represent themselves as a liquid under the conditions of the reaction, for example mineral acids, such as, for example, sulfuric acid and phosphoric acid, and such catalysts as known from JP-A-56-092228, which is incorporated herein by reference.

Suitable catalysts for the conversion of the olefin oxide with carbon dioxide 10 may be, for example, resins which comprise quaternary phosphonium halide groups or quaternary ammonium halide groups on a styrene/divinylbenzene copolymer matrix, wherein the halide may be in particular chloride or bromide. Such catalysts for this conversion are known from T. Nishikubo, A. Kameyama, J. Yamashita and M. Tomoi, *Journal of Polymer Science, Pt. A. Polymer Chemist*, 31, 939 - 947 (1993), 15 which is incorporated herein by reference. More suitable catalysts comprise a metal salt immobilized in a solid carrier, wherein the metal salt may comprise a cation of a metal selected from those in the third Period and Group 2, the fourth Period and Groups 2 and 4-12, the fifth Period and Groups 2, 4-7, 12 and 14, and the sixth Period and Groups 2 and 4-6, of the Periodic Table of the Elements, and wherein the carrier 20 contains a quaternary ammonium, quaternary phosphonium, quaternary arsenonium, quaternary stibonium or a quaternary sulfonium cation, which cation may be separated from the backbone of the carrier by a spacer group of the general formula -(CH₂-O-)_m-(CH₂)_n-, m and n being integers, with for example n being at most 10, for example 1, 2, 3 or 6, when m is 0, and n being from 1 to 8, for example 2 or 4, when 25 m is 1. The metal salt may be selected in particular from the halides, acetates, laureates, nitrates and sulfates of one or more selected from magnesium, calcium, zinc, cobalt, nickel, manganese, copper and tin, for example zinc bromide, zinc iodide, zinc acetate, or cobalt bromide. The solid carrier for immobilizing the metal salt may be, for example silica, a silica-alumina, or a zeolite, or it may be a resin with 30 a polystyrene/divinylbenzene copolymer backbone, or a silica-based polymeric backbone, such as in polysiloxanes, or a resin incorporating quaternized vinylpyridine monomers. Other suitable catalysts for the conversion of the olefin oxide with carbon dioxide are, for example, quaternary phosphonium halides, quaternary ammonium halides, and certain metal halides. An example is methyltributylphosphonium iodide.

More suitably, the catalysts comprise an organic base neutralized with a hydrogen halide, wherein the organic base has a pK_a greater than 8 and comprises a carbon-based compound containing one or more nitrogen and/or phosphorus atoms with at least one free electron pair. The hydrogen halide may be hydrogen bromide or

5 hydrogen iodide. Examples of such organic bases having a pK_a greater than 8 are 2-*tert*-butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorin, as such or on polystyrene, 1,1,3,3-tetramethylguanidine, and triethanolamine. In this context, the term "neutralized" means that the organic base and the hydrogen halide have reacted in amounts relative to each other such that an aqueous solution of the reaction

10 product would be essentially neutral, i.e. having a pH between 6 and 8.

Another suitable catalyst for the conversion of the olefin oxide with carbon dioxide comprises from 10 to 90 mole-%, based on the mixture, of an organic base and from 10 to 90 mole-%, based on the mixture, of the salt of the organic base and a hydrogen halide, wherein the organic base comprises a carbon-based compound

15 containing one or more nitrogen and/or phosphorus atoms with at least one free electron pair, and has a pK_a high enough that it is capable of binding carbon dioxide under the reaction conditions. The hydrogen halide may be hydrogen bromide or hydrogen iodide. Examples of such organic bases having capability of binding carbon dioxide are 2-*tert*-butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-

20 diazaphosphorin, as such or on polystyrene, 1,1,3,3-tetramethylguanidine, and triethanolamine. An exemplary catalyst may be based upon 1,1,3,3-tetramethylguanidine, hydrogen iodide and molybdenum trioxide in a mole ratio of about 6.6:4.71:1. When using these catalysts in the presence of water and carbon dioxide, the formed 1,2-carbonate may be at least partly converted in situ to the

25 corresponding 1,2-glycol.

The catalyst, when present as a solid material under the condition of the reaction, may be installed in the second section of the one or more process microchannels by known methods and applicable methods include, for example, filling at least a portion of the second section to form a packed bed, or covering at

30 least a portion of the walls of the second section with the catalyst, for example by wash coating. Some of the methods related to the installation of an epoxidation catalyst, as set out hereinbefore, may be applicable to these catalysts in an analogous manner. The use of a catalyst which is present as a solid material under the condition of the reaction is less preferred. In embodiments in which the catalyst represents

itself as a liquid under the conditions of the reaction, the catalyst may be fed to the second section of the one or more process microchannels through the second feed channel and the one or more second orifices, suitably together with feed comprising water, the alcohol, carbon dioxide and/or the amine. When the conversion is a

5 thermal conversion, the temperature may be in the range of from 100 to 300 °C, in particular from 150 to 250 °C. When the conversion is a catalytic conversion, the temperature may be in the range of from 30 to 200 °C, in particular from 50 to 150 °C. The molar ratio of the total of water, the alcohol, carbon dioxide and the amine to the olefin oxide may be more than 10, for example at most 20 or at most 30. However, as

10 described hereinbefore, it is a benefit of this invention that adequate control of the temperature can be achieved when the molar ratio of the total of water, the alcohol, carbon dioxide and the amine is kept relatively low, albeit that the selectivity to the desired product may become lower. The molar ratio of the total of water, the alcohol, carbon dioxide and the amine to the olefin oxide may be at most 10, in particular in

15 the range of from 1 to 8, more in particular from 1.1 to 6, for example from 1.2 to 4. The feed fed to the second section of the process microchannels may comprise a total quantity of the olefin oxide and water, the alcohol, carbon dioxide and the amine of at least 60 %w, in particular at least 80 %w, more in particular at least 90 %w, for example at least 95 %w, relative to the total weight of the said feed. The pressure

20 may be in the range of from 500 to 3500 kPa, as measured at the second feed channel, described hereinbefore. The reaction conditions may be selected such that the conversion of the olefin oxide is at least 50 mole-%, in particular at least 80 mole-%, more in particular at least 90 mole-%, for example at least 95 mole-%. Suitable alcohols for the conversion of the olefin oxide may be methanol, ethanol, propanol,

25 isopropanol, 1-butanol and 2-butanol. Methanol is a preferred alcohol. Mixtures of alcohols and mixtures of water and one or more alcohols may be used. Suitable amines for the conversion of the olefin oxide into alkanol amine may be ammonia or a primary amine or a secondary amine. Suitable primary amines are, for example. Suitable secondary amines are, for example, dimethylamine, diethylamine,

30 ethylmethylamine, methyl(1-propyl)amine, di(2-propyl)amine and di(1-butyl)amine. Mixtures of alcohols, mixtures of amines and mixtures of water and one or more alcohols or one or more amines may be used.

The temperature of the epoxidation reaction mixture, including the olefin oxide, may be controlled before the olefin oxide enters the second section of the one

or more process microchannels, so that the olefin oxide may adopt the desired temperature for the conversion to the 1,2-diol, the 1,2-diol ether, the 1,2-carbonate or the alkanol amine. Thus, the one or more process microchannels may comprise additionally an intermediate section downstream from the first section and upstream from the second section, which intermediate section is adapted to control the temperature of the olefin oxide. In particular, the reactor may comprise additionally one or more third heat exchange channels adapted to exchange heat with the intermediate section of the said process microchannels.

The 1,2-diols and 1,2 diol ethers, for example ethylene glycol, 1,2-propylene glycol and ethylene glycol ethers may be used in a large variety of industrial applications, for example in the fields of food, beverages, tobacco, cosmetics, thermoplastic polymers, curable resin systems, detergents, heat transfer systems, etc. The 1,2-carbonates, for example ethylene carbonate, may be used as a diluent, in particular as a solvent. Ethanol amines may be used, for example, in the treating (“sweetening”) of natural gas.

Unless specified otherwise, the organic compounds mentioned herein, for example the olefins, alcohols, 1,2-diols, 1,2-diol ethers, 1,2-carbonates, ethanol amines and organic halides, have typically at most 40 carbon atoms, more typically at most 20 carbon atoms, in particular at most 10 carbon atoms, more in particular at most 6 carbon atoms. Typically, the organic compounds have at least one carbon atom. As defined herein, ranges for numbers of carbon atoms (i.e. carbon number) include the numbers specified for the limits of the ranges.

The following example is intended to illustrate the advantages of the present invention and is not intended to unduly limit the scope of the invention.

25 Example

This prophetic example describes how an embodiment of this invention may be practiced.

A microchannel reactor will comprise process microchannels, first heat exchange microchannels, second heat exchange microchannels, third heat exchange channels, first feed channels and second feed channels. The process microchannels will comprise an upstream end, a first section, a first intermediate section, and a second section.

The first section will be adapted to exchange heat with a heat exchange fluid flowing in the first heat exchange microchannels. The third heat exchange

microchannels will comprise two sets of third heat exchange microchannels adapted to exchange heat with the first intermediate section, such that in the downstream portion of the first intermediate section a lower temperature will be achieved than in the upstream portion of the first intermediate section. A first feed microchannel will

5 end in the first section of the process microchannel through first orifices. The first orifices will be positioned at approximately equal distances into the downstream direction of the first section from the upstream end of the microchannel till two thirds of the length of the first section, and in the perpendicular direction the orifices will be positioned at approximately equal distances approximately across the entire width of

10 the process microchannel. Second orifices will be positioned in a similar manner relative to the second section, and will connect the second feed microchannels with the second section of the process microchannels. The second heat exchange microchannels will comprise one set of second heat exchange microchannels adapted to exchange heat with the second sections, such that in the second section a selected

15 temperature will be maintained.

The first section will comprise an epoxidation catalyst comprising silver, rhenium, tungsten, cesium and lithium deposited on a particulate carrier material, in accordance with the present invention. The particulate carrier material will be an α -alumina having a surface are of $1.5 \text{ m}^2/\text{g}$, a total pore volume of 0.4 ml/g , and a pore size distribution such that that pores with diameters in the range of from 0.2 to $10 \mu\text{m}$ represent 95% of the total pore volume, and that pores with diameters in the range of from 0.3 to $10 \mu\text{m}$ represent more than 92% , of the pore volume contained in the pores with diameters in the range of from 0.2 to $10 \mu\text{m}$.

The microchannel reactor will be assembled in accordance with methods known from WO-A-2004/099113, and references cited therein. The carrier material will be deposited on the walls of the first section of the process microchannels by wash coating. Thereafter, the process microchannels will be assembled, and after assembly silver, rhenium, tungsten, cesium and lithium will be deposited on the carrier material by using methods, which are known per se from US-A-5380697.

30 As an alternative, the microchannel reactor will be assembled, without prior wash coating, and after assembly the first section will be filled with a particulate epoxidation catalyst which will be prepared by milling and sieving a commercial HS-

PLUS epoxidation catalyst, which may be obtained from CRI Catalyst Company, Houston, Texas, USA.

In either alternative, the first section will be heated at 220 °C by heat exchange with the heat exchange fluid flowing in the first heat exchange microchannel, while

5 ethylene is fed through an opening positioned at the upstream end of the process microchannels. A mixture of oxygen and ethyl chloride (3 parts by million by volume) will be fed through the feed channels. The molar ratio of oxygen to ethylene will be 1:1. The mixture exiting the first section and entering the first intermediate section of the process microchannels will be quenched in the first intermediate section

10 in two steps, initially to a temperature of 150 °C and subsequently to a temperature of 80 °C. The temperature and the feed rate of the ethylene and oxygen will be adjusted such that the conversion of ethylene is 97 mole-%. Then, the quantity of ethyl chloride in the mixture of oxygen and ethyl chloride will be adjusted so as to optimize the selectivity to ethylene oxide.

15 The quenched mixture, comprising ethylene oxide, exiting the first intermediate section and entering the second section will react in the second section in the presence of a 1%-w aqueous solution of sulfuric acid, to convert ethylene oxide into ethylene glycol. The aqueous sulfuric acid solution will enter the second section through the second orifices. The molar ratio of water to ethylene oxide will be 3:1.

20 The temperature in the second section is maintained at 80 °C by heat exchange with a heat exchange fluid flowing in the second heat exchange microchannel.

The reaction product, including ethylene glycol, may be separated and purified.

C L A I M S

1. A process for the preparation of a 1,2-diol, a 1,2-diol ether, a 1,2-carbonate or an alkanol amine, which process comprises

- reacting a feed comprising an olefin and oxygen in the presence of an epoxidation catalyst contained in a first section of one or more process microchannels of a microchannel reactor to form an olefin oxide, and
- converting the olefin oxide with water, an alcohol, carbon dioxide or an amine to form the 1,2-diol, 1,2-diol ether, 1,2-carbonate or alkanol amine in a second section of the one or more process microchannels positioned downstream of the first section.

2. A process as claimed in claim 1, wherein the epoxidation catalyst comprises a Group 11 metal in a quantity of from 50 to 500 g/kg, relative to the weight of the catalyst.

3. A process as claimed in claim 1 or 2, wherein the epoxidation catalyst comprises silver deposited in a carrier material.

4. A process as claimed in claim 3, wherein the catalyst comprises, as promoter component(s), one or more elements selected from rhenium, tungsten, molybdenum, chromium, and mixtures thereof, and additionally one or more alkali metals selected from lithium, potassium, and cesium.

5. A process as claimed in claim 3 or 4, wherein the carrier material is an alumina having a surface area at least 0.3 m²/g and at most 10 m²/g, relative to the weight of the carrier and having a pore size distribution such that pores with diameters in the range of from 0.2 to 10 µm represent more than 80 % of the total pore volume.

6. A process as claimed in any of claims 1-5, wherein the feed comprises the olefin and oxygen in a total quantity of at least 50 mole-%, relative to the total feed.

7. A process as claimed in claim 6, wherein the feed comprises the olefin and oxygen in a total quantity of from 80 to 99.5 mole-%, relative to the total feed.

8. A process as claimed in any of claims 1-7, wherein the feed comprises saturated hydrocarbons in a quantity of at most 5 mole-%, relative to the total feed, and the feed comprises inert gases in a quantity of at most 5 mole-%, relative to the total feed.

9. A process as claimed in claim 8, wherein the quantity of saturated hydrocarbons is at most 2 mole-%, relative to the total feed, and the quantity of inert gases is at most 2 mole-%, relative to the total feed.
10. A process as claimed in any of claims 1-9, which process additionally comprises quenching the olefin oxide in an intermediate section, which is positioned downstream of first section and upstream of second section.
11. A process as claimed in claim 10, wherein quenching comprises decreasing the temperature of the first mixture to a temperature in the range of from 20 to 200 °C.
12. A process as claimed in claim 10 or 11, wherein the process comprises quenching by heat exchange with a heat exchange fluid.
13. A process as claimed in any of claims 10-12, wherein the process comprises quenching in more than one stage by heat exchange with a plurality of heat exchange fluids having different temperatures.
14. A process as claimed in any of claims 1-13, wherein the process comprises converting the olefin oxide with water, an alcohol, carbon dioxide or an amine applying a molar ratio of the total of water, the alcohol, carbon dioxide and the amine to the olefin oxide of at most 30.
15. A process as claimed in claim 14, wherein the molar ratio is at most 10.
16. A process as claimed in claim 15, wherein the molar ratio is in the range of from 1 to 8.
17. A process as claimed in claim 16, wherein the molar ratio is in the range of from 1.1 to 6.
18. A process as claimed in any of claims 1-17, wherein the process comprises catalytically converting the olefin oxide with water, an alcohol, carbon dioxide or an amine at a temperature in the range of from 30 to 200 °C, and at a pressure in the range of from 500 to 3500 kPa, as measured at the second feed channel.
19. A process as claimed in claim 18, wherein the temperature is in the range of from 50 to 150 °C.
20. A process as claimed in claim 18 or 19, wherein converting the olefin oxide with water, an alcohol, carbon dioxide or an amine comprises converting olefin oxide in the presence of a catalyst selected from
 - strongly acid or strongly basic ion exchange resins,
 - silicas and oxides of metals selected from Groups 3-6 of the Periodic Table of the Elements,

- mineral acids,
- resins which comprise quaternary phosphonium halide groups or quaternary ammonium halide groups on a styrene/divinylbenzene copolymer matrix;
- catalysts comprising a metal salt immobilized in a solid carrier, wherein the metal salt comprises a cation of a metal selected from those in the third Period and Group 2, the fourth Period and Groups 2 and 4-12, the fifth Period and Groups 2, 4-7, 12 and 14, and the sixth Period and Groups 2 and 4-6, of the Periodic Table of the Elements, and wherein the carrier contains a quaternary ammonium, quaternary phosphonium, quaternary arsenonium, quaternary stibonium or a quaternary sulfonium cation, which cation may or may not be separated from the backbone of the carrier by a spacer group of the general formula $-(CH_2-O-)_m-(CH_2)_n-$, m and n being integers, with n being at most 10, when m is 0, and n being from 1 to 8, when m is 1;
- quaternary phosphonium halides, quaternary ammonium halides, and metal halides;
- catalysts comprising an organic base neutralized with a hydrogen halide, wherein the organic base has a pK_a greater than 8 and comprises a carbon-based compound containing one or more nitrogen and/or phosphorus atoms with at least one free electron pair; and
- catalysts comprising from 10 to 90 mole-%, based on the mixture, of an organic base and from 10 to 90 mole-%, based on the mixture, of the salt of the organic base and a hydrogen halide, wherein the organic base comprises a carbon-based compound containing one or more nitrogen and/or phosphorus atoms with at least one free electron pair, and has a pK_a high enough that it is capable of binding carbon dioxide under the reaction conditions.

21. A process as claimed in claim 20, wherein

- the strongly acid ion exchange resin comprises sulfonic acid groups on a styrene/divinylbenzene copolymer matrix, or
- the mineral acid is selected from sulfuric acid and phosphoric acid, or
- the oxide of a metal selected from Groups 3-6 of the Periodic Table of the Elements is zirconium oxide or titanium oxide, or
- the metal salt is a metal salt selected from halides, acetates, laureates, nitrates and sulfates of one or more selected from magnesium, calcium, zinc, cobalt, nickel, manganese, copper and tin, or
- the solid carrier for immobilizing the metal salt is selected from a silica-alumina, a zeolite, a resin with a polystyrene/divinylbenzene copolymer backbone, a silica-based polymeric backbone, and a resin incorporating quaternized vinylpyridine monomers; or

- the catalyst is methyltributylphosphonium iodide; or
- the organic base is selected from 2-*tert*-butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorin, as such or on polystyrene, 1,1,3,3-tetramethylguanidine, and triethanolamine.

22. A process as claimed in any of claims 1-21, wherein the alcohol is selected from methanol, ethanol, propanol, isopropanol, 1-butanol and 2-butanol; or the amine is selected from ammonia, methylamine, ethylamine, 1-propylamine, 2-propylamine, 1-butylamine, dimethylamine, diethylamine, ethylmethylamine, methyl(1-propyl)amine, di(2-propyl)amine and di(1-butyl)amine.

23. A process for the preparation of a 1,2-diol, a 1,2-diol ether, a 1,2-carbonate or an alkanol amine, which process comprises reacting in one or more process microchannels of a microchannel reactor an olefin oxide with water, an alcohol, carbon dioxide or an amine to form the 1,2-diol, 1,2-diol ether, 1,2-carbonate or alkanol amine.

24. A reactor suitable for the preparation of a 1,2-diol, a 1,2-diol ether, a 1,2-carbonate or an alkanol amine, which reactor is a microchannel reactor comprising one or more process microchannels comprising

- an upstream end,
- a downstream end,
- a first section which is adapted to contain an epoxidation catalyst, to receive a feed comprising an olefin and oxygen, and to cause conversion of at least a portion of the feed to form an olefin oxide in the presence of the epoxidation catalyst, and
- a second section positioned downstream of the first section which is adapted to receive the olefin oxide; to receive water, an alcohol, carbon dioxide or an amine; and to cause conversion of the olefin oxide to form the 1,2-diol, 1,2-diol ether, 1,2-carbonate or alkanol amine.

25. A reactor as claimed in claim 24, which reactor comprises additionally one or more first heat exchange channels adapted to exchange heat with the first section of the said process microchannels, and one or more second heat exchange channels adapted to exchange heat with the second section of the said process microchannels.

26. A reactor as claimed in claim 25, which reactor comprises additionally an intermediate section downstream from the first section and upstream from the second section, which intermediate section is adapted to control the temperature of the olefin oxide.

27. A reactor as claimed in claim 26, which reactor comprises additionally one or more third heat exchange channels adapted to exchange heat with the intermediate section of the said process microchannels.

28. A reactor as claimed in any of claims 24-27, wherein the second section is additionally adapted to contain a catalyst.

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Examiner: Stephen Quick

Claims searched: 1-23

Date of search: 20 April 2007

Patents Act 1977: Search Report under Section 17

Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance
X	1 & 23 at least	WO 2001/96324 A2 (SHELL OIL). See page 10 lines 14-34 and examples Pt II (pages 11-12).
Y	1 & 23 at least	WO 2003/072246 A2 (SHELL OIL). See especially page 4 lines 19-24, page 18 lines 21-22 and page 22 line 10 to page 23 line 2.
Y	23 at least	JP 2004275933 A (NIPPON NYUKAZAI) 07.10.2004 & WPI Abstract Accession No 2004-712491 [70]. See WPI abstract, and paragraphs 0001, 0008, 0021 & 0022 and (for example) examples 1 & 6-8.
Y	1 & 23 at least	WO 2003/000641 A1 (EXXONMOBIL CHEMICAL PATENTS). See especially page 5 line 28 to page 6 line 3 and examples 5 & 6; see also page 22 lines 16-29.
Y	1 & 23 at least	US 6265592 B1 (BASF). See especially column 1 lines 6-10.
Y	1 & 23 at least	EP 0069494 A1 (STANDARD OIL). See especially page 1 line 9 to page 3 line 4, page 5 lines 12-13, and examples 1-10.
Y	1 & 23 at least	US 4892954 A (HOECHST). See especially column 1 lines 8-11 and column 2 lines 8-20 & 36ff.
Y,A	1 & 23 at least	WO 2004/099113 A1 (VELOCYS). [Y] See especially page 1 (paragraph 3), page 12 line 13ff, and figures 3A & 3B. [A] See figure 3B and references thereto. Acknowledged in this application.
Y,A	1 & 23 at least	WO 2001/12312 A2 (BATTELLE MEMORIAL INSTITUTE). [Y] See especially page 3 lines 15-20 and page 12 lines 16 & 22. [A] See (for example) figure 1 and paragraph bridging pages 7 & 8. Acknowledged in this application.
Y	1 & 23 at least	US 6284217 B1 (BATTELLE MEMORIAL INSTITUTE). See especially column 2 lines 64-67; acknowledged in this application.

Y	1 & 23 at least	US 6451864 B1 (BATTELLE MEMORIAL INSTITUTE). See especially column 2 lines 63-67; acknowledged in this application.
Y	1 & 23 at least	US 6491880 B1 (BATTELLE MEMORIAL INSTITUTE). See especially column 7 line 59ff; acknowledged in this application.
A	-	US 6192596 B1 (BATTELLE MEMORIAL INSTITUTE). See figure 2a and column 5 line 51 to column 6 line 20; acknowledged in this application.

Categories:

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category	P	Document published on or after the declared priority date but before the filing date of this invention
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application

Field of Search:

Search of GB, EP, WO & US patent documents classified in the following areas of the UKC^X :

Worldwide search of patent documents classified in the following areas of the IPC

C07C; C07D

The following online and other databases have been used in the preparation of this search report

EPODOC, WPI

International Classification:

Subclass	Subgroup	Valid From
C07D	0301/10	01/01/2006
B01J	0019/00	01/01/2006
B01J	0019/24	01/01/2006
C07B	0035/00	01/01/2006
C07B	0041/02	01/01/2006
C07C	0029/10	01/01/2006
C07C	0031/20	01/01/2006
C07D	0303/04	01/01/2006