EPOXIDATION CATALYST AND PROCESS

The invention relates to silver-containing catalysts suitable for the epoxidation of olefins having no allylic hydrogen, in particular for the preparation of ethylene oxide and to the use of the catalysts. The catalysts are prepared using a unique alpha alumina-based catalyst carrier.

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. 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, 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.

The use of porous ceramic catalyst carriers has been previously described in a number of patents such as, for example, U.S. Patent No. 5,380,697, issued January 10, 1995, U.S. Patent No. 5,100,859, issued March 31, 1992, U.S. Patent No. 5,055,442, issued October 8, 1991, U.S. Patent No. 5,037,794, issued August 6, 1991, and U.S. Patent No. 4,874,739, issued October 17, 1989. Such catalyst carriers have a wide variety of potential applications in the catalytic field and are especially

useful where the ceramic base is an alumina such as alpha alumina.

A catalyst support needs to possess, in combination, at least a minimum surface area on which the catalytic component may be deposited, high water absorption and crush strength. The problem is that usually an increase in one can mean a reduction in another property. Thus, high crush strength may mean low porosity. Often the balance is achieved by trial and error making the catalyst carrier art even more unpredictable than other chemical process art.

Carriers need to have a uniform degree of porosity and this may be achieved in a number of ways including the incorporation of burnout materials that are eliminated when the ceramic is fired to form the finished product. Typical burnout materials include charcoal, petroleum coke, ground walnut shells and the like. The problem is that such materials usually leave leachable residues that can significantly impair the performance of catalysts supported on carriers made using such burnout materials. Furthermore, the actual content of such leachable material varies widely from batch to batch so that predictability is unsatisfactory. In an attempt to circumvent this problem, it has been proposed to incorporate organic polymeric burnout materials with very low metallic leachables content (PCT/EP 96/0444). However, such burnout materials still may leave traces of residue which may affect the results.

There is therefore a need to design catalysts in which one can have confidence with respect to the final property balance. The catalysts of the present invention have an excellent balance of crush strength, abrasion resistance, porosity and catalytic performance that make them ideal for a wide range of catalytic applications. More importantly, the amount of metallic leachables has

been significantly reduced without parallel negative effects on the physical properties of the catalyst. The present invention therefore results in catalysts which have improved selectivity and/or activity stability.

This invention therefore relates to a catalyst suitable for the epoxidation of olefins having no allylic hydrogen, in particular for the vapour phase production of ethylene oxide from ethylene and oxygen, comprising a catalytically effective amount of silver and a promoting amount of alkali metal(s) deposited on a carrier prepared by a process which comprises: a) mixing with a liquid medium in an amount sufficient to sender it stupable a mixture consisting essentially of: i) ceramic components comprising at least 80 percent by weight of alpha alumina, from 0.01 to 10 percent by weight (measured as the oxide) of an alkaline earth metal oxide, from 0.01 to 10 percent by weight (measured as the silica) of a silicon oxide, and from zero to 15 percent by weight (measured as the dioxide) of zirconium in the form of an oxide; and ii) a total amount of from zero to 15 percent by weight of ceramic bond, lubricant and/or forming aids; b) shaping the mixture to form a carrier precursor; c) drying the carrier precursor to remove the liquid from the carrier medium; and d) firing the precursor to form a carrier with a porosity of from 15 percent to 60 percent, wherein the particle sizes of the ceramic components are chosen such that the packing density of the dried precursor is not greater than that of the fired carrier.

The catalysts of the present invention comprise a catalytically effective amount of silver and a promoting amount of alkali metal supported on an alpha alumina-based catalyst carrier produced by a novel production method which does not require the presence of pore-inducing burnout materials.

The Carrier

The process provides a carrier that has no metallic oxide leachables originating from the burnout of the pore formers. Some leachables, and particularly some metallic leachables, are known to adversely affect the stability of the selectivity and/or the activity of a catalyst deposited on the carrier in that, using prior art catalysts on carriers with conventional amounts of metallic leachables, these parameters decline over time. Since the amount of leachables in organic burnout materials is subject to considerable variability, the impact on the performance from batch to batch likewise varies. Thus, predictability in performance is significantly and adversely impacted by the leachables. Leachables may arise from several sources but by eliminating one very significant source, the organic burnout material, the variability of performance impact is reduced. Moreover, while with the carriers of the present invention there is still a decline in selectivity over time, the rate of such decline is greatly reduced making the catalysts prepared using such carriers able to perform at acceptable levels for significantly longer periods.

The term "metallic leachables", as used in this specification, refers to the total amount of the elements sodium, potassium, calcium and aluminium present in the carrier measured in parts by weight per million. It can be determined by boiling a standard amount of the finished carrier in a standard volume of 10% nitric acid for 30 minutes. This extracts the metals in the form of the soluble nitrates which may then be analyzed for the residual metallic values.

The above process introduces porosity in the form of the natural porosity that results when large particles are sintered together, modified by the presence of

smaller particles that fill up some of the spaces between the larger particles until exactly the desired degree of porosity is achieved. This is in contrast to the prior art approach of forming porosity by inclusion of material subsequently burned out. As a result of the absence of the conventional burnout material, the process of the invention can also be characterized in that the loss of weight upon firing the dried extrudate is less than about 15 percent, which is the maximum amount of residual liquid carrier medium (with water this is usually about 2 percent by weight), lubricants and extrusion aids that might conventionally be used to produce such carriers.

Because there are essentially no burnout pore formers present (though some small amounts, for example up to 5 percent of the weight of the ceramic components, may be added to assist in pore forming without departing from the essence of the invention), the dried precursor of the carrier usually has a porosity that is at least 95 percent of that of the finished (fired) carrier, after making allowance for the presence of lubricants and extrusion aids. Some slight reduction of the porosity will be expected to occur upon firing as a result of the sintering together of the ceramic particles. There will, however, be no significant increase in porosity such as results when a burnout material is volatilized from the precursor.

Another indicator of the products made by the process of the invention is that the packing density, (as measured by ASTM 4699-87), is frequently less than 10 percent greater for the green, unfired carrier than for the fired carrier. Indeed, typically the density of the fired carrier is, if anything, slightly higher than that of the unfired carrier. A typical carrier made with organic burnout materials conventionally comprises 20 to 35 percent by weight, based on the weight of the ceramic

components, of material that is removed during firing and, of this amount from 50 to 75 percent is provided by the burnout materials. Thus the green packing density is typically from 8 to 15 percent greater than the density of the corresponding fired carrier materials for conventionally formed carriers. By contrast, the difference in green packing density and fired density for the products of the invention is very small and usually the green pack density is up to 2 percent greater than the unfired density. After making allowance for the presence of lubricants and extrusion aids in the unfired material, the density difference is insignificant.

Manipulation of the porosity can be achieved according to the invention in a number of ways. For example, it is possible to use a bimodal particle size distribution, consisting of relatively large particles of a first alumina component such as particles from 15 to 120 micrometer in average particle size and relatively small alumina particles of a second component with average particle sizes of from 1 to 15 micrometer. The proportions in which the components appear is dictated by the final desired porosity and the desired average pore size.

When a bimodal particle size distribution is chosen, the larger particle size component can be supplied by monolithic particles or alternatively, and sometimes preferably, they may be supplied in the form of lightly sintered alpha alumina agglomerates. This is often the form of commercial alpha alumina components which can relatively easily be comminuted to a uniform fine particle size by a conventional milling operation. The intensity of the milling required will depend largely on the degree of sintering that accompanied the conversion to the alpha phase. By initiating the process with agglomerated alumina components and then subjecting the

agglomerates to a milling operation sufficient to generate exactly the correct amount of the finer particles, a blend of particle sizes can be generated with exactly the desired porosity in the final carrier. With lightly sintered alumina agglomerates, this milling operation can be supplied by the normal mixing and extruding operations involved in producing the carrier material and this is often a preferred way of operating especially where the unmilled agglomerated product has properties that are reasonably consistent from batch to batch. Therefore in a preferred manner of operating the alumina is provided in the form of unmilled agglomerated particles having a median agglomerated particle size of from 15 to 120, more preferably from 30 to 90, and most preferably from 40 to 80 micrometer, with the particles formed upon comminution having median particle sizes of from 1 to 6, and preferably from 1.5 to 4 micrometer.

It is often preferred to use mixtures of ground alpha alumina agglomerates with known particle size distribution and unground alpha alumina agglomerates and to ensure that the production process includes no operations that could result in unacceptable reduction in the average particle size of the agglomerate components.

The particles can have any desired configuration but since the objective is to produce a carrier material with a high but uniform porosity, this is most efficiently achieved if the larger particles have a generally blocky, i.e., more nearly spherical, configuration. In the same way, the smaller particles are also preferably somewhat blocky in shape.

The material from which the carrier is made is based predominantly on alpha alumina, with at least 80 and preferably 85 or even 90 percent or more of the weight of the finished carrier being provided by alpha alumina. However minor amounts of other ceramic oxides such as

zirconia, titania, silica and/or alkaline earth metal oxides, (calcia, magnesia and strontia), may be present.

The calcium or magnesium oxide component of the carrier composition of the invention this can be present in an amount that represents from 0.01 to 10 percent by weight (measured as the oxide, MO,) of the carrier weight, but preferably the amount present is from 0.03 to 5.0 and especially from 0.05 to 2.0 percent by weight.

The calcium and magnesium compounds that may be used to prepare the carriers for the catalyst of the present invention are oxides or compounds that are decomposable to or which form oxides upon calcination. Examples include carbonates, nitrates, and carboxylates. Other suitable compounds include the oxides themselves, and mixed oxides such as the aluminates, silicates, aluminosilicates, zirconates and the like. The preferred compounds are calcium silicate and magnesium silicate.

The silicon compounds used to prepare the carriers for the catalyst of the present invention are oxides or compounds decomposable to the oxides upon calcination. Suitable compounds include silicon dioxide itself, as well as the mixed oxides such as the alkaline earth metal silicates, zirconium silicates, aluminosilicates such as zeolites, hydrolyzable silicon compounds, polysiloxanes and the like. The amount used should be such as to provide, in the final carrier composition, from 0.01 to 15.0 percent by weight, such as from 0.03 to 10.0 percent by weight and most conveniently from 0.05 to 5.0 percent by weight (measured as silica).

The zirconia component, while optional, is preferably present in an amount that is from 0.01 to 10.0 percent by weight, such as from 0.3 to 5.0 percent by weight and especially from 0.05 percent by weight to 2.0 percent by weight based on the carrier weight. Where the zirconia is

generated in situ, the amount used should be selected to give a final proportion within these parameters.

The zirconium compounds which may be used to prepare the carriers are oxides or compounds which are decomposable to or which form oxides upon calcination. Examples include carbonates, nitrates and carboxylates. Suitable compounds include zirconium nitrate, zirconium dioxide, as well as the mixed oxides such as zirconium silicates, zirconium aluminosilicates, zirconates and the like. The preferred compound is zirconium dioxide.

The alpha alumina component is most preferably combined with calcium silicate itself but, as indicated above, it is also possible to use a calcium oxide-generating compound and silica or a silica-generating compound in such proportions that on heating calcium silicate is produced. These components are mixed with zirconia or a zirconia-generating compound, (where present), a ceramic bond material, lubricants and/or extrusion aids and water, formed into shapes and calcined.

The formulation from which the carriers of the present catalyst is formed can also comprise a "binding agent" and this term, as used herein, refers to an agent that holds together the various components of the carrier prior to calcination to form an extrudable paste, i.e., the so-called low temperature binding agent. The binding agent also facilitates the extrusion process by adding lubricity. Typical binding agents include alumina gels, particularly in combination with a peptizing agent such as nitric or acetic acid. Also suitable are the carbon based materials, including celluloses and substituted celluloses such as methylcellulose, ethylcellulose and carboxyethylcellulose, stearates such as organic stearate esters, e.g. methyl or ethyl stearate, waxes, polyolefin

oxides and the like. Preferred binding agents are petroleum jelly and polyolefin oxides.

The use of calcium or magnesium silicate, whether prepared directly or formed in situ with the constraints described above, can completely replace the need for a ceramic bond component. Even where it is considered necessary to use a ceramic bond component it is often possible to use ceramic bonds containing, overall, a lower amount of silica then is present in conventional bonds. It also permits the avoidance of an excess of silicon dioxide which typically contains deleterious amounts of sodium, iron and/or potassium impurities, especially when present in clays, bentonite and the like. As is known, the avoidance of such metallic impurities is a highly desirable objective.

The role of the zirconia, where used, is not fully understood but it appears to stabilize certain partial oxidation catalyst recipes. Calcium silicate appears to stabilize at least a proportion of the zirconia in the more active tetragonal form instead of the monoclinic form to which the mixed phase reverts when heated in the absence of calcium silicate.

The carrier and catalyst prepared therefrom may comprise a number of other ceramic-forming components chosen to contribute to the desired physical properties, including crush strength and the like. For example, components such as titania in amounts of up to 5 percent by weight, are often found to confer particular advantage on such carrier materials. The titania can be added as a component of the initial mixture or it can be added to the porous calcined carrier by impregnation using a titanium salt that, for purposes of this specification, is presumed to decompose to the oxide during the firing operation.

After the components of the carrier are mixed together, for example by milling, the mixed material is formed, for example by extruding or pressing, into shaped pellets, for example, cylinders, rings, trilobes, tetralobes and the like. The formed material is dried to remove water that would convert to steam during calcination and destroy the physical integrity of the shapes. The drying and calcination can be combined in one step by suitable programming of the time and temperature. Calcining is carried out under conditions sufficient to volatilize lubricants, extrusion aids and binding agents and to fuse the alpha alumina particles into a porous, hard mass.

Calcination is typically carried out in an oxidizing atmosphere, such as oxygen gas or more preferably air and at a maximum temperature over 1300 °C and preferably ranging from 1350 °C to 1500 °C. Times at these maximum temperatures can range from 0.5 to 200 minutes.

The calcined carriers and catalysts prepared therefrom typically have pore volumes (water) ranging from 0.2 to 0.6 ml/g, and more preferably from 0.3 to 0.5 ml/g, and surface areas ranging from 0.15 to 3.0 m^2/g, and preferably from 0.3 to 2.0 m^2/g.

As indicated above, it may be necessary to add a ceramic bond material to the mixture to give added strength to the fired carrier. Conventional ceramic bond materials can be used in amounts of from 0.2 to 5 percent by weight, based on the weight of the ceramic components in the composition, and after firing these typically comprise components, (expressed as the oxides), such as silica, alumina, aluminosilicates, alkaline earth metal oxides, alkali metal oxides and minor trace amounts of iron oxide and titanium oxide, with the first two being the dominant components.

The preferred porous alpha alumina based carriers for use in the catalyst of the instant invention have a metallic leachables content below 2000 ppm and more preferably below 1000 ppm. By comparison with carriers having similar porosities and packing densities made using the same ceramic components and with conventional burnout materials, these carriers display a significantly greater selectivity stability in the oxidation of ethylene to ethylene oxide.

The carriers described above are particularly suited for preparing ethylene oxide catalysts which have improved selectivity and/or activity stability.

The Catalyst

The catalysts of the present invention comprise a catalytically effective amount of silver and a promoting amount of alkali metal(s) deposited on a carrier as described above. Other promoters in promoting amounts may be optionally present on the catalysts such as rare earths, magnesium, rhenium and rhenium co-promoters selected from sulphur, chromium, molybdenum, tungsten, phosphorus, boron and mixtures thereof.

In general, the catalysts of the present invention are prepared by impregnating the carrier with silver ions or compound(s), complex(es) and/or salt(s) dissolved in a suitable solvent sufficient to cause deposition on the support of from 1 to 40, preferably from 1 to 30 percent by weight, basis the weight of the total catalyst, of silver. The impregnated support is then separated from the solution and the deposited silver compound is reduced to metallic silver. Also deposited on the support either prior to, coincidentally with, or subsequent to the deposition of the silver will be suitable ions, or compound(s) and/or salt(s) of alkali metal dissolved in a suitable solvent. Also deposited on the carrier coincidentally with the deposition of the silver and/or

alkali metal will be suitable optional promoter compound(s), complex(es) and/or salt(s) dissolved in an appropriate solvent.

The catalysts of the present invention are prepared by a technique in which the alkali metal promoter as well as any additional promoters in the form of soluble salts and/or compounds are deposited on the catalyst and/or support prior to, simultaneously with, or subsequent to the deposition of the silver, alkali metal, and any other promoters. The preferred method is to deposit silver, alkali metal and any other promoters simultaneously on the support, that is, in a single impregnation step, although it is believed that the individual or concurrent deposition of the alkali metal prior to and/or subsequent to the deposition of the silver would also produce suitable catalysts.

Promoting amounts of alkali metal or mixtures of alkali metal are deposited on a porous support using a suitable solution. Although alkali metals exist in a pure metallic state, they are not suitable for use in that form. They are used as ions or compounds of alkali metals dissolved in a suitable solvent for impregnation purposes. The carrier is impregnated with a solution of alkali metal promoter ions, salt(s) and/or compound(s) before, during or after impregnation of the silver ions or salt(s), complex(es), and/or compound(s) has taken place. An alkali metal promoter may even be deposited on the carrier after reduction to metallic silver has taken place. The promoting amount of alkali metal utilized will depend on several variables, such as, for example, the surface area and pore structure and surface chemical properties of the carrier used, the silver content of the catalyst and the particular ions used in conjunction with the alkali metal cation, optional co-promoters. 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 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 active free alkali metals, although for convenience purposes in this specification and claims they are referred to as "alkali metal" or "alkali metal promoters" even though they are not present on the catalyst as metallic elements. Without intending to limit the scope of the invention, it is believed that the alkali metal compounds are oxidic compounds.

In a preferred embodiment, at least a major proportion (greater than 50% wt.) of the alkali metals are selected from the group consisting of potassium, rubidium, cesium, and mixtures thereof. As used herein, the term "alkali metal" and cognates thereof refers to the alkali metals selected from the group consisting of lithium, sodium, potassium, rubidium, cesium and mixtures thereof. As used herein, the term "mixtures of alkali metals" or cognates of these terms refers to the use of two or more of the alkali metals, as appropriate, to provide a promoting effect. Non-limiting examples include cesium plus rubidium, cesium plus potassium, cesium plus sodium, cesium plus lithium, cesium plus rubidium plus sodium, cesium plus potassium plus sodium, cesium plus lithium plus sodium, cesium plus rubidium plus potassium plus sodium, cesium plus rubidium plus potassium plus lithium, cesium plus potassium plus lithium and the like. A preferred alkali metal promoter is cesium. A particularly preferred alkali metal promoter is cesium plus at least one additional alkali metal. The additional alkali metal is preferably

selected from sodium, lithium and mixtures thereof, with lithium being preferred.

Non-limiting examples of other promoters include rhenium, sulphate, molybdate, tungstate and chromate (see U.S. Patent no. 4,766,105, issued August 23, 1988), as well as phosphate and borate; sulphate anion, fluoride anion, oxyanions of Groups 3b to 6b (see U.S. Patent No. 5,102,848, issued April 7, 1992); (i) oxyanions of an element selected from Groups 3 through 7b and (ii) alkali(ne) metal salts with anions of halides, and oxyanions selected from Groups 3a to 7a and 3b through 7b (see U.S. Patent no. 4,908,343, issued March 13, 1990).

There are several known methods to add the silver and promoters to the carrier or support.

One method of preparing the silver containing catalyst can be found in U.S. Patent 3,702,259, issued November 7, 1972. Other methods for preparing the silver-containing catalysts which in addition contain higher alkali metal promoters can be found in U.S. Patent 4,010,115, issued March 1, 1977; and U.S. Patent 4,356,312, issued October 26, 1982; U.S. Patent 3,962,136, issued June 8, 1976 and U.S. Patent 4,012,425, issued March 15, 1977. Methods for preparing silver-containing catalysts containing higher alkali metal and rhenium promoters can be found in U.S. Patent No. 4,761,394, issued August 2, 1988 and methods for silver-containing catalysts containing higher alkali metal and rhenium promoters and a rhenium co-promoters can be found in U.S. Patent No. 4,766,105, issued August 2, 1988. Methods for preparing silver-containing catalysts with a variety of different promoters are found in U.S. patents 4,908,343, issued March 13, 1990 and 5,057,481, issued October 15, 1991.

A particularly preferred process of impregnating the carrier consists of impregnating the carrier with an

aqueous solution containing a silver salt of a carboxylic acid, an organic amine and a salt of cesium and a salt of an additional alkali dissolved therein. Silver oxalate is a preferred salt.

The impregnated carriers are heated to a temperature between about 50 °C and about 600 °C, preferably between about 75 °C and about 400 °C to evaporate the liquid and produce a metallic silver.

In general terms, the impregnation process comprises impregnating the support with one or more solutions comprising silver, alkali metal and optional other promoters. The concentration of the silver (expressed as the metal) in the silver-containing solution will range from 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 1×10^{-3} up to 12 g/l and preferably, from 10×10^{-3} to about 12 g/l when a single impregnation step is utilized. Concentrations selected within the above noted ranges will depend upon the pore volume of the catalyst, the final amount desired in the final catalyst and whether the impregnation is single or multiple. Appropriate concentrations can be readily determined by routine experimentation.

It is observed that independent of the form in which the silver is present in the solution before precipitation on the carrier, the term "reduction to metallic silver" is used, while in the meantime often decomposition by heating occurs. We prefer to use the term "reduction", since Ag^+ ion is converted into a metallic Ag atom. Reduction times may generally vary from 0.5 to 8 hours, depending on the circumstances.

The Process

In commercial operation, ethylene and oxygen are converted to ethylene oxide in an ethylene oxide reactor

which comprises a large fixed tube heat exchanger containing several thousand tubes filled with catalysts. A coolant is used on the shell side of the reactor to remove the heat of reaction. Coolant temperatures are frequently utilized as an indication of catalyst activity, with high coolant temperatures corresponding to lower catalyst activities.

In the reaction of ethylene oxide with oxygen to produce ethylene oxide, the ethylene is typically present in at least a double amount (on a molar basis) compared with oxygen, but the amount of ethylene employed is generally much higher. The conversion is therefore conveniently calculated according to the mole percentage of oxygen which has been consumed in the reaction to form ethylene oxide and any oxygenated by-products. The oxygen conversion is dependent on the reaction temperature, and the reaction temperature at which a given conversion is reached is a measure of the activity of the catalyst employed. The value T_{40} indicates the temperature, expressed in °C, at 40 percent oxygen conversion in the reactor. 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 percent oxygen conversion.

The conditions for carrying out 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, diluent materials such as nitrogen, carbon dioxide, steam, argon, methane or other saturated hydrocarbons, to the presence of moderating agents to control the catalytic action, for example, 1-2-dichloro-

ethane, vinyl chloride, ethyl chloride or chlorinated polyphenyl compounds, to the desirability of employing recycle operations or applying successive conversions 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. Pressures in the range of from atmospheric to 3500 kPa are generally employed. Higher pressures, however, are not excluded. Molecular oxygen employed as reactant can be obtained from conventional sources. The suitable oxygen charge may consist 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 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 and which are also suitable for the instant process.

TABLE I

*GHSV	1500-10,000
Inlet Pressure	1034-2756 kPa
Inlet Feed	
Ethylene	1-40%
O_2	3-12%
Ethane	0-3%
Chlorohydrocarbon moderator	0.3-50 ppmv total
Argon and/or methane and/or nitrogen diluent	Balance
Coolant temperature	180-315 °C
Catalyst temperature	180-325 °C
O_2 conversion level	10-60%
EO Production (Work Rate)	26-325 kg/l of catalyst/hr.

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

In a preferred application of the silver catalysts according to the 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 a temperature in the range of from 200 °C to 325 °C.

While the catalysts of the present invention are preferably used to convert ethylene and oxygen to ethylene oxide, other olefins having no allylic hydrogens can be oxidized using the silver catalysts of the present invention to produce a high selectivity of epoxide derivatives thereof by contacting the olefin feed with an oxygen-containing gas in the presence of an organic halide and the silver catalyst described above under defined oxidation conditions.

The process for the selective epoxidation of olefins having no allylic hydrogens comprises contacting the feed olefin, preferably an olefin having at least 4 carbon atoms, with a sufficient quantity of an oxygen-containing gas so as to maintain the molar ratio of olefin to oxygen in the range of 0.01 up to 20, in the presence of an organic halide and a silver catalyst at a reaction pressure in the range of 10 to 10000 kPa and a temperature in the range of 75° up to 325 °C for a reaction time sufficient to obtain olefin conversions per pass in the range of 0.1 up to 75 mole percent.

Exemplary olefins having no allylic hydrogen include butadiene, tertiary butylethylene, vinyl furan, methyl vinyl ketone, N-vinyl pyrrolidone, and the like.

The process is carried out in the presence of 0.1 to 1000 parts per million (by volume of total feed) of organic halide. Preferred quantities of organic halide for use in the practice of the present invention fall within the range of 1 up to 100 parts per million, by volume of total feed.

Prior to use for oxidizing olefins having no allylic hydrogens, the silver catalysts (either before or after further treatment with promoter), are optionally calcined in an oxygen-containing atmosphere (air or oxygen-supplemented helium) at about 350C for about 4 hours. Following calcination, the silver catalysts are typically subjected to an activation treatment at a temperature in the range of 300°-350 °C in an atmosphere initially containing 2-5% hydrogen in an inert carrier such as helium or nitrogen. The hydrogen content of the activating atmosphere is gradually increased up to a final hydrogen concentration of 20-25% at a controlled rate so that the activation temperature does not exceed 350 °C. After the temperature is maintained for about

1 hour at a hydrogen concentration in the range of 20-25%, catalyst is ready for use.

More detailed descriptions of the silver catalysts and their use in oxidizing olefins having no allylic hydrogens are found in U.S. Patent Nos. 4,897,498, issued January 30, 1990 and 5,081,096, issued January 14, 1992.

The invention will be illustrated by the following Examples.

Examples

Carrier Preparation

Carriers A, C and E were prepared according to the invention, i.e., without organic burnout material. Carriers B, D and F were prepared in a manner similar to Carrier A, except that an organic burnout material was used, i.e. they were comparative carriers.

Carrier A:

Carrier A was made as follows:

An alpha alumina powder sold in the form of lightly sintered agglomerates was used. These highly agglomerated particles, having a volume average particle size of about 60 micrometer (as measures using a laser light scattering device), were subjected to a milling operation which reduced the agglomerates to the primary particles which had a median particle size of 3.0-3.4 micrometer, an average crystallite size of 1.8-2.2 micrometer and a soda content of 0.02-0.06% by weight. These milled particles were then used with agglomerated particles which had not been subjected to any previous milling operation in a 50/50 weight ratio.

The alumina component was used to prepare a formulation of the following ceramic components: 98.8% by weight alpha alumina; 1.0% by weight of zirconia; and 0.2% by weight of magnesium silicate. To this mixture were added 0.1 percent by weight of boric acid, and the components were thereafter mixed for 45 seconds. Water

was then added in an amount necessary to make the mixture extrudable. The mixture was mixed for a further 4 minutes and then 5% by weight of Vaseline was added to form an extrudable mixture. The mixture was then mixed for a further 3 minutes before being extruded in the form of hollow cylinders and dried to less than 2% uncombined water. These were then fired in a tunnel kiln with a maximum temperature of about 1385-1390 °C for about 4 hours. The carrier is described in terms of its physical properties in Table 1.

Carrier B:

Carrier B was prepared in a manner similar to Carrier A except that 25% ground walnut shells, i.e., traditional burnout material, was added to the carrier formulation, and only agglomerated particles subjected to a milling operation were used. The carrier is described in terms of its physical properties in Table 1.

Carrier C:

Carrier C was made in a manner similar to Carrier A, except that the milled particles had an average crystallite size of 1.6-2.2 μm, and calcium silicate was used in the place of magnesium silicate. The carrier is described in terms of its physical properties in Table 1.

Carrier D:

Carrier D was prepared in a manner similar to Carrier B (containing 25% ground walnut shells), except that the milled particles had an average crystallite size of 1.6-2.2 μm, and calcium silicate was used in the place of magnesium silicate (as in carrier C). The carrier is described in terms of its physical properties in Table 1.

Carrier E:

Carrier E was made in a manner similar to Carrier A, except that the highly agglomerated particles having a volume average particle size of about 62 μm, the milled particles had an average crystallite size of 1.0-1.4 μm,

the alumina component contained 98.85% by weight alpha alumina and 0.15% calcium silicate was used in the place of magnesium silicate. The carrier is described in terms of its physical properties in Table 1.

Carrier F:

Carrier F was prepared in a manner similar to Carrier B (containing 25% ground walnut shells), except that the milled particles had an average crystallite size of 1.0-1.4 μm, the alumina component contained 98.7% by weight alpha alumina and 0.3% calcium silicate was used in the place of magnesium silicate (similar to carrier E). The carrier is described in terms of its physical properties in Table 1.

TABLE 1

CARRIER PROPERTIES

PROPERTY	Carrier A	Carrier B	Carrier C	Carrier D	Carrier E	Carrier F
Fired Temp. (C)	1390	1385	1390	1390	1393	1413
Surface Area [1] (m^2/g)	0.99	0.77	0.92	0.51	0.99	0.66
Pack. Den. [2]	0.766	0.813	0.738	0.798	0.738	0.705
Water Absorp. [3] (%)	40.1	38.3	43.1	38.3	42.4	49.5
Average C.S. [4] (kg)	8.7	13.1	3.2	9.6	5.3	6.5
Leachable Na [5] (ppm)	120	128	71	188	64	48
Leachable K [5] (ppm)	44	103	28	66	32	30
Leachable Al [5] (ppm)	418	660	558	486	348	510
Leachable Ca [5] (ppm)	176	428	700	790	484	1298
Total Leachables [5]	758	1319	1357	1530	928	1886

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[1] "Surface Area" is the BET surface area measured using nitrogen or krypton as the adsorbate.

[2] "Packing Density" is the settled packing density as measured by ASTM D-4699-87, modified by the use of cylinder with an inside diameter of 9.5 cm and a length of 45.7 cm, or an equivalent.

[3] "Water Absorption" is a measure of the increase in weight of the carrier after being immersed in water and weighed.

[4] "Crush Strength" is measured on a Compton Tensile Tester, model 50-OP.

[5] "Leachables" were measured using the nitric acid solution technique.

Catalyst Preparation

The following illustrative embodiment describes preparative techniques for making the catalysts of the instant invention (Catalysts A, C and E) and the comparative catalysts (Comparative Catalysts B, D and F) and the technique for measuring the properties of these catalysts.

Part A: Preparation of stock silver oxalate/ethylene-diamine 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 (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 100 g 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 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.

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 which provides the "stock solution" used in the preparation of Catalysts A, C and E and Comparative Catalysts B, D and F below.

Part B: Preparation of impregnation solutions

For Catalyst A:

For preparing impregnated catalyst A, into a 10 millilitre (ml) beaker is added 0.188 grams of NH_4ReO_4 dissolved in approximately 2 ml of 50:50 ethylene-diamine:H_2O, 0.092 grams $Li_2SO_4H_2O$ dissolved in 1 gram water, and 0.329 grams $LiNO_3$ dissolved in 2 grams water were added to 180.3 grams of the above-prepared silver solution (specific gravity 1.54 gram/ml), and the resulting solution was diluted with 16.2 grams of water.

0.1572 Grams of stock cesium hydroxide solution containing 46.2% weight cesium was added to 50 grams of the silver oxalate/dopant solution to prepare the impregnation solution.

For Comparative Catalyst B:

For preparing impregnated comparative catalyst B, into a 10 ml beaker is added 0.161 grams NH_4ReO_4 dissolved in approximately 2 ml of 50:50 ethylene-diamine:H_2O, 0.079 grams $Li_2SO_4.H_2O$ dissolved in 1 gram water, and 0.339 grams $LiNO_3$ dissolved in 2 grams water were added to 182.7 grams of the above-prepared silver solution (specific gravity 1.55 grams/ml), and the resulting solution was diluted with 13.3 grams of water. 0.1387 grams of stock cesium hydroxide solution containing 45.5% weight cesium was added to 50 grams of the silver oxalate/dopant solution to prepare the impregnation solution.

For Catalyst C:

For preparing impregnated catalyst C, into a 10 ml beaker is added 0.149 grams NH_4ReO_4 dissolved in approximately 2 ml of 50:50 ethylenediamine:H_2O 0.073 grams $LiSO_4.H_2O$ dissolved in 1 gram water, and 0.313 grams $LiNO_3$ dissolved in 2 grams water were added to 168.8 grams of the above-prepared silver solution (specific gravity 1.55 grams/ml), and the resulting solution was diluted with 27.7 grams of water. 0.1424 Grams of stock cesium hydroxide solution containing 46.5% weight cesium was added to 50 grams of the silver oxalate/dopant solution to prepare the impregnation solution.

For Comparative Catalyst D:

For preparing impregnated comparative catalyst D, into a 10 ml beaker is added 0.166 grams of NH_4ReO_4 dissolved in approximately 2 ml of 50:50 ethylene-diamine:H_2O, 0.079 grams $Li_2SO_4.H_2O$ dissolved in 1 gram

water, and 0.342 grams $LiNO_3$ dissolved in 2 grams water were added to 181.1 grams of the above-prepared silver solution (specific gravity 1.57 grams/ml), and the resulting solution was diluted with 16.9 grams of water. 0.0939 Grams of stock cesium hydroxide solution containing 46.2% weight cesium was added to 50 grams of the silver oxalate/dopant solution to prepare the impregnation solution.

For Catalyst E:

For preparing impregnated catalyst E, into a 10 ml beaker is added 0.201 grams NH_4ReO_4 dissolved in approximately 2 ml of 50:50 ethylenediamine:H_2O, 0.096 grams $Li_2SO_4.H_2O$ dissolved in 1 gram water, and 0.103 grams $LiNO_3$ dissolved in 2 grams water were added to 182.3 grams of the above-prepared silver solution (specific gravity 1.56 grams/ml), and the resulting solution was diluted with 13.7 grams of water. 0.1779 Grams of stock cesium hydroxide solution containing 45.8% weight cesium was added to 50 grams of the silver oxalate/dopant solution to prepare the impregnation solution.

For Comparative Catalyst F:

For preparing impregnated comparative catalyst F, into a 10 ml beaker is added 0.179 grams NH_4ReO_4 dissolved in approximately 2 ml of 50:50 ethylene-diamine:H_2O, 0.086 grams $Li_2SO_4.H_2O$ dissolved in 1 gram water, and 0.092 grams $LiNO_3$ dissolved in 2 grams water were added to 166 grams of the above-prepared silver solution (specific gravity 1.56 grams/ml), and the resulting solution was diluted with 32 grams of water. 0.1195 Grams of stock cesium hydroxide solution containing 49% weight cesium was added to 50 grams of the silver oxalate/dopant solution to prepare the impregnation solution.

Part C: Catalyst impregnation and curing

Catalyst A:

Approximately 30 g of carrier A (described above in Table 1) is placed under 3.33 kPa vacuum for 3 minutes at room temperature. Approximately 50 to 60 g of doped impregnating solution (as described in Part B above under "For Catalyst A") 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 excess impregnating solution is removed from the carrier by centrifugation for 2 minutes at 500 rpm. The impregnated carrier is then cured by being continuously shaken in a 8500 l/hr. air stream flowing across a cross-sectional area of approximately 19.4-32.3 cm^3 at 240-270 °C for 3-6 minutes. The cured catalyst is then ready for testing. The properties of Catalyst A are shown in Table 2 below.

Comparative Catalyst B:

Comparative Catalyst B was prepared in the same manner as Catalyst A, except that Catalyst carrier B was used in place of Catalyst carrier A and the impregnating solution used was that described in Part B above under "For Comparative Catalyst B". The properties of Comparative Catalyst B are shown in Table 2 below.

Catalyst C:

Catalyst C was prepared in the same manner as Catalyst A, except that Catalyst carrier C was used in place of Catalyst carrier A and the impregnating solution used was that described in Part B above under "For Catalyst C". The properties of Catalyst C are shown in Table 2 below.

Comparative Catalyst D:

Comparative Catalyst D was prepared in the same manner as Catalyst A, except that Catalyst carrier D was used in place of Catalyst carrier A and the impregnating solution used was that described in Part B above under

"For Comparative Catalyst D". The properties of Comparative Catalyst D are shown in Table 2 below.

Catalyst E:

Catalyst E was prepared in the same manner as Catalyst A, except that Catalyst carrier E was used in place of Catalyst carrier A and the impregnating solution used was that described in Part B above under "For Catalyst E". The properties of Catalyst E are shown in Table 2 below.

Comparative Catalyst F:

Comparative Catalyst F was prepared in the same manner as Catalyst A, except that Catalyst carrier F was used in place of Catalyst carrier A and the impregnating solution used was that described in Part B above under "For Comparative Catalyst F". The properties of Comparative Catalyst F are shown in Table 2 below.

TABLE 2

CATALYST PROPERTIES

	Ag (wt%)	Cs (ppm)	Li_2SO_4 (μmol/g)	$LiNO_3$ (mol/g)	Re (μmol/g)
Catalyst A	13.2	738	1.8	12.0	1.8
Comp. Cat. B	13.2	645	1.5	12.0	1.5
Catalyst C	13.2	727	1.5	12.0	1.5
Comp. Cat. D	13.2	444	1.5	12.0	1.5
Catalyst E	14.5	828	2	4.0	2.0
Comp. Cat. F	14.5	599	2	4.0	2.0

Part D: Standard Microreactor Catalyst Test Conditions/Procedure

A. For Catalysts A and Comparative Catalysts B:

3 to 5 Grams of crushed catalyst (1.41-0.84 mm, i.e. 14-20 mesh) are loaded into a 5.3 inch 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. The outlet gas pressure is 1448 kPa.

The gas mixture passed thorough 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 0.5 to 6 ppmv ethyl chloride with the balance being nitrogen/argon.

The start-up procedure involved ramping the temperature from 225 °C to 245 °C in the following fashion: 1 hour at 225 °C, 1 hour at 235 °C, and 1 hour at 245 °C, and then the temperature was adjusted so as to achieve a constant oxygen conversion level of (T_{40}). The moderator level is varied and run for 4-24 hours at each level to determine maximum selectivity. 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 standard reference catalyst which was S_{40} = 81.0% and T_{40} = 230 °C.

Catalysts A and Comparative Catalyst B prepared above were tested using the above procedure, measurements were taken continuously and are reported in Table 3 below at 150 days, 200 days and 250 days to provide an indication of the selectivity stability of the catalysts over time. All selectivity values are expressed as % and all activity values are expressed as °C.

TABLE 3

CATALYST PERFORMANCE OVER TIME

	S_{40}, %			T_{40}, °C		
	150 Days	200 Days	250 Days	150 Days	200 Days	250 Days
Catalyst A	84.8	83.8	83.0	269	277	279
Comparative Catalyst B	84.8	82.6	81.5	277	281	284

B. For Catalyst C and Comparative Catalyst D:

Catalyst C and Comparative Catalyst D were tested in a manner similar to Catalyst A and Comparative Catalyst B above, except that an accelerated aging test as set forth hereinafter was utilized. After the initial performance values for selectivity and activity at 40% oxygen conversion were obtained as above, the catalysts were brought to 85% oxygen conversion or to a maximum temperature of 285 °C to a ten day period to accelerate the aging of the catalyst. After this ten day aging period, the oxygen conversion is reduced to 40% and the performance is re-optimized using the ethyl chloride moderator under standard conditions. This cycle is then repeated so that the selectivity and activity decline of the catalyst is measured under the standard 40% oxygen conversion conditions after each ten day period at 85% oxygen conversion or a maximum temperature of 285 °C. Table 4 shows the performance at 40% oxygen conversion aging for the number of days indicated at 85% oxygen conversion or a maximum temperature of 285 °C.

TABLE 4

CATALYST PERFORMANCE OVER TIME

	S_{40}, %				T_{40}, °C			
	Days				Days			
	20	40	60	80	20	40	60	80
Catalyst C	86.7	85.9	83.7	83	260	268	275	280
Comparative Catalyst D	83.8	82.4	80.5	77.8	259	265	267	275

C. For Catalyst E and Comparative Catalyst F:

Catalyst E and Comparative Catalyst F were tested in a manner similar to Catalyst A and Comparative Catalyst B above, except that a higher severity accelerated aging test as set forth hereinafter was utilized. 0.7-0.8 Grams of crushed catalyst (0.420-0.177 mm, i.e. 40-80 mesh) were loaded into a 3.8 millimetre (inside diameter) stainless steel U-shaped tube. The weight of the catalyst used and the inlet gas flow rate are adjusted to achieve a gas hourly space velocity of 16,500. The outlet gas pressure is 1448 kPa. Prior to being contacted with the reactant gases, the catalysts were treated with nitrogen gas at 225 °C for twenty-four hours.The gas mixture passed thorough the catalyst bed (in once-through operation) during the entire test run (including start-up) consists of 30% ethylene, 8.5% oxygen, 7% carbon dioxide, 54.5% nitrogen, and with 4 ppmv ethyl chloride and 4 ppmv vinyl chloride as moderators. The start-up procedure involved ramping the temperature from 225 °C to 245 °C in the following fashion: 1 hour at 225 °C, 1 hour at 235 °C, and 1 hour at 245 °C, and then the temperature was adjusted so as to achieve a constant oxygen conversion level of (T_{40}). The selectivity and activity loss relative to the initial

performance as a function of days on stream are given in Table 5 below.

TABLE 5

CATALYST SELECTIVITY AND ACTIVITY LOSS OVER TIME

	S_{40}, %				T_{40}, °C			
	Days				Days			
	10	20	30	40	10	20	30	40
Catalyst E	2.2	2.2	3.5	5.2	18	21	31	34
Comparative Catalyst F	1.8	3.5	8.5	9.0	15	25	38	41

As can be seen in the above examples and specifically in Tables 3, 4, and 5, the catalysts which were prepared without organic burnout materials, i.e., Catalysts A, C and E, have improved selectivity stabilities over catalysts which were prepared using organic burnout materials, i.e., Comparative Catalysts B, D and F.



C L A I M S

1. A catalyst suitable for the epoxidation of olefins having no allylic hydrogen, in particular for the vapour phase production of ethylene oxide from ethylene and oxygen, comprising a catalytically effective amount of silver and a promoting amount of alkali metal(s) deposited on a carrier prepared by a process which comprises: a) mixing with a liquid medium in an amount sufficient to sender it stupable a mixture consisting essentially of: i) ceramic components comprising at least 80 percent by weight of alpha alumina, from 0.01 to 10 percent by weight (measured as the oxide) of an alkaline earth metal oxide, from 0.01 to 10 percent by weight (measured as the silica) of a silicon oxide, and from zero to 15 percent by weight (measured as the dioxide) of zirconium in the form of an oxide; and ii) a total amount of from zero to 15 percent by weight of ceramic bond, lubricant and/or forming aids; b) shaping the mixture to form a carrier precursor; c) drying the carrier precursor to remove the liquid from the carrier medium; and d) firing the precursor to form a carrier with a porosity of from 15 percent to 60 percent, wherein the particle sizes of the ceramic components are chosen such that the packing density of the dried precursor is not greater than that of the fired carrier.

2. The catalyst of claim 1 wherein, in the carrier, the ceramic components of the mixture comprise at least 85 percent by weight of alpha alumina, from 0.01 to 6.0 percent by weight of an alkaline earth metal silicate selected from the group consisting of calcium and magnesium silicates and from 0.01 to 10 percent by weight of zirconia.

3. The catalyst of claim 1 wherein, in the carrier, the alpha alumina component has a bimodal particle size distribution with a first mode having an average particle size of from 15 to 120 micrometer and a second mode having an average particle size that is less than one-half that of the first mode and is between 1 and 15 micrometer.

4. The catalyst of claim 1 wherein, in the carrier, the alpha alumina component selected comprises lightly sintered agglomerates with a median particle size of from 15 to 120 micrometer.

5. The catalyst of claim 4 wherein, in the carrier, the alpha alumina component selected comprises lightly sintered agglomerates with a median particle size of from 30 to 90 micrometer.

6. The catalyst of claim 1 wherein, in the carrier, the ceramic components further comprise a compound that forms titania when the carrier is fired in an amount sufficient to provide the equivalent of from 0.01 to 5 percent by weight of titania.

7. The catalyst of claim 1 wherein the silver ranges from 1 to 40 percent by weight of the total catalyst and the alkali metal ranges from 10 to 3000 parts per million, expressed as the metal, by weight of the total catalyst.

8. The catalyst of claim 7 wherein said alkali metal promoter is selected from the group consisting of potassium, rubidium, cesium, lithium and mixtures thereof.

9. The catalyst of claim 1 wherein the catalyst additionally comprises a promoting amount of rhenium, and optionally a rhenium co-promoter selected from the group consisting of sulphur, molybdenum, tungsten, chromium, phosphorus, boron and mixtures thereof.

10. A process for the epoxidation of olefins having no allylic hydrogens wherein an olefin having no allylic hydrogen is contacted in the vapour phase with an oxygen-containing gas at epoxide forming conditions at a temperature in the range of from 75 °C to 325 °C in the presence of an organic halide and a catalyst according to claim 1.

11. A process for the production of ethylene oxide wherein ethylene is contacted in the vapour phase with an oxygen-containing gas at ethylene oxide forming conditions at a temperature in the range of from 180 °C to 330 °C in the presence of a catalyst according to claim 1.