

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
28 October 2004 (28.10.2004)

PCT

(10) International Publication Number
WO 2004/092148 A2

(51) International Patent Classification⁷: **C07D 301/10**

(21) International Application Number:
PCT/US2004/010457

(22) International Filing Date: 5 April 2004 (05.04.2004)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/460,901 7 April 2003 (07.04.2003) US

(71) Applicant (for all designated States except US): **SHELL OIL COMPANY** [US/US]; One Shell Plaza, P.O. Box 2463, Houston, TX 77252-2463 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **EVANS, Wayne, Errol** [US/US]; 1019 Lively Court, Richmond, TX 77469 (US). **MATUSZ, Marek** [US/US]; 14515 Meeting Lane, Houston, TX 77084 (US).

(74) Agent: **LEMUTH, Richard, F.**; Shell Oil Company, One Shell Plaza, P.O. Box 2463, Houston, TX 77252-2463 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— without international search report and to be republished upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: PROCESS FOR THE PRODUCTION OF AN OLEFIN OXIDE

(57) Abstract: A process for the production of an olefin oxide, which process comprises reacting a feed comprising an olefin and oxygen in the presence of a silver-containing catalyst, wherein before the catalyst has reached an advanced stage of ageing the reaction temperature is above 255 °C and the olefin content of the feed is above 25 mole-%, relative to the total feed.

WO 2004/092148 A2

PROCESS FOR THE PRODUCTION OF AN OLEFIN OXIDE

Field Of The Invention

5 The present invention relates to a process for the production of an olefin oxide, a 1,2-diol, a 1,2-diol ether or an alkanolamine.

Background Of The Invention

10 In olefin epoxidation an olefin is reacted with oxygen to form an olefin epoxide, using a catalyst comprising a silver component, usually with one or more further elements deposited therewith on a support. The olefin oxide may be reacted with water, an alcohol or an amine to form a 1,2-diol, a 1,2-diol ether or an alkanolamine. Thus, 1,2-diols,
15 1,2-diol ethers and alkanolamines may be produced in a multi-step process comprising olefin epoxidation and converting the formed olefin oxide with water, an alcohol or an amine.

20 The performance of the epoxidation process may be assessed on the basis of the selectivity, the catalyst's activity and stability of operation. The selectivity is the molar fraction of the converted olefin yielding the desired olefin oxide. The catalyst is subject to an ageing-related performance decline during normal operation. The ageing manifests itself by a reduction in the activity of the
25 catalyst. Usually, when a reduction in activity of the catalyst is manifest, the reaction temperature is increased in order to compensate for the reduction in activity, however at the expense of selectivity. In the typical operation of a fresh catalyst, the process is operated at a reaction
30 temperature of at most 255 °C. Upon catalyst ageing the reaction temperature may gradually be increased to values substantially above 255 °C until the reaction temperature becomes undesirably high, at which point in time the catalyst is deemed to be at the end of its lifetime and would need to
35 be exchanged. It goes without saying that from an economical

point of view it is highly desirable to improve the performance of the catalyst and to extend its lifetime as much as possible. Quite modest improvements in the maintenance of selectivity over long periods yields huge
5 dividends in terms of efficiency in the olefin epoxidation process and, if applicable, also in the overall process for the production of a 1,2-diol, a 1,2-diol ether or an alkanolamine.

Therefore, for decades much research has been devoted to
10 improving the activity, the selectivity and the lifetime of the catalysts, and to find process conditions which enable to fully exploit the catalyst performance.

An organic halide, for example a chlorohydrocarbon, may be added to the feed to an epoxidation reactor as a reaction
15 modifier for increasing the selectivity. The reaction modifier suppresses the undesirable oxidation of olefin or olefin oxide to carbon dioxide and water, relative to the desired formation of olefin oxide.

US-A-4766105 and US-A-4761394 disclose that rhenium may
20 be employed as a further element in the silver-containing catalyst with the effect that the selectivity of the olefin epoxidation is increased.

US-B-6372925 and WO-01/96324 teach that when operating with a catalyst which exhibits an improved selectivity, for
25 example a catalyst known from US-A-4766105 or US-A-4761394, it is advantageous to increase the ethylene content of the feed when the catalyst has reached a certain stage of ageing. The increased ethylene content substantially improves the selectivity of the conversion of ethylene into ethylene
30 oxide.

Notwithstanding the improvements already achieved, there is a desire to further improve the performance of the silver-containing catalysts in the production of the production of

an olefin oxide, a 1,2-diol, a 1,2-diol ether or an alkanolamine.

Summary Of The Invention

The present invention provides a process for the
5 production of an olefin oxide, which process comprises
reacting a feed comprising an olefin and oxygen in the
presence of a supported silver-containing catalyst, wherein
before the catalyst has reached an advanced stage of ageing
the reaction temperature is above 255 °C and the olefin
10 content of the feed is above 25 mole-%, relative to the total
feed.

The invention also provides a process for the production
of an olefin oxide, which process comprises reacting a feed
comprising an olefin and oxygen at a reaction temperature
15 above 255 °C and an olefin content of the feed above
25 mole-%, relative to the total feed, in the presence of a
silver-containing catalyst which has not reached an advanced
stage of ageing.

The invention also provides a method of using an olefin
20 oxide for making a 1,2-diol, a 1,2-diol ether or an
alkanolamine comprising converting the olefin oxide into the
1,2-diol, the 1,2-diol ether or the alkanolamine, wherein the
olefin oxide has been obtained by the process according to
this invention.

Detailed Description Of The Invention

In accordance with this invention, when a fresh catalyst
is used at a relatively high temperature, i.e. above 255 °C,
the performance of the catalyst, in particular the activity,
the selectivity, and the ageing related performance decline,
30 are improved when the olefin content of the feed is
increased. Such improvements have not become apparent when
the catalyst was used at a relatively low temperature.

This is unobvious over the teachings of US-B-6372925 and WO-01/96324. These documents show the performance of fresh catalysts at their typical use temperature of at most 255 °C and the performance of aged catalysts at their typical use
5 temperature of above 255 °C. These documents are silent about the performance of fresh catalysts at reaction temperatures above 255 °C.

As used herein, "an advanced stage of ageing" of the catalyst is defined by a cumulative olefin oxide production
10 of at least 10,000 kmole, in particular at least 5000 kmole, more in particular at least 2000 kmole, most in particular at least 1000 kmole, of olefin oxide per m³ of catalyst bed. As used herein, "fresh catalyst" means a catalyst immediately after its preparation or rejuvenation, or a catalyst which,
15 in the course of operation, has not yet reached an advanced stage of ageing.

Although the present epoxidation process may be carried out in many ways, it is preferred to carry it out as a gas phase process, i.e. a process in which the feed is contacted
20 in the gas phase with the catalyst which is present as a solid material, typically in a packed bed. Generally the process is carried out as a continuous process.

The olefin for use in the present epoxidation process may be any olefin, such as an aromatic olefin, for example
25 styrene, or a di-olefin, whether conjugated or not, for example 1,9-decadiene or 1,3-butadiene. 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.

30 The olefin content of the feed is above 25 mole-%, typically at least 30 mole-%, more typically at least 35 mole-%, relative to the total feed. Typically the olefin content of the feed is at most 80 mole-%, more typically at

most 70 mole-%, relative to the total feed. In preferred
embodiments, amongst others, the olefin content of the feed
is maintained at a value of at least 25 mole-%, typically at
least 30 mole-%, more typically at least 35 mole-%, relative
5 to the total feed, when the catalyst has reached an advanced
stage as ageing. Also at an advanced stage of ageing the
olefin content of the feed is typically at most 80 mole-%,
more typically at most 70 mole-%, relative to the total feed.
Typically the olefin content of the feed is maintained at the
10 value as defined for at least a period which is sufficient to
effect an olefin oxide production of at least 1000 kmole,
more typically at least 5000 kmole, most typically at least
10,000 kmole, of olefin oxide per m³ catalyst bed, preferably
up to the end of the catalyst's lifetime, that is when the
15 catalyst will be exchanged and/or rejuvenated. As used
herein, the feed is considered to be the composition which is
contacted with the catalyst.

The direct oxidation of an olefin to the corresponding
olefin oxide can be air-based or oxygen-based, see Kirk-
20 Othmer's *Encyclopedia of Chemical Technology*, 3rd ed., Vol. 9
(1980) p. 445-447. In the air-based processes air or air
enriched with oxygen is fed directly to the system while in
the oxygen-based processes high-purity (above 95 mol-%)
oxygen is employed as the source of the oxidizing agent.
25 Presently most ethylene oxide production plants are oxygen-
based and this is the preferred embodiment of the present
invention.

The oxygen content of the feed is within the broad range
of from 3 to 20 mole-%, preferably from 5 to 12 mole-%,
30 relative to the total feed.

In order to remain outside the flammability limit of the
reaction mixture, the oxygen content of the feed is usually
balanced with the olefin content. The actual safe operating

ranges depend, along with the gas composition (reactants and balance gases), also on individual plant conditions such as temperature and pressure.

In addition to the olefin and oxygen, the feed may
5 contain one or more optional components, such as carbon dioxide, a reaction modifier and balance inert gases.

Carbon dioxide is a by-product of the olefin oxidation process. Since frequently unconverted olefin is continuously recycled, and since a content of carbon dioxide in the feed
10 which is much in excess of 15 mole-% will have an adverse effect on catalyst activity, accumulation of carbon dioxide will be avoided by continuously removing carbon dioxide from the recycle gas. This may be done by venting and by continuous absorption of the formed carbon dioxide.

15. Currently contents of carbon dioxide as low as 1 mole-% are practical, for example in the range of from 0.5 to 1 mole-%, and in future even lower contents may be reached. The process of the present invention is independent of the presence or absence of carbon dioxide in the reaction
20 mixture.

A reaction modifier may be added to the feed for increasing the selectivity, suppressing the undesirable oxidation of olefin and of the olefin oxide to carbon dioxide and water. Many organic compounds, especially organic
25 halides but also amines, organometallic compounds and aromatic hydrocarbons are known to be effective in this respect. Organic halides are the preferred reaction modifiers and they are effective without suppressing the desired reaction when used in quantities ranging from 0.1 to
30 25 parts per million by volume (ppmv), in particular from 0.3 to 20 ppmv, relative to the total feed. Dependent of the silver-containing catalyst employed, the reaction modifier content of the feed may be optimized from time to time during

operation if the maximum achievable selectivity is to be maintained. Preferred organic halides are C_1 to C_8 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 reaction modifiers are ethyl chloride and ethylene dichloride.

The balance inert gases usually present in the feed comprise, for example, nitrogen, argon, and/or saturated hydrocarbon such as methane or ethane. When unconverted olefin is continuously recycled, and oxygen added, the accumulation of balance gases is avoided. The process of the present invention is independent of the amount of balance inert gases in the reaction mixture.

"GHSV", or Gas Hourly Space Velocity, is the unit volume of gas at standard temperature and pressure (0°C , 1 atm, i.e. 101.3 kPa) passing over one unit volume of packed catalyst per hour. Preferably, if the process is carried out as a gas phase process, the GHSV is in the range of from 1500 to 10000. The reactor inlet pressure is preferably in the range of from 1000 to 3500 kPa.

The reaction temperature is typically at least 260°C , more typically at least 265°C , most typically at least 270°C . The reaction temperature is typically at most 325°C , more typically at most 310°C . In preferred embodiments, amongst others, the reaction temperature is maintained at a value of above 255°C , typically at least 260°C , more typically at least 265°C , most typically at least 270°C when the catalyst has reached an advanced stage of ageing. Also at an advanced stage of ageing the reaction temperature is typically at most 325°C , more typically at most 310°C . Typically the reaction temperature is maintained at the value as defined for at least a period which is sufficient to

effect an olefin oxide production of at least 1000 kmole, more typically at least 5000 kmole, most typically at least 10,000 kmole, of olefin oxide per m³ catalyst bed, preferably up to the end of the catalyst's lifetime, that is when the catalyst will be exchanged and/or rejuvenated.

The present process may be started-up by using procedures known in the art, for example from US-A-4874879 and US-5155242, which are incorporated herein by reference. After passing the start-up phase, and at some point in time before the catalyst has reached an advanced stage of ageing, the catalyst may be subjected to the conditions of reaction temperature and olefin content of the feed as defined in accordance with this invention, until the catalyst has reached an advanced stage of ageing. In this context, the stage of ageing of the catalyst is considered on the basis of the total quantity of olefin oxide produced, that is including for example the olefin oxide production, if any, during the start-up procedure.

The material of the support of the supported silver-containing catalysts may be selected from a wide range of conventional materials which are considered to be inert in the presence of the olefin oxidation feed, products and reaction conditions. Such conventional materials can be natural or artificial and they may include aluminum oxides, magnesia, zirconia, silica, silicon carbide, clays, pumice, zeolites and charcoal. Alpha alumina is the most preferred material for use as the main ingredient of the porous support.

The support is typically porous and has preferably a surface area, as measured by the B.E.T. method, of less than 20 m²/g and more in particular from 0.05 to 20 m²/g. Preferably the B.E.T. surface area of the support is in the range of 0.1 to 10, more preferably from 0.1 to 3.0 m²/g.

The B.E.T. method of measuring the surface area has been described in detail by Brunauer, Emmet and Teller in *J. Am. Chem. Soc.* 60 (1938) 309-316.

The catalyst comprises silver as a catalytically active metal. Appreciable catalytic activity is obtained by employing a silver content of the catalyst of at least 10 g/kg, relative to the weight of the catalyst. Preferably, the catalyst comprises silver in a quantity of from 50 to 500 g/kg, more preferably from 100 to 400 g/kg, relative to the weight of the catalyst.

The catalyst preferably comprises, in addition to silver, a further element or compound thereof. Eligible further elements may be selected from the group of nitrogen, sulfur, phosphorus, boron, fluorine, Group IA metals, Group IIA metals, rhenium, molybdenum, tungsten, chromium, titanium, hafnium, zirconium, vanadium, thallium, thorium, tantalum, niobium, gallium and germanium and mixtures thereof.

Preferably the Group IA metals are selected from lithium, potassium, rubidium and cesium. Most preferably the Group IA metal is lithium, potassium and/or cesium. Preferably the Group IIA metals are selected from calcium and barium.

Typically, the further element is present in the catalyst in a quantity of from 0.01 to 500 mmole/kg, more typically from 0.05 to 100 mmole/kg, calculated as the element on the total catalyst. Where possible, the further element may suitably be provided as an oxyanion, for example, as a perrhenate, sulfate, nitrate, nitrite, borate or molybdate, in salt or acid form. Salts of Group IA metals or Group IIA metals are suitable.

Preferably, the silver-containing catalyst is one which, when operated fresh, exhibits at 260 °C a theoretical selectivity at zero oxygen conversion, S_0 , of at least 6/7 or 85.7 mole-%, more preferably 88 mole-%, most preferably

89 mole-%. The value of S_0 for a given catalyst is found by operating the catalyst at 260 °C in a range of oxygen conversions, resulting in a range of selectivity values S corresponding to the range of oxygen conversions. These values S are then extrapolated back to the theoretical value of S at zero oxygen conversion, by the use of conventional curve-fitting algorithms.

Preferred supported highly selective silver-containing catalysts to be used in the present invention are rhenium-containing catalysts. Such catalysts are known from US-A-4766105 and US-A-4761394, which are incorporated herein by reference. Broadly, these catalysts contain a catalytically effective amount of silver, a promoting amount of rhenium or compound thereof, a promoting amount of at least one further metal or compound thereof and optionally a co-promoting amount of a rhenium co-promoter selected from tungsten, molybdenum, chromium, sulfur, phosphorus, boron, and compounds thereof. More specifically the at least one further metal of these rhenium-containing catalysts is/are selected from the group of Group IA metals, Group IIA metals, titanium, hafnium, zirconium, vanadium, thallium, thorium, tantalum, niobium, gallium and germanium and mixtures thereof. Preferably the at least one further metal is/are selected from the Group IA metals such as lithium, potassium, rubidium and cesium and/or from the Group IIA metals such as calcium and barium. Most preferably it is lithium, potassium and/or cesium.

Preferred amounts of the components of these rhenium-containing catalysts are, when calculated as the element on the total catalyst:

- silver from 10 to 500 g/kg, more preferably from 10 to 400 g/kg,
- rhenium from 0.01 to 50 mmol/kg,

- further metal or metals from 10 to 3000 mg/kg, and
- optional rhenium co-promoter from 0.1 to 10 mmol/kg.

More preferably, the rhenium content of these catalysts is at least 0.5 mmole/kg, in particular at least

5 1.0 mmole/kg, more in particular at least 1.5 mmole/kg, when calculated as the element on the total catalyst. More preferably, the rhenium content of these catalysts is at most 40 mmole/kg, when calculated as the element on the total catalyst. Alternatively, the rhenium content of these
10 catalysts, expressed relative to the surface area of the support, is preferably at least 0.0005 mmole/m², in particular at least 0.001 mmole/m², more in particular at least 0.0015 mmole/m². Preferably the rhenium content of these catalysts is at most 0.1 mmole/m², more preferably at
15 most 0.05 mmole/m², relative to the surface area of the support.

As used herein, the quantity of Group IA metal present in the catalysts is deemed to be the quantity in so far as it can be extracted from the catalysts with de-ionized water at
20 100 °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 relevant metals by using a known method, for example atomic absorption
25 spectroscopy.

As used herein, the quantity of Group IIA metal present in the catalysts is deemed to be the quantity in so far as it can be extracted from the catalysts with 10 %w nitric acid in de-ionized water at 100 °C. The extraction method involves
30 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.

The olefin oxide produced may be recovered by using methods known in the art, for example by absorbing the olefin
5 oxide in water and optionally recovering the olefin oxide from the aqueous solution by distillation. At least a portion of the aqueous solution containing the olefin oxide may be applied in a subsequent process for converting the olefin oxide into a 1,2-diol, a 1,2-diol ether or an
10 alkanolamine.

The olefin oxide produced in the epoxidation process may be converted into a 1,2-diol, into a 1,2-diol ether or into an alkanolamine.

The conversion into the 1,2-diol or the 1,2-diol ether
15 may comprise, for example, reacting the olefin oxide with water, suitably using an acidic or a basic catalyst. For example, for making predominantly the 1,2-diol and less 1,2-diol ether, the olefin oxide may be reacted with a ten fold molar excess of water, in a liquid phase reaction in presence
20 of an acid catalyst, e.g. 0.5-1.0 %w sulfuric acid, based on the total reaction mixture, at 50-70 °C at 1 bar absolute, or in a gas phase reaction at 130-240 °C and 20-40 bar absolute, preferably in the absence of a catalyst. If the proportion of water is lowered the proportion of 1,2-diol ethers in the
25 reaction mixture is increased. The 1,2-diol ethers thus produced may be a di-ether, tri-ether, tetra-ether or a subsequent ether. Alternative 1,2-diol ethers may be prepared by converting the olefin oxide with an alcohol, in particular a primary alcohol, such as methanol or ethanol, by
30 replacing at least a portion of the water by the alcohol.

The conversion into the alkanolamine may comprise reacting the olefin oxide with an amine, such as ammonia, an alkyl amine or a dialkylamine. Anhydrous or aqueous ammonia

may be used. Anhydrous ammonia is typically used to favour the production of monoalkanolamine. For methods applicable in the conversion of the olefin oxide into the alkanolamine, reference may be made to, for example US-A-4845296, which is
5 incorporated herein by reference.

The 1,2-diol and the 1,2-diol ether 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
10 systems, etc. The alkanolamine may be used, for example, in the treating ("sweetening") of natural gas.

Unless specified otherwise, the organic compounds mentioned herein, for example the olefins, 1,2-diols, 1,2-diol ethers, alkanolamines and organic halides, have
15 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. As defined herein, ranges for numbers of carbon atoms (i.e. carbon number) include the numbers specified for the limits of the ranges.

20 Having generally described the invention, a further understanding may be obtained by reference to the following examples, which are provided for purposes of illustration only and are not intended to be limiting unless otherwise specified.

25 EXAMPLE 1 - 5 (Example 1 for comparison, Examples 2-5 according to the invention)

A catalyst as defined in US-A-4766105, containing silver, rhenium and rhenium co-promoter and having in the fresh state a theoretical selectivity S_0 at 260 °C of 93%, was used to
30 produce ethylene oxide from ethylene and oxygen. To do this, 2.1-g samples of the crushed catalyst (0.8-1.4 mm) were each loaded into a stainless steel U-shaped tube. The tube was immersed in a molten metal bath (heat medium) and the ends

were connected to a gas flow system. The flow rate of the feed was adjusted to give a gas hourly space velocity of 15,200 NL/(l.h), as calculated for uncrushed catalyst. The flow rate was 35.7 NL/h. The inlet pressure was 1450 kPa.

5 The feed passed through the catalyst bed in a "once-through" operation consisted of ethylene, oxygen, 3 mole-% carbon dioxide, 2.0 to 6.0 ppmv ethyl chloride and balance nitrogen. In each Example different contents of olefin and oxygen were chosen, and such that the oxygen content was the
10 maximum considered to be allowable avoiding conditions of flammability.

 The initial reactor temperature was 225 °C and this was ramped up at a rate of 10 °C per hour to 245 °C and then adjusted so as to achieve a constant ethylene oxide content
15 of 2 mole-% in the outlet stream. For each of the ethylene/oxygen contents combinations, the ethyl chloride content of the feed was varied to identify and then apply the level that provided the optimum selectivity.

 The initial performance data of the catalyst (Table I)
20 were obtained when the catalysts had been on stream for a total of at least 1-2 days. A lower reaction temperature needed to accomplish a certain ethylene oxide content in the outlet stream is indicative for a higher activity of the catalyst.

25

TABLE I

Example	Ethylene in feed (mole-%)	Oxygen in feed (mole-%)	Selectivity (mole-%)	Activity (°C)
1 ¹⁾	25	8.3	85.5	290
2 ²⁾	30	8.0	86	289
3 ²⁾	35	7.6	87.5	283
4 ²⁾	40	7.2	87.5	283
5 ²⁾	45	6.8	88	280
¹⁾ comparative ²⁾ invention				

EXAMPLES 6-10 (for comparison)

The procedure as outlined for Examples 1-5 was repeated,
 5 except that the gas hourly space velocity was 4,100 Nl/(l.h),
 as calculated for uncrushed catalyst, and that the flow rate
 was 9.6 Nl/h.

The initial performance data of the catalyst (Table II)
 were obtained when the catalysts had been on stream for a
 10 total of at least 1-2 days.

TABLE II

Example	Ethylene in feed (mole-%)	Oxygen in feed (mole-%)	Selectivity (mole-%)	Activity (°C)
6 ¹⁾	25	8.3	90	250
7 ¹⁾	30	8.0	89.5	249
8 ¹⁾	35	7.6	90	250
9 ¹⁾	40	7.2	90.5	250
10 ¹⁾	45	6.8	90.5	251
¹⁾ comparative				

A comparison of Examples 2-5 (according to the invention) with Comparative Example 1 shows that when the process is operated at a high temperature, i.e. above 255 °C, the activity of the catalyst becomes progressively higher when the olefin content of the feed is progressively increased to values above 25 mole-%, despite the fact that the content of the other reactant in the feed, oxygen, is decreased. In addition, a gain in selectivity is achieved. Comparative Examples 6-10 show that a similar increase in activity is not seen when the process is operated at a lower temperature. Instead, the activity tends to decrease with increasing olefin content.

EXAMPLE 11 (according to the invention)

The procedure as outlined for Examples 1-5 was repeated, except that the oxygen content of the feed was 8 mole-%, the gas hourly space velocity of 16,500 Nl/(l.h), as calculated for uncrushed catalyst, the flow rate was 38.6 Nl/h, and the ethylene oxide content in the outlet stream was 1.8 mole-%. Further, the decline in catalyst performance was measured over a time period providing a cumulative ethylene oxide (EO) production of 1800 kmole/m³. Then the ethylene content in the feed was increased to 45 mole-%, with unchanged oxygen content, and again the decline in catalyst performance was

measured over a time period providing a cumulative ethylene oxide production of 1800 kmole/m³.

The results have been given in Table III.

Example 11 (according to the invention) shows that when
5 the process is operated at a high temperature, i.e. above 255 °C, the catalyst maintains its performance better as the olefin content in the feed is higher.

TABLE III

Ethylene in feed (mole-%)	Selectivity (mole-%)	Activity (°C)	Selectivity decline after 1800 kmole/m ³ EO production, (mole-%)	Activity decline after 1800 kmole/m ³ EO production, (°C)
30	86.5	278	1.5	10
45	88	270	0.5	0

C L A I M S

1. A process for the production of an olefin oxide, which process comprises reacting a feed comprising an olefin and oxygen in the presence of a silver-containing catalyst, wherein before the catalyst has reached an advanced stage of ageing the reaction temperature is above 255 °C and the olefin content of the feed is above 25 mole-%, relative to the total feed.

2. A process as claimed in claim 1, wherein the olefin is ethylene.

3. A process as claimed in claim 1 or 2, wherein the olefin content of the feed is in the range of from 30 to 80 mole-%.

4. A process as claimed in claim 3, wherein the olefin content of the feed is in the range of from 35 to 70 mole-%.

5. A process as claimed in any of claims 1-4, wherein the olefin content of the feed is maintained at the value as defined for at least a period which is sufficient to effect an olefin oxide production of at least 1000 kmole of olefin oxide per m³ catalyst bed.

6. A process as claimed in any of claims 1-5, wherein the reaction temperature is in the range of from 260 to 325 °C.

7. A process as claimed in claim 6, wherein the reaction temperature is in the range of from 270 to 310 °C.

8. A process as claimed in any of claims 1-7, wherein the reaction temperature is maintained at the value as defined for at least a period which is sufficient to effect an olefin oxide production of at least 1000 kmole of olefin oxide per m³ catalyst bed.

9. A process as claimed in any of claims 1-8, wherein "an advanced stage of ageing" of the catalyst is defined by a cumulative olefin oxide production of at least 10,000 kmole of olefin oxide per m³ of catalyst bed.

5 10. A process as claimed in any of claims 1-8, wherein "an advanced stage of ageing" of the catalyst is defined by a cumulative olefin oxide production of at least 2000 kmole of olefin oxide per m³ of catalyst bed.

10 11. A process as claimed in any of claims 1-8, wherein "an advanced stage of ageing" of the catalyst is defined by a cumulative olefin oxide production of at least 1000 kmole of olefin oxide per m³ of catalyst bed.

15 12. A process as claimed in any of claims 1-11, wherein the catalyst comprises, in addition to silver, rhenium or compound thereof, and a rhenium co-promoter selected from tungsten, molybdenum, chromium, sulfur, phosphorus, boron, and compounds thereof.

20 13. A process for the production of an olefin oxide, which process comprises reacting a feed comprising an olefin and oxygen at a reaction temperature above 255 °C and an olefin content of the feed above 25 mole-%, relative to the total feed, in the presence of a silver-containing catalyst which has not reached an advanced stage of ageing.

25 14. A method of using an olefin oxide for making a 1,2-diol, a 1,2-diol ether or an alkanolamine comprising converting the olefin oxide into the 1,2-diol, the 1,2-diol ether or the alkanolamine, wherein the olefin oxide has been obtained by a process as claimed in any of claims 1-13.