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(54) Title: EPOXIDATION CATALYST AND A PROCESS FOR ITS PREPARATION		
(57) Abstract This invention relates to an epoxidation catalyst having improved selectivity stability, comprising silver, a promoting amount of alkali metal, a promoting amount of rhenium, a promoting amount of nickel and, optionally, a promoting amount of rhenium co-promoter selected from sulphur, molybdenum, tungsten, chromium and mixtures thereof, on a porous refractory support. Preferably, the nickel has been deposited on the catalyst by post-impregnating the catalyst by a non-aqueous solution of the nickel.		

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EPOXIDATION CATALYST AND A PROCESS FOR ITS PREPARATION

The invention relates to a silver-containing epoxidation catalyst, to a process for its preparation and to its use for the epoxidation of olefins having no allylic hydrogen, in particular ethylene.

5 Catalysts for the production of ethylene oxide from ethylene and molecular oxygen are generally supported silver catalysts. Such catalysts are typically promoted with alkali metals. The use of small amounts of the alkali metals potassium, rubidium and cesium were noted as useful promoters in supported silver catalysts in U.S. Patent No. 3,962,136, issued June 8, 1976, and U.S. Patent No. 10 4,010,115, issued March 1, 1977. The use of other co-promoters, such as rhenium, or rhenium along with sulphur, molybdenum, tungsten and chromium is disclosed in U.S. Patent No. 4,766,105, issued August 23, 1988, and U.S. Patent No. 4,808,738, issued February 28, 15 1989. U.S. Patent No. 4,908,343, issued March 13, 1990, discloses a supported silver catalyst containing a mixture of a cesium salt and one or more alkali metal and alkaline earth metal salts.

US Patent No. 4,897,498, issued January 30, 1990, discloses the use of silver-based, alkali metal-promoted, supported catalysts in 20 the epoxidation of olefins having no allylic hydrogens.

It has now been found that silver-based, alkali metal/rhenium-doped supported catalysts containing (and especially post-doped or post-impregnated with) a promoting amount of nickel, have higher selectivity stabilities than those obtained with catalysts 25 containing no nickel.

Accordingly, the present invention relates to a process for the preparation of a catalyst for the vapour phase epoxidation of olefins having no allylic hydrogen, in particular ethylene, which process comprises depositing a catalytically effective amount of 30 silver, a promoting amount of alkali metal, a promoting amount of

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rhenum and optionally, a promoting amount of a rhenum co-promoter selected from sulphur, molybdenum, tungsten, chromium and mixtures thereof, on a porous, refractory support, at least partially drying the support, depositing a promoting amount of nickel on the support, and thereafter drying the support.

Generally, in the vapour phase reaction of ethylene with oxygen to produce ethylene oxide, the ethylene is present in at least a double amount (on a molar basis) compared with oxygen. Therefore, the conversion is calculated according to the mole percentage of oxygen which has been consumed in the reaction to ethylene oxide and any oxygenated by-products. The oxygen conversion is dependent on the reaction temperature, and the reaction temperature is a measure of the activity of the catalyst employed. The value T_{40} indicates the temperature (in °C) at 40 mole percent oxygen conversion in the reactor. This temperature for any given catalyst is higher when the conversion of oxygen is higher. The selectivity (to ethylene oxide) indicates the molar amount of ethylene oxide in the reaction product compared with the total molar amount of ethylene converted. In this specification, the selectivity is indicated as S_{40} , which means the selectivity at 40 mole percent oxygen conversion. The selectivity of silver-based ethylene oxide catalysts can and will decrease over a period of time of usage. Therefore, from an economic and practical standpoint, it is not only the initial selectivity of a catalyst which is important, but also the rate at which the selectivity declines. In fact, significant improvement in lowering the decline rate of a catalyst can prove more economically attractive than a high initial selectivity. Thus, the rate at which a catalyst loses selectivity is a predominant factor influencing the efficiency of any particular catalyst, and lowering this decline rate can lead to significant savings in terms of minimizing waste of the ethylene starting material. As used herein, "selectivity" is used to refer to the selectivity of ethylene oxide catalysts when measured at a given constant oxygen conversion level of 40% at a gas hourly space velocity of approximately 3300 and when measured after

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the catalyst has been placed on stream for at least several days.

The carrier or support employed in these catalysts can be any of the large number of conventional, porous refractory catalyst carriers or support materials which are considered relatively inert in the presence of ethylene oxidation feeds, products and reaction conditions. Such conventional materials are known to those skilled in the art and may be of natural or synthetic origin and preferably are of a macroporous structure, i.e., a structure having a surface area below 10 and preferably below 3 m²/g. Particularly suitable supports are those of aluminous composition. Examples of supports which have been used as supports for different catalysts and which could be used as supports for ethylene oxide catalysts are the aluminium oxides (including the materials sold under the trade name "Alundum"), charcoal, pumice, magnesia, zirconia, keiselguhr, fuller's earth, silicon carbide, porous agglomerates comprising silica and/or silicon carbide, silica, magnesia, selected clays, artificial and natural zeolites and ceramics. Refractory supports especially useful in the preparation of catalysts in accordance with this invention comprise the aluminous materials, in particular those comprising alpha alumina. In the case of alpha alumina-containing supports, preference is given to those having a specific surface area as measured by the B.E.T. method of from 0.03 to 10, preferably from 0.05 to 5, more preferably from 0.1 to 3 m²/g, and a water pore volume as measured by conventional water absorption techniques of from 0.1 to 0.75 ml/g. The B.E.T. method for determining specific surface area is described in detail in Brunauer, S., Emmet, P. Y. and Teller, E., J. Am. Chem. Soc., 60, 309-16 (1938).

Certain types of alpha alumina containing supports are particularly preferred. These alpha alumina supports have relatively uniform pore diameters and are more fully characterized by having B.E.T. specific surface areas of from 0.1 to 3, preferably from 0.1 to 2 m²/g, and water pore volumes of from 0.10 to 0.55 ml/g. Typical properties of some supports found particularly useful in the present invention are presented in Table I. Suitable

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manufacturers of carriers comparable to those in Table I include Norton Company and United Catalysts, Inc. (UCI).

TABLE I

Carrier	A	B	C	D	E	F
B.E.T. Surface Area, m ² /g (a)	0.21	0.42	0.51	0.48	0.57	2.06
Water Pore Volume, ml/g	0.26	0.36	0.38	0.49	0.44	0.65
Crush Strength, FPCS, lbs (b)	100%	97%	21	14	15	No Data
	20 lbs	15				
Total Pore Volume, Hg, ml/g (c)	1.26	0.42	0.40	0.46	0.42	0.65
Average Pore Diameter, Hg, nm (c)	62	56		55	77	100
Median Pore Diameter, Hg, microns (c,d)	3.7	2.7	3.5	3.4	2.4	2.5
Percent Pore Volume in Pores Greater Than 35 nm (c)	90.0%	88.5%	93.0%	89.1%	91.5%	94.1%
Percent Pore Volume in Pores Greater Than 1 μm (c)	87.0%	82.5%	77.0%	82.3%	83.5%	61.0%
% Wt. Alpha Alumina	99.5	98	98.8	98.5	98	70-75
Water Leachable Na, ppmw	12	53	69	24	18	No Data
Acid-Leachable Na, ppmw	40	96	188	51	45	No Data
Water Leachable K, ppmw	5	22	32	22	10	No Data
Acid-Leachable Fe, ppmw	2	5	No Data	1	5	No Data
% Wt. SiO ₂	.5	2	0.1	15	2	25-30

(a) Method of Brunauer, Emmet and Teller, loc. cit.

(b) Flat Plate Crush Strength, single pellet.

(c) Determined by mercury intrusion to 380,000 kPa using Micromeritics Autopore 9200 or 9210

(130° Contact angle, 0.473 N/m surface tension of Hg).

(d) Median pore diameter represents the pore diameter wherein 50% of the total pore volume is found pores having less than (or greater than) the median pore diameter.

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Of the carriers listed in TABLE I, B and C are preferred because they provide catalysts which have high initial selectivities.

5 The support, irrespective of the character of the support or carrier used, is preferably shaped into particles, chunks, pieces, pellets, rings, spheres, wagon wheels, and the like of a size suitable for use in fixed bed reactors. Conventional commercial fixed bed reactors are typically in the form of a plurality of parallel elongated tubes (in a suitable shell) filled with catalyst.
10 In such reactors, it is desirable to use a support formed into a rounded shape, such as, for example, spheres, pellets, rings, tablets and the like, having diameters from 2.5 to 20 mm.

Particular supports having differing properties such as surface area and pore volume may be selected in order to provide particular catalytic properties.
15

The catalysts of the present invention are prepared by a technique in which the alkali metal promoters, the rhenium, and the rhenium co-promoter, if present, in the form of soluble salts and/or compounds are deposited on the catalyst and/or support prior to,
20 simultaneously with, or subsequent to the deposition of the silver and each other. Nickel may also be deposited simultaneously. However, it is preferred that, following the deposition of the silver, alkali metal, rhenium and rhenium co-promoter, if present, on the support, the catalyst is subjected to partial drying or to a thermal treatment sufficient to allow deposition of a promoting
25 amount of nickel and thereafter, a nickel promoter in the form of soluble salts and/or compounds is deposited on the catalyst. The alkali metals may be deposited at one step of the process and the rhenium and/or the rhenium co-promoter, if present, at a different
30 step or steps. The preferred method is to deposit silver, alkali metal, rhenium and rhenium co-promoter simultaneously on the support, that is, in a single impregnation step. The nickel, however is preferably deposited on the catalyst after all of the other catalyst components have been added, and after the catalyst has

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been at least partially dried to a degree sufficient to permit a promoting amount of nickel to be impregnated onto the catalyst. The post-impregnation or post-doping of the catalyst with a promoting amount of nickel compounds results in a catalyst having particularly improved selectivity stability.

Promoting amounts of alkali metal or mixtures of alkali metal are deposited on a porous support using a suitable solution of alkali metal promoter ions, salt(s) and/or compound(s). An alkali metal promoter may even be deposited on the carrier after reduction to metallic silver has taken place. The amount of alkali metal promoter deposited upon the support or present on the catalyst generally lies between 10 and 3000, preferably between 15 and 2000, more preferably between 20 and 1500 and most preferably between 50 and 1000 parts per million by weight of the total catalyst. The effects of these variations in properties are readily determined by experimentation. The alkali metal promoters are present on the catalysts in the form of cations (ions) or compounds of complexes or surface compounds or surface complexes rather than as the extremely reactive free alkali metals, although for convenience purposes in this specification and claims they are referred to as "alkali metal" or "alkali metal promoters". It is believed that the alkali metal compounds are oxidic compounds, probably in the form of mixed surface oxides or double surface oxides or complex surface oxides with the aluminium of the support and/or the silver of the catalyst, possibly in combination with species contained in or formed from the reaction mixture, such as, for example, chlorides or carbonates or residual species from the impregnating solution(s).

In a preferred embodiment, at least a major proportion (greater than 50%) of the alkali metals comprise the higher alkali metals, selected from the group consisting of potassium, rubidium, cesium and mixtures thereof. A preferred alkali metal promoter is cesium. A particularly preferred alkali metal promoter is cesium plus at least one additional alkali metal, which is preferably selected from sodium, lithium and mixtures thereof, with lithium being preferred.

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The carrier is also impregnated with rhenium ions, salt(s), compound(s), and/or complex(es). This may be done at the same time that the alkali metal promoter is added, or before or later; or at the same time that the silver is added, or before or later; or at the same time that the rhenium co-promoter, if present, is added, or before or later. Preferably, rhenium, alkali metal, rhenium co-promoter, if present, and silver are in the same impregnating solution. The preferred amount of rhenium, calculated as the metal, deposited on or present on the carrier or catalyst ranges from 0.1 to 10, more preferably from 0.2 to 5 micromoles per gram of total catalyst, or, alternatively stated, from 19 to 1860, preferably from 37 to 930 parts per million by weight of total catalyst. For purposes of convenience, the amount of rhenium present on the catalyst is expressed as the metal, irrespective of the form in which it is present.

The rhenium compounds used in the preparation of the instant catalysts are rhenium compounds that can be solubilized in an appropriate solvent. Preferably, the solvent is a water-containing solvent. More preferably, the solvent is the same solvent used to deposit the silver and the alkali metal promoter. Examples of suitable rhenium compounds include the rhenium salts such as rhenium halides, the rhenium oxyhalides, the rhenates, the perrhenates, the oxides and the acids of rhenium. A preferred compound for use in the impregnation solution is the perrhenate, preferably ammonium perrhenate. However, the alkali metal perrhenates, alkaline earth metal perrhenates, silver perrhenates, other perrhenates and rhenium heptoxide can also be suitably utilized. Rhenium heptoxide, Re_2O_7 , when dissolved in water, hydrolyzes to perrhenic acid, HReO_4 , or hydrogen perrhenate. Thus, for purposes of this specification, rhenium heptoxide can be considered to be a perrhenate, i.e., ReO_4 . It is also understood that there are many rhenium compounds that are not soluble per se in water. However, these compounds can be solubilized by utilizing various acids, bases, peroxides, alcohols, and the like. In a preferred embodiment of the instant invention,

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the rhenium present on the catalyst is present in a form that is extractable in a dilute aqueous base solution.

It was found in U.S. Patent No. 4,766,105, issued August 23, 1988, that if a rhenium co-promoter is added to an alkali metal/rhenium doped supported silver catalyst, an improvement in initial selectivity is obtained. When a co-promoter is utilized, it is selected from the group consisting of sulphur, molybdenum, tungsten, chromium and mixtures thereof, preferably a compound of sulphur, molybdenum, tungsten, chromium and mixtures thereof. The co-promoter, it is believed, is not present on the catalyst in the elemental form since it is applied to catalyst in the form of ions, salts, compounds and/or complexes and the reducing conditions generally used to reduce the silver to metallic silver are not usually sufficient to reduce the sulphur, molybdenum, tungsten or chromium to the elemental form. It is believed that the co-promoter deposited on the support or present on the catalyst is in the compound form, and probably in the form of an oxygen-containing or oxidic compound. In a presently preferred embodiment, the co-promoter is applied to the catalyst in the oxyanionic form, i.e., in the form of an anion, or negative ion which contains oxygen. Examples of anions of sulphur that can be suitably applied include sulfate, sulphite, bisulfite, bisulphate, sulfonate, persulfate, thiosulfate, dithionate, etc. Preferred compounds to be applied are ammonium sulfate and the alkali metal sulfates. Examples of anions of molybdenum, tungsten and chromium that can be suitably applied include molybdate, dimolybdate, paramolybdate, other iso- and hetero-polymolybdates, etc.; tungstate, paratungstate, metatungstate, other iso- and hetero-polytungstates, etc.; and chromate, dichromate, chromite, halochromate, etc. Preferred are sulfates, molybdates, tungstates and chromates. The anions can be supplied with various counter-ions. Preferred are ammonium, alkali metal and hydrogen (i.e. acid form). The anions can be prepared by the reactive dissolution of various non-anionic materials such as the oxides such as SO_2 , SO_3 , MoO_3 , WO_3 , Cr_2O_3 , etc., as well as

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other materials such as halides, oxyhalides, hydroxyhalides, hydroxides, sulphides, etc., of the metals.

The preferred amount of co-promoter compound present on or deposited on the support or catalyst ranges from 0.1 to 10, preferably from 0.2 to 5 micromoles, expressed as the element, per gram of total catalyst. For purposes of convenience the amount of co-promoter present on the catalyst is expressed as the element irrespective of the form in which it is present.

The co-promoter compounds, salts and/or complexes suitable for use in the preparation of the instant catalysts are compounds, salts and/or complexes which can be solubilized in an appropriate solvent. Preferably, the solvent is a water-containing solvent. More preferably, the solvent is the same solvent used to deposit the silver, alkali metal promoter and rhenium.

In a preferred embodiment, following the impregnation of the carrier with silver, alkali metal, rhenium and rhenium co-promoter, if present, the impregnated carrier is at least partially dried to a degree sufficient to allow for impregnation of the carrier with nickel ions, salt(s), compound(s) and/or complex(es). It is necessary for purposes of this invention that the nickel be added after the other components, i.e., the silver, alkali metal, rhenium and rhenium co-promoter, if present, have been impregnated or deposited on the support and the impregnated support or catalyst has been at least partially dried to an extent sufficient to allow an essentially non-aqueous solution of nickel ions to be adsorbed into the pore structure of the support or catalyst. The solution of nickel ions must be essentially non-aqueous in order to prevent the potential redissolution and redistribution of the other components, i.e., the silver, alkali metal, rhenium and rhenium co-promoter, if present, which have already been deposited on the support. The nickel is used as an ion or compound of nickel dissolved in a suitable solvent for impregnation purposes. The catalyst is post-impregnated or post-doped with a solution of nickel promoter ions, salt(s) and/or compound(s). The amount of nickel promoter deposited

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upon the support or present on the catalyst generally lies between 10 and 1000, and preferably between 15 and 500, most preferably between 30 and 250 parts per million by weight of the total catalyst. The nickel promoter or promoters are presumably present on the catalyst in the form of oxides or oxygen-bound species, or surface compounds or surface complexes rather than as metals. For purposes of convenience, the amount of nickel deposited on the support or present on the catalyst is expressed as the element.

In a preferred embodiment, the nickel compound is selected from the group consisting of nickel carbonate, nitrate, acetate, acetylacetonate, chloride, sulfate and mixtures thereof, with nickel carbonate, nitrate, sulfate and mixtures thereof being particularly preferred. Particularly preferred nickel promoters are nickel carbonate and nickel nitrate.

Generally, the carrier is contacted with a silver salt, compound or complex which has been dissolved in an aqueous solution, so that the carrier is impregnated with said aqueous solution; thereafter the impregnated carrier is separated from the aqueous solution, e.g., by centrifugation or filtration and then dried. The thus obtained impregnated carrier is heated to reduce the silver to metallic silver. It is understood that the reduction of the silver to metallic silver may take place, at least in part, during the partial drying step which takes place before the deposition of the nickel promoter. It is conveniently heated to a temperature in the range of from about 50°C to about 600°C, during a period sufficient to cause reduction of the silver salt, compound or complex to metallic silver and to form a layer of finely divided silver, which is bound to the surface of the carrier, both the exterior and pore surface. Air, or other oxidizing gas, reducing gas, an inert gas or mixtures thereof may be conducted over the carrier during this heating step.

One method of preparing the silver containing catalyst can be found in U.S. Patent 3,702,259. Other methods for preparing the silver-containing catalysts which in addition contain higher alkali

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metal promoters can be found in U.S. Patent 4,010,115, U.S. Patent 4,356,312, U.S. Patent 3,962,136 and U.S. Patent 4,012,425. Methods for preparing silver-containing catalysts containing higher alkali metal and rhenium promoters can be found in U.S. Patent
5 No. 4,761,394, and methods for silver-containing catalysts containing higher alkali metal and rhenium promoters and rhenium co-promoters can be found in U.S. Patent No. 4,766,105.

The alkali metal and rhenium promoters and rhenium co-promoters, if present, may be deposited on the carrier (support) or
10 on the catalyst, depending upon the particular impregnation technique or sequence utilized. In this specification and claims, the term "on the catalyst" when referring to the deposition or presence of promoters and/or co-promoters refers to the catalyst which comprises the combination of carrier (support) and silver.
15 Thus, the promoters, i.e., alkali metal, rhenium and rhenium co-promoter may be found individually or in a mixture thereof on the catalyst, on the support or on both the catalyst and the support. There may be, for example, alkali metal, rhenium and rhenium co-promoter on the support; alkali metal, rhenium and rhenium co-promoter on the catalyst; alkali metal, and rhenium on the support
20 and rhenium co-promoter on the catalyst; alkali metal and rhenium co-promoter on the support and rhenium on the catalyst; alkali metal, rhenium and rhenium co-promoter on the support and rhenium and rhenium co-promoter on the catalyst and any of the other
25 possible distributions of alkali metal, rhenium and/or rhenium co-promoter between the support and/or the catalyst.

A particularly preferred process of impregnating the carrier with silver, alkali metal, rhenium and rhenium co-promoter consists of impregnating the carrier with an aqueous solution containing a
30 silver salt of a carboxylic acid, an organic amine, a salt of cesium, ammonium perrhenate and ammonium sulfate dissolved therein. Silver oxalate is a preferred salt. It can be prepared by reacting silver oxide (slurry in water) with (a) a mixture of ethylenediamine and oxalic acid, or (b) oxalic acid and then ethylenediamine, which

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latter is preferred, so that an aqueous solution of silver oxalate-ethylenediamine complex is obtained, to which solution is added a certain amount of cesium compound, ammonium perrhenate and ammonium sulfate. While addition of the amine to the silver oxide before adding the oxalic acid is possible, it is not preferred since it can give rise to solutions which are unstable or even explosive in nature. Other diamines and other amines, such as ethanolamine, may be added as well. A cesium-containing silver oxalate solution may also be prepared by precipitating silver oxalate from a solution of cesium oxalate and silver nitrate and rinsing with water or alcohol the obtained silver oxalate in order to remove the adhering cesium salt until the desired cesium content is obtained. The cesium-containing silver oxalate is then solubilized with ammonia and/or an amine in water and ammonium perrhenate and ammonium sulfate is added. Rubidium-, potassium-, sodium-, lithium- and mixtures of alkali metal-containing solutions may be prepared also in these ways. The impregnated carriers are then partially dried at a temperature between 50°C and 600°C, preferably between about 75°C and about 400°C to evaporate the liquid. It is believed that these partial drying temperatures also result in substantial reduction of the silver to produce a metallic silver. Thereafter, the impregnated carriers are post-impregnated or post-doped with an essentially alcoholic solution containing nickel cations. The solution can be prepared by dissolving a suitable soluble nickel salt in a substantially non-aqueous solvent such as, for example, a lower alcohol solvent. The post-doped or post-impregnated carriers are then heated to a temperature between 50°C and 600°C, preferably between 75°C and 400°C.

In the impregnation process, the concentration of the silver (expressed as the metal) in the silver-containing solution will range from about 1 g/l up to the solubility limit when a single impregnation is utilized. The concentration of the alkali metal (expressed as the metal) will range from about 1×10^{-3} to 12 and preferably, from 10×10^{-3} to 12 g/l when a single impregnation step

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is utilized. The concentration of the rhenium (expressed as the metal) will range from 5×10^{-3} to 20 and preferably from 50×10^{-3} to 20 g/l when a single impregnation step is utilized. The concentration of rhenium co-promoter (expressed as the element) will
5 range from 1×10^{-3} to 20 and preferably from 10×10^{-3} to 20 g/l when a single impregnation step is utilized. In the post-impregnation step, the concentration of the nickel (expressed as the element) will range from about 1×10^{-5} to 1 and preferably, from 5×10^{-4} to 0.1 g/l when a single post-impregnation step is
10 utilized.

The silver catalysts according to the present invention have been shown to have a particularly high selectivity stability for ethylene oxide production in the direct oxidation of ethylene with molecular oxygen to ethylene oxide. The conditions for carrying out
15 such an oxidation reaction in the presence of the silver catalysts according to the present invention broadly comprise those already described in the prior art. This applies, for example, to suitable temperatures, pressures, residence times, to the presence of diluent materials and moderating agents, to the desirability of employing
20 recycle operations or applying successive conversations in different reactors to increase the yields of ethylene oxide, and to any other special conditions which may be selected in processes for preparing ethylene oxide. Oxygen employed as reactant can be obtained from conventional sources. The suitable oxygen charge may consist
25 essentially or relatively pure oxygen, a concentrated oxygen stream comprising oxygen in major amount with lesser amounts of one or more diluents, such as nitrogen and argon, or another oxygen-containing stream, such as air. It is therefore evident that the use of the present silver catalysts in ethylene oxide reactions is in no way
30 limited to the use of specific conditions among those which are known to be effective. For purposes of illustration only, the following table shows the range of conditions that are often used in current commercial ethylene oxide reactor units.

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TABLE II

*GHSV	1500-10,000
Inlet Pressure	1000-3800 kPa
<u>Inlet Feed</u>	
Ethylene	1-40%
O ₂	3-12%
Ethane	0-3%
Argon and/or methane and/or nitrogen diluent	Balance
Chlorohydrocarbon Moderator	0.3-50 ppmv total
Coolant temperature	180-315°C
Catalyst temperature	180-325°C
O ₂ conversion level	10-60%
EO Production (Work Rate)	32-320 kg EO/m ³ / catalyst/hr.

* Volume units of gas at standard temperature and pressure passing over one volume unit of packed catalyst per hour.

In a preferred application of the silver catalysts according to the present invention, ethylene oxide is produced when an oxygen-containing gas is contacted with ethylene in the presence of the present catalysts at a temperature in the range of from 180°C to 330°C and preferably 200°C to 325°C.

While the catalysts of the present invention are preferably used to convert ethylene to ethylene oxide, they can be also used to epoxidise other olefins having no allylic hydrogens, such as are broadly defined in U.S. Patent No. 4,897,498. Exemplary such olefins are butadiene, tertiary butyl ethylene, vinyl furan, methyl vinyl ketone, N-vinyl pyrrolidone, and the like. A presently preferred olefin for use in the practice of this process is butadiene, because of its ready availability, relative low cost, and the wide range of possible uses for the epoxide reaction product. U.S. Patent No. 5,081,096, issued January 14, 1992, discloses a silver-based,

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alkali metal-promoted, supported catalyst which is adapted to the epoxidation of butadiene by treating the pro-catalyst, after its impregnation with a silver compound, with a hydrogen containing gas at a temperature not exceeding 350 °C. The same can be done with the catalysts according to the present invention.

The invention will be illustrated by the following embodiments.

Illustrative Embodiments

Illustrative Embodiment 1

This embodiment describes typical preparative techniques for making the catalysts of the instant invention (and comparative catalysts) and the typical technique for measuring the properties of these catalysts.

Part A: Preparation of stock silver oxalate/ethylenediamine solution for use in catalyst preparation:

1) Dissolve 415 grams (g) of reagent-grade sodium hydroxide in 2340 millilitres (ml) deionized water. Adjust the temperature to 50°C.

2) Dissolve 1699 g of "Spectropure" (high purity) silver nitrate in 2100 ml deionized water. Adjust the temperature to 50°C.

3) Add sodium hydroxide solution slowly to silver nitrate solution with stirring while maintaining a temperature of 50°C. Stir for 15 minutes after addition is complete, and then lower the temperature to 40°C.

4) Insert clean filter wands and withdraw as much water as possible from the precipitate created in step (3) in order to remove sodium and nitrate ions. Measure the conductivity of the water removed and add back as much fresh deionized water as was removed by the filter wands. Stir for 15 minutes at 40°C. Repeat this process until the conductivity of the water removed is less than 90 µmho/cm. Then add back 1500 ml deionized water.

5) Add 630 g of high-purity oxalic acid dihydrate in approximately 100g increments. Keep the temperature at 40°C and stir to mix thoroughly. Add the last portion of oxalic acid dihydrate slowly and monitor pH to ensure that pH does not drop

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below 7.8.

6) Remove as much water from the mixture as possible using clean filter wands in order to form a highly concentrated silver-containing slurry. Cool the silver oxalate slurry to 30°C.

5 7) Add 699 g of 92 percent weight (%w) ethylenediamine (8% deionized water). Do not allow the temperature to exceed 30°C during addition.

The above procedure yields a solution containing approximately 27-33%w silver.

10 Part B: Preparation of impregnated catalysts

For preparing the impregnated catalyst, into a 10 ml beaker is added 0.166 g of $(\text{NH}_4)\text{ReO}_4$ and approximately 2.0 g of ethylenediamine/ H_2O (50/50 by weight), and the mixture is allowed to dissolve with stirring. 0.079 g of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ is dissolved in 1 ml
15 of water in a weighing dish, and then added to the perrhenate solution. 0.3416 g of LiNO_3 is dissolved in 2 ml of water and added to the perrhenate solution. The perrhenate/lithium sulfate/lithium nitrate solution is allowed to stir, ensuring complete dissolution. This dopant solution is then added to 184 g of the above-prepared
20 silver solution (specific gravity = 1.556 g/ml), and the resulting solution is diluted with water to a total weight of 204 g. One-fourth of this solution is used to prepare a catalyst. 0.0444 - 0.0475 g of CsOH is added to a 51 g portion of the silver oxalate/dopant solution to prepare the final impregnation solution.

25 The final impregnation solution thus prepared is then used to impregnate a catalyst carrier in the manner described below. Catalyst carrier C which is described in Table 1 is a preferred support for the instant invention and is used in the following examples and illustrative embodiments unless otherwise stated.

30 Approximately 30 g of carrier C are placed under vacuum at 3.33 kPa for 3 minutes at room temperature. Approximately 50 g of doped impregnating solution is then introduced to submerge the carrier, and the vacuum is maintained at 3.33 kPa for an additional 3 minutes. At the end of this time, the vacuum is released, and

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excess impregnating solution is removed from the carrier by centrifugation for 2 minutes at 500 rpm. If the impregnating solution is prepared without monoethanolamine, then the impregnated carrier is cured by being continuously shaken in a 8500 litre/hr. air stream flowing across a cross-sectional area of approximately 19-32 cm² at 250-270°C for 5-6 minutes. If significant monoethanolamine is present in the impregnating solution, then the impregnated carrier is cured by being continuously shaken in a 8500 litre/hr. air stream at 250°C for 2.5 minutes, followed by a 2830 litre/hr. air stream at 270°C for 7.5 minutes (all over a cross-section area of approximately 19-32 cm²). The cured nickel-free catalyst (Catalyst C) is then ready for testing.

Part C: Catalyst post-doping procedure

A standard solution of nickel ions is prepared using the following procedure. Into a 50 millilitre (ml) volumetric flask is added 12.2911 g of nickel nitrate hexahydrate, 31.06 g of a 50/50 mixture of ethylenediamine and water, and approximately 2.5 millilitres of concentrated aqueous ammonium hydroxide. 10 millilitres of saturated ammonium carbonate solution is also added. The solution is then allowed to stand overnight and is then diluted with water to 50 millilitres. The solution prepared contains 0.0491 grams of nickel per millilitre of solution.

For Catalyst A, in order to deposit 88 parts per million (ppm) of nickel ions, the following solution is made. 0.1389 ml of the above standard solution of nickel ions is added to 30 millilitres of absolute (100%) ethanol. 36.1 grams of Catalyst C (as prepared above) is then impregnated at 3.33-6.66 kPa for three minutes. At the end of this time, the vacuum is released and the excess solution is decanted from the catalyst pellets. The catalyst pellets are then dried by continuous shaking in a 8500 litre/hr. air stream at 60-80°C, three minutes at 120-150°C, and four minutes at 250°C.

For Catalyst B, the post-doping procedure for Catalyst A above was carried out, except that no nickel solution was added to the absolute (100%) ethanol. Catalyst B was thus post-doped with

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ethanol only.

The procedures set forth above for Catalysts A and C will yield catalysts on this carrier which contain approximately 13.5%w Ag with the following approximate dopant levels (expressed in parts per million by weight basis the weight of the total catalyst, i.e., ppmw) and which are approximately optimum in cesium for the given silver and rhenium and sulphur levels and support with regard to initial selectivity under the test conditions described below.

	<u>Cs, ppmw</u>	<u>Nickel, ppmw</u>	<u>Re, ppmw</u>	<u>S, ppmw</u>
Catalyst A	460	88	280	48
Catalyst B	460	None	280	48
Catalyst C	430	None	280	48

The actual silver content of the catalyst can be determined by any of a number of standard, published procedures. The actual level of rhenium on the catalysts prepared by the above process can be determined by extraction with 20 mm aqueous sodium hydroxide, followed by spectrophotometric determination of the rhenium in the extract. The actual level of nickel on the catalyst can be determined by standard atomic emission spectroscopy. The actual level of cesium on the catalyst can be determined by employing a stock cesium hydroxide solution, which has been labelled with a radioactive isotope of cesium, in catalyst preparation. The cesium content of the catalyst can then be determined by measuring the radioactivity of the catalyst. Alternatively, the cesium content of the catalyst can be determined by leaching the catalyst with boiling deionized water. In this extraction process cesium, as well as other alkali metals, is measured by extraction from the catalyst by boiling 10 grams of whole catalyst in 20 millilitres of water for 5 minutes, repeating the above two more times, combining the above extractions and determining the amount of alkali metal present by comparison to standard solutions of reference alkali metals using atomic absorption spectroscopy (using Varian Techtron Model 1200 or

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equivalent).

Part D: Standard Microreactor Catalyst Test Conditions/Procedure

3 to 5 grams of crushed catalyst of 1.410-0.841 mm (14-20 mesh) are loaded into a 6 mm diameter stainless steel U-shaped tube. The U tube is immersed in a molten metal bath (heat medium) and the ends are connected to a gas flow system. The weight of the catalyst used and the inlet gas flow rate are adjusted to achieve a gas hourly space velocity of 3300 ml of gas per ml of catalyst per hour. The inlet gas pressure is 1548 kPa.

The gas mixture passed through the catalyst bed (in once-through operation) during the entire test run (including start-up) consists of 30% ethylene, 8.5% oxygen, 5% carbon dioxide, 54.5% nitrogen, and 2.0 to 6.0 ppmv ethyl chloride.

The initial reactor (heat medium) temperature is 225°C. After 1 hour at this initial temperature, the temperature is increased to 235°C for 1 hour, and then adjusted to 245°C for 1 hour. The temperature is then adjusted so as to achieve a constant oxygen conversion level of 40%. Performance data at this conversion level are usually obtained when the catalyst has been onstream for a total of at least 2-3 days. Due to slight differences in feed gas composition, gas flow rates, and the calibration of analytical instruments used to determine the feed and product gas compositions, the measured selectivity and activity of a given catalyst may vary slightly from one test run to the next. To allow meaningful comparison of the performance of catalysts tested at different times, all catalysts described in this illustrative embodiment were tested simultaneously with a reference catalyst. All performance data reported in this illustrative embodiment are corrected relative to the average initial performance of the reference catalyst ($S_{40} = 81.0\%$; $T_{40} = 230^\circ\text{C}$).

After obtaining initial performance values for selectivity at 40% conversion the catalysts are subjected to high severity ageing conditions. Under these conditions, the catalyst is brought to either 85% conversion or a maximum of 285°C for a 10-day period to

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accelerate the ageing of the catalyst. After this 10-day ageing period, the catalysts are again brought to 40% conversion and reoptimized under standard conditions. The selectivity is again measured, and compared to the original value of the fresh catalyst.

5 After the new selectivity value is determined, this cycle is repeated, and the selectivity decline of the catalyst is continuously measured under standard 40% conversion conditions in 10-day cycles relative to its fresh initial performance. The results are presented below in Table III. All selectivity values are expressed as %. Catalysts A and C have initial S_{40} values of 86.0-86.5% at T_{40} values of $259^{\circ}\text{C} \pm 4^{\circ}\text{C}$. Catalyst B (post-doped with ethanol) showed an initial S_{40} value of approximately 84%, and therefore was not tested in a long term run due to its poor initial performance relative to Catalyst A (post-doped with nickel) and

10 Catalyst C (standard impregnated with no post-doped nickel).

15

$$\text{Loss of Selectivity (\%)} = [S_{40}, \text{ (Aged)}] - [S_{40}, \text{ (Fresh)}]$$

TABLE III

<u>Loss of Selectivity from Fresh Catalyst</u>					
<u>Total Days at Either 85% Conversion or 285°C</u>					
(Data Obtained at 40% Conversion Conditions)					
<u>Catalyst</u>	<u>10 Days</u>	<u>20 Days</u>	<u>30 Days</u>	<u>40 Days</u>	<u>50 Days</u>
A (Re/Ni)	0.1%	0.1%	0.8%	2.4%	4.3%
C (Re)	1.2%	2.3%	3.4%	5.0%	6.1%

As mentioned previously, selectivity decline is of tremendous economic importance when choosing a catalyst, and retarding this decline rate can lead to significant savings in costs. As can be seen from Table III, Catalyst C, which does not contain a post-

20 doped, i.e., post-impregnated, nickel promoter in combination with Re, decreases in selectivity much more rapidly than do the catalysts which contain a post-doped nickel promoter. Catalysts which contain post-doped nickel promoters in combination with rhenium maintain their selectivity significantly longer than catalysts without post-

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doped nickel promoters and are thus significantly advantaged.
Catalyst B's poor initial performance shows that the advantages
which are seen with Catalyst A are not due to the presence of the
ethanol or the post-doping step, but rather due to the addition of
5 the nickel during the post-doping or post-impregnation step.

C L A I M S

1. A catalyst for the vapour phase epoxidation of olefins having no allylic hydrogen, in particular ethylene, comprising a catalytically effective amount of silver, a promoting amount of alkali metal, a promoting amount of rhenium and a promoting amount of nickel on a support having a surface area in the range of 0.05 to 10 m²/g.
2. The catalyst of claim 1 wherein the support comprises alpha alumina having a surface area in the range of from 0.05 to 5 m²/g.
3. The catalyst of claim 1 wherein, based on the total catalyst, the amount of silver is in the range of from 1 to 40 percent by weight, the amount of alkali metal promoter is in the range of from 10 to 3000 parts per million, expressed as the metal, by weight, the amount of rhenium promoter is in the range of from 0.1 to 10 micromoles of rhenium, expressed as the metal, per gram, and the amount of nickel promoter is in the range of from 10 to 1000 parts per million, expressed as the element.
4. The catalyst of claim 1 wherein the alkali metal is selected from potassium, rubidium, cesium, and mixtures thereof.
5. A process for preparing a catalyst for the vapour phase epoxidation of olefins having no allylic hydrogen, in particular ethylene, which process comprises depositing a catalytically effective amount of silver, a promoting amount of alkali metal and a promoting amount of rhenium on a support having a surface area in the range of from 0.05 to 10 m²/g, at least partially drying the support, depositing a promoting amount of nickel on the support, and thereafter drying the support.
6. The process of claim 5 wherein the nickel is applied to the support as a solubilized nickel compound.
7. The process of claim 5 wherein the nickel compound is selected from nickel carbonate, nickel nitrate, nickel acetate, nickel

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acetylacetonate, nickel chloride, nickel sulfate and mixtures thereof.

5 8. The process of claim 5 wherein there is added a rhenium copromoter selected from sulphur, molybdenum, tungsten, chromium and mixtures thereof in an amount of from 0.1 to 10 micromoles, expressed as the element, per gram of total catalyst.

9. The process of any one of claims 5-8, which comprises impregnating a porous refractory support with one or more solutions comprising silver, alkali metal, rhenium and optionally rhenium co-promoter, wherein the concentration (expressed as the respective
10 element) of the silver in the solution ranges from 1 gram/litre to the solubility limit of silver in the solution, the concentration of alkali metal in the solution ranges from 1×10^{-3} to 12 grams/litre, the concentration of the rhenium in the solution ranges from 5×10^{-3}
15 to 20 grams/litre and the optional concentration of the rhenium co-promoter in the solution ranges from 1×10^{-3} to 20 grams/litre, partially drying the impregnated support, post-impregnating the impregnated support with one or more essentially non-aqueous solutions comprising nickel, wherein the concentration of the nickel
20 in the solution ranges from 1×10^{-5} to 1 gram/litre, and drying the post-impregnated support, to provide the catalyst with a catalytically effective amount of silver, a promoting amount of alkali metal, a promoting amount rhenium, optionally a promoting amount of rhenium co-promoter and a promoting amount of nickel.

INTERNATIONAL SEARCH REPORT

International Application No

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A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B01J23/68 C07D301/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 B01J C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 480 537 (UNION CARBIDE CHEMICALS AND PLASTICS CO., INC.) 15 April 1992 see the whole document ---	1,5
A	EP,A,0 480 539 (UNION CARBIDE CHEMICALS AND PLASTICS CO., INC.) 15 April 1992 see the whole document ---	1,5
A	EP,A,0 266 015 (SHELL INTERNATIONALE RESEARCH MAATSCAPPIJ B. V.) 4 May 1988 cited in the application -----	

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

information on patent family members

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