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EPOXIDATION CATALYST AND PROCESS

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

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

The use of alumina-based catalyst carriers has been previously described in a number of patents such as, for example, 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. These alumina carriers have a wide variety of potential applications in the catalytic field and are especially useful where the alumina base is alpha alumina and the application is one in which abrasion resistance is a desirable feature.

This invention relates to a catalyst suitable for the epoxidation of olefins having no allylic hydrogen, in particular ethylene, with oxygen in the vapour phase which catalyst comprises a catalytically effective amount of silver and a promoting amount of alkali metal supported on an alpha alumina based carrier having a crush strength of at least 2.3 kg and a settled packing density of at least 0.48 kg/litre which comprises first and second alpha alumina components with a first alpha alumina component in the form of particles having a median crystallite size of from 0.4 to 4 μm providing from 95% to 40% of the total weight of alpha alumina in the carrier and a second alpha alumina component generated in situ by a sol-gel process and providing the balance of the alpha alumina in the carrier.

It has been found that catalysts having this unique alumina carrier have improved selectivities and/or activities over catalysts having conventional alumina carriers. These catalysts also have improved selectivity stabilities and/or activity stabilities.

Descriptions of the carrier, the catalyst prepared with the carrier and the use of the catalyst are provided in detail below.

The Carrier

The catalyst carrier in the present invention is a novel alpha alumina based catalyst carrier having a crush strength, (as measured on a Compton Tensile Tester, model 50-OP), of at least 2.3 kg and a settled packing density, (as measured by ASTM D-4699-87, modified by the use of a

cylinder with an inside diameter of 9.52 cm and a length of 45.7 cm), of at least 0.48 kg/litre, preferably at least 0.56 kg/litre, and more preferably at least 0.61 kg/litre, which comprises first and second alpha alumina components with a first alpha alumina component in the form of particles having a median crystallite size of from 0.4 to 4 μm providing from 95% to 40%, preferably from 95% to 65% of the total weight of alpha alumina in the carrier and, and a second alpha alumina component generated in situ by a sol-gel process and providing the balance of the alpha alumina in the carrier.

As used herein, the term "sol-gel process" refers to a process which comprises heating an alumina sol and/or gel (i.e, hydrated alumina) to a temperature which converts at least a portion of the alumina sol and/or gel to an alumina having the corundum crystalline structure (i.e., a hexagonal close-packed structure). Temperatures of at least 400°C, preferably above 1100°C, and more preferably from 1100°C to 1500°C, are generally used for the conversion.

The catalyst carrier is prepared by a process which comprises:

a) forming a mixture comprising:

i) at least one alpha alumina component with a median particle size of from 3 to 8 μm and;

ii) a hydrated precursor of alpha alumina in an amount sufficient to provide from 5% by weight to 60% by weight of the total weight of alpha alumina in the catalyst carrier product;

iii) from 5% to 40%, based on the weight of the alpha alumina, of a burnout material; and

iv) water in sufficient quantity to extrude the above mixture;

b) extruding the mixture into the desired shapes; and

c) firing to convert the precursor of alpha alumina to

alpha alumina so as to produce a catalyst carrier in which alpha alumina particles with a median particle size of from 3 to 8 μm are dispersed in a matrix of alpha alumina derived from the precursor material.

The catalyst carrier may be composited with a number of alpha alumina constituents chosen to contribute to the desired physical properties, including porosity, pore volume, crush strength and the like. Often a combination of two different alpha aluminas is preferred, with a first constituent having larger particles mixed with a second constituent having smaller particles, in weight ratios of from 10:90 to 90:10. The first constituent typically comprises from 10% to 90%, preferably from 40% to 80%, by weight of the first alpha alumina component, and the second constituent typically comprises from 10% to 90%, preferably from 20% to 60%, by weight of the first alpha alumina component. The objective of this is to end up with a surface area in the final calcined carrier of from 0.4 to 5 m^2/g. As used herein, "surface area" is used to refer to the BET surface area measured using nitrogen or krypton as the adsorbed gas. The surface area in the finished carrier is somewhat less than for the free alumina particles. Thus, a convenient mixture may comprise, for example, two types of alpha alumina particles, the first having a surface area of 0.9 to 1.4 and preferably 1 m^2/g, a median particle size of from 2 to 4 and preferably 3 to 3.4 μm and a median crystallite size of from 1.6 to 2.2 μm; and the second having a surface area of 3 to 5 m^2/g, a median particle size of from 4 μm to 8 μm, and a median crystallite size of from 0.4 to 0.8 μm.

The hydrated precursor of alpha alumina is preferably based on a monohydrate such as boehmite, but good results are also obtained if the precursor comprises a mixture of boehmite with an aluminium trihydrate such

as gibbsite or bayerite. Where such a mixture is used it is often preferred to use a weight ratio of the monohydrate, (boehmite), to trihydrate of from 1:10 to 1:3 and more preferably from 1:8 to 1:4. When the precursor of alpha alumina contains alumina trihydrate, it typically contains from 10% to 35% by weight of alumina trihydrate, based on the total weight of alpha alumina in the carrier. Although other alumina trihydrates can be utilized, the alumina trihydrate most frequently utilized is gibbsite having a median particle size of from 4 to 20 μm.

In a preferred embodiment, the hydrated precursor of alpha alumina is seeded. The seed used can be any material that is effective to produce nucleation sites in the precursor so as to reduce the transition temperature at which a transition alumina converts to alpha alumina. Seeds that accomplish this goal generally have the same crystal lattice type as alpha alumina itself and lattice dimensions that do not differ by too much from those of alpha alumina. Clearly the most convenient seed is alpha alumina itself and sub-μm sized particles of alpha alumina are the preferred seed. In a preferred embodiment, the alpha alumina seed has a median particle size of less than 0.1 micro-meter, and comprises from 0.2% to 5% by weight based on the total weight of alumina, measured as alpha alumina, in the catalyst carrier. It is however possible to use other seeds such as alpha ferric oxide and chromium oxide and certain complex oxides of titanium.

The alpha alumina formed from the seeded precursor when the extruded mixture is fired generally has a much finer crystal size than the alpha alumina particles with which the seeded precursor is mixed unless, during firing, it is maintained at a high temperature for a prolonged period. As produced, the seeded sol-gel

material has a sub-μm crystal structure, but if it is held at temperatures over 1400°C for extended periods, crystal growth begins and the size differentiation may become less apparent.

The final calcined carrier preferably has a porosity of at least 50% and more desirably from 60% to 75%, a crush strength of at least 2.3 kg, and a settled packing density of at least 0.5 kg per litre, preferably at least 0.6 kg litre. The surface area of the final calcined carrier is preferably from 0.4 to 5 m^2/g, and more preferably from 0.6 to 1.2 m^2/g.

It is often found advantageous to add titania to the mixture to be extruded in an amount that represents from 0.05% to 1%, preferably from 0.05% to 0.5%, more preferably from 0.08% to 0.40%, and most preferably, from 0.08% to 0.25%, of the weight of the fired carrier. Certain forms of alumina and bond material may also contain titania as impurities or components. The contribution of such forms of titania are not included in the amounts specified above. The titania can be added as the dioxide, as a titanate or as a precursor of titania. In the following description, all of the above options are understood to be included under the term "titania". It is believed that the titania may function as a form of crystal growth inhibitor in the alpha alumina formed as a result of the conversion of the seeded precursor. It may be anticipated therefore that other such materials such as, for example, zirconia or magnesia, which can act in this capacity might have utility as replacements for titania. It is believed that complex solid state reactions between alumina/bond, impurities and titania added to the carrier occur and result in increased strength and density of the carrier.

The titania is preferably in the form of a powder with a relatively high surface area, i.e., at least 8 and

preferably from 8 to 300 m^2/g. In practice, the preferred titanias have an amorphous or anatase structure. While not wishing to be bound by any theory, it is believed that the rutile structure of titania does not generally show the advantages which can be obtained with the amorphous and anatase structures of titania because it typically has a much smaller surface area. Commercial pigment grades of titania can also give good results.

The carrier alumina components are then typically mixed with a burnout and/or binding agent and water, formed into shapes and calcined.

The burnout agent is a material that is added to the mixture such that upon calcination, it is completely removed from the carrier, leaving a controlled porosity in the carrier. These materials are carbonaceous materials such as coke, carbon powders, graphite, powdered plastics such as polyethylene, polystyrene and polycarbonate, rosin, cellulose and cellulose based materials, sawdust and other plant materials such as ground nut shells, e.g. pecan, cashew, walnut and filbert shells. Carbon-based burnout agents can also serve as binding agents. The burnout agents are provided in an amount and size distribution to provide a final carrier having a water pore volume (water absorption) ranging from 0.2 to 0.6 ml/g, preferably 0.3 to 0.5 ml/g. The burnout agents typically comprise from 5% to 40% by weight, based on the weight of alpha alumina in the carrier. Preferred burnout agents are cellulose-derived materials, such as ground nut shells.

The term "binding agent" as used herein refers to an agent that holds together that various components of the carrier after they have been shaped into the final form, say by extrusion or pelleting. These binding agents allow the shaped materials to be dried and calcined without

crumbling. Such binding agents are usually "sticky" organic materials such as polyvinyl alcohols or cellulosic materials. Binding agents may also serve as extrusion aids. In certain cases peptizing acids may be used in lieu of binding agents.

While it would appear that the alpha alumina formed from the seeded precursor acts in some sense as a matrix binder holding the rest of the alpha alumina particles together, it is usually preferred to add a ceramic bond material to the mixture to give added strength to the fired carrier. The ceramic bond material is typically present in an amount of from 1% to 3% by weight based on the total weight of the alumina components, expressed as alpha alumina. Conventional ceramic bond materials can be used and after firing these typically comprise components, (expressed as the oxides), such as silica, alumina, alkali metal oxides, alkaline earth metal oxides, iron oxide and titanium oxide, with the first two being the dominant components. In a preferred embodiment, the ceramic bond comprises the following components, expressed as the oxides, in the following approximate proportions: 60% wt. silica, 29% wt. alumina, 3% wt. calcium oxide, 2% magnesia, 4% wt. alkali metal oxides and less than 1% wt. each of ferric oxide and titania.

After the components of the carrier are mixed together, say by mulling, the mixed material is extruded into shaped pellets, for example, cylinders, rings, trilobes, tetralobes and the like. "Extrusion aids" such as Vaseline Petroleum Jelly and other organic lubricating materials may be used to facilitate extrusion. The extruded material is dried to remove water that could convert to steam during calcination and destroy the extrudate shapes. After drying to a low water content, i.e., less than 2%, the extruded material is calcined

under conditions sufficient to remove burnout agents, 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, say oxygen gas or preferably air and at a maximum temperature greater than 1300°C and preferably ranging from 1350°C to 1500°C. Times at these maximum temperatures typically range from 0.1 to 10, preferably from 0.5 to 5 hours.

The calcined carriers and catalysts made therefrom will typically have pore volumes (water) ranging from 0.2 to 0.6, preferably from 0.3 to 0.5 ml/g and surface areas ranging from 0.15 to 3, preferably from 0.3 to 2 m^2/g.

The carrier formulation preferably has a low soda content which is less than 0.06% by weight. In practice it is very difficult to obtain a sodium-free formulation and soda contents from 0.02 to 0.06% by weight are usually found acceptable.

The carriers described above are particularly suited for preparing ethylene oxide catalysts which have high initial selectivities.

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 such as rare earths, magnesium, rhenium and rhenium co-promoters selected from sulphur, chromium, molybdenum, tungsten and mixtures thereof.

In general, the catalysts of the present invention are prepared by impregnating porous refractory supports comprising alpha alumina 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 and each other. The preferred method is to deposit silver and alkali metal 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 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 and more preferably, between 20 and 1500 parts per million by weight of total catalyst. Most preferably, the amount ranges between 50 and 1000 parts per million by weight of the total catalyst.

For purposes of convenience, the amount of alkali metal deposited on the support or present on the catalyst is expressed as the metal. Without intending to limit the scope of the invention, it is believed that the alkali metal compounds are oxidic compounds. More particularly, it is believed that the alkali metal compounds are 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% wt.) of the alkali metals are 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. The additional alkali metal is preferably selected from sodium, lithium and mixtures thereof, with lithium being preferred.

It should be understood that the amounts of alkali metal promoters on the catalysts are not necessarily the total amounts of these metals present in the catalyst. Rather, they are the amounts of alkali metal promoters which have been added to the catalyst by impregnation with a suitable solution of ions, salts and/or compounds and/or complexes of alkali metals. These amounts do not include amounts of alkali metals which are locked into the support, for example, by calcining, or are not extractable in a suitable solvent such as water or lower alkanol or amine or mixtures thereof and do not provide a promoting effect. It is also understood that a source of the alkali metal promoter ions, salts and/or compounds used to promote the catalyst may be the carrier. That is, the carrier may contain extractable amounts of alkali metal that can be extracted with a suitable solvent, such as water or lower alkanol, thus preparing an impregnating solution from which the alkali metal ions, salts and/or compounds are deposited or redeposited on the support.

The catalyst may also contain moderating amounts of chloride for purposes of enhancing the start-up procedure for the catalysts. When chloride is added to the catalyst, the carrier can be impregnated with a solution of chloride moderator 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 and before, during or after impregnation of the promoter ions or salt(s), complex(es), and/or compound(s) has taken place. The chloride moderator may even be deposited on the carrier after reduction to metallic silver has taken place. Suitable chloride-containing salts used to prepare the impregnating solutions include promoter chlorides such as lithium chloride, sodium chloride, potassium chloride, rubidium chloride and cesium chloride as well as ammonium chloride. Ammonium

chloride is a preferred salt for use in preparing the chloride-containing impregnating solutions. Other compounds which decompose to the chloride ion upon processing of the catalyst are also suitable. The chloride-containing impregnating solutions will normally contain at least a small amount of water to enhance solubility of the chloride-containing salt or compound. Other promoters and co-promoters can be used in conjunction with the silver and alkali metal promoters.

Non-limiting examples of other promoters include rhenium, sulfate, molybdate, tungstate and chromate (see U.S. Patent No. 4,766,105); sulfate anion, fluoride anion, oxyanions of Groups 3b to 6b (see U.S. Patent No. 5,102,848); (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).

The thus obtained impregnated carrier is heated to reduce the silver to metallic silver. It is conveniently heated to a temperature in the range of from 50°C to 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 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 No. 4,761,394, 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. Methods for preparing silver-containing catalysts with a variety of different promoters are found in U.S. patents 4,908,343 and 5,057,481.

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 x 10^{-3} g/l up to 12 g/l and preferably, from 10 x 10^{-3} g/l to 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.

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 about 0.5 minute to about 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

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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 is a measure of the activity of the catalyst employed. The value T_{40} indicates the temperature at 40 percent oxygen conversion in the reactor and the value T is expressed in °C. This temperature for any given catalyst is higher when the conversion of oxygen is higher. Moreover, this temperature is strongly dependent on the employed catalyst and the reaction conditions. 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-dichloroethane, vinyl chloride, ethyl chloride or chlorinated polyphenyl compounds, to the desirability of

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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	1000-3800 kPa
Inlet Feed Ethylene O_2 Ethane Chlorohydrocarbon moderator Argon and/or methane and/or nitrogen diluent	 1-40% 3-12 0-3% 0.3-50 ppmv total Balance
Coolant temperature	180-315 °C
Catalyst temperature	180-325 °C
O_2 conversion level	10-60%
EO Production (Work Rate)	32-400 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 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 from 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, 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

Carrier Preparation

Carrier A:

The ceramic components are mixed with a burn-out material (walnut shell flour) and boric acid for about a minute. Water and the seed component are then added, the water being added in an amount that is necessary to make the mixture extrudable. Generally this is about 30% by weight of the total solids present. The mixture is mixed for two to four minutes and then 5% by weight of petroleum gelly (Vaseline (Vaseline is a trademark)) based on the weight of the ceramic components, is added as an extrusion aid. The mixture is then mixed for a further 2 to 4 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 1500 °C for about 4 hours. The carrier is described in terms of its formulation in Table I and in terms of its physical properties in Table II.

Carrier B:

Carrier B was prepared in a manner similar to Carrier

A except that titania was added to the carrier formulation. The carrier is described in terms of its formulation in Table I and in terms of its physical properties in Table II.

Carrier C:

Carrier C was prepared in a manner similar to Carrier A except that the carrier contains no alpha alumina component generated by a sol-gel process, and no seed component, i.e., Alpha Alumina #5, was added to the carrier formulation. The carrier is described in terms of its formulation in Table I and in terms of its physical properties in Table II.

Carrier D:

Carrier D was prepared in a manner similar to Carrier A except that the carrier contains no alpha alumina component generated by a sol-gel process, and no seed component, i.e., Alpha Alumina #5, was added to the carrier formulation. The carrier is described in terms of its formulation in Table I and in terms of its physical properties in Table II.

TABLE II

CARRIER COMPOSITIONS

	Carrier A, % wt	Carrier B, % wt	Carrier C, % wt	Carrier D, % wt
Alpha Alumina #1[1,2]	46.6	46.6	None	98.8
Alpha Alumina #2[1,3]	28.0	28.0	None	None
Alpha Alumina #3[1,4]	None	None	74	-
Alpha Alumina #4[1,5]	None	None	25	-
Alpha Alumina # 5 (Seed)[1,6]	0.9	0.9	None	None
TiO_2[1]	None	0.2	None	None
ZrO_2[1]	None	None	None	1
Gibbsite[1,7]	18.7	18.7	None	None
Boehmite [1,8]	4.5	4.5	None	None
Ceramic Bond[1,9,11,12]	1.3	1.3	1.0	0.2
Organic Burnout[10]	11.0	11.0	30	28
Vaseline[10]	5.0	5.0	5	5
Boric Acid[10]	0.15	0.15	0.1	0.1
Water (to make extrudable)[13]	~30	~30	~30	~30

1 Indicates "ceramic components" and percentages given are based on 100% of the ceramic components.

2 "Alpha Alumina #1" is an alpha alumina that had a median particle size of 3 to 3.4 µm, a BET surface area of 0.9 to 1.4 m^2/g, a crystallite size of 1.6 to 2.2 µm and a soda content of 0.02% to 0.06%.

3 "Alpha Alumina #2" is an alpha alumina with a median particle size of 4.0 to 8.0 μm, a surface area of 3.0 to 5.0 m^2/g, a crystallite size of from 0.4 to 0.8 μm and a soda content of 0.1% to 0.3%.

4 "Alpha Alumina #3" is an alpha alumina that had a median particle size of 3.6 to 4.2 μm, a BET surface area of 0.8 to 1.0 m^2/g, a crystallite size of 3 to 4 μm and a soda content of 0.05%.

5 "Alpha Alumina #4" is an alpha alumina that had a median particle size of 2.5 to 3.5 μm, a BET surface area of 3 to 4 m^2/g, a crystallite size of 3 to 4 μm and a soda content of 0.1%.

6 "Alpha Alumina #5" is an alpha alumina that was used as the seed for the gibbsite and boehmite precursors of alpha alumina. Its median particle size was less than 0.1 μm.

7 The gibbsite had a median particle size of from 4.0 to 20 μm.

8 The boehmite was dispersible as a sol.

9 The ceramic bond for carriers A and B contained components, expressed as the oxides, in the following approximate proportions: 60% wt. silica, 29% wt. alumina, 3% wt. calcium oxide, 2% magnesia, 4% wt. alkali metal oxides and less than 1% wt. each of ferric oxide and titania.

10 Percentages are based on the total weight of the ceramic components.

11 The ceramic bond for Carrier C contained components, expressed as oxides, in the following approximate proportions: 67% wt. silica, 30% wt. alumina, about 1% wt. each of ferric oxide and titania, and a trace of alkali metal and alkaline earth oxides.

12 The ceramic bond used for Carrier D was calcium silicate.

13 Percentages are based on total weight of solids.

TABLE III

CARRIER PROPERTIES

	Carrier A	Carrier B	Carrier C	Carrier D
Water Absorption, % [1]	44.5	38.3	46.4	41.5
Packing Density, kg/litre	0.737	0.815	0.720	0.774
Crush Strength, kg[3]	6.350	6.758	7.711	9.979
Surface Area, m^2/g[4]	0.97	1.01	0.51	0.50
Acid Leachables, ppm	217	350	42	50.5
Na	80	76	30	41
K	189	149	n.a.	850
Ca	520	579	n.a.	534
Al				
TiO_2, %	None	0.2	None	None
Firing Temperature, °C	1480	1450	1420	1390

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

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 88 mm and a length of 45.7 cm, or an equivalent.

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

4 "Surface Area" is the BET surface area measured using

nitrogen or krypton as the adsorbate.

Catalyst Preparation

The following illustrative embodiment describes preparative techniques for making the catalysts of the instant invention (Catalysts A, B, C, D, and F) and the comparative catalysts (Comparative Catalysts E and G) and the 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 g of reagent-grade sodium hydroxide in 2340 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, B, C, D and F and Comparative Catalysts E and G below.

Part B: Preparation of impregnation solutions

For Catalyst A:

161.3 Grams of silver stock solution with a specific gravity of 1.543 was diluted with 4.2 grams of water and 13.5 grams of monoethanolamine. 0.0350 Grams of NH_4F were dissolved in 2 ml of water and added to the silver solution. CsOH (50% solution in water) in an amount of 0.1367 grams was added to 60 grams of the above diluted silver solution and the resulting mixture was used for the carrier impregnation.

For Catalyst B:

175.4 Grams of silver stock solution with a specific gravity of 1.53 was diluted with 3.6 grams of water. 0.0387 Grams of NH_4F were dissolved in 2 cc of water and added to the silver solution. CsOH (50% solution in water) in an amount of 0.1536 grams was added to 60 grams of the above diluted silver solution and the resulting mixture was used for the carrier impregnation.

For Catalyst C:

165.3 Grams of silver stock solution with a specific

gravity of 1.55 was diluted with 13.9 grams of monoethanolamine. 0.0426 Grams of NH_4F were dissolved in 2.5 grams of water and added to the silver solution. CsOH (50% solution in water) in an amount of 0.1406 grams was added to 60 grams of the above diluted silver solution and the resulting mixture was used for the carrier impregnation.

For Catalyst D:

161.2 grams of silver stock solution with a specific gravity of 1.555 was diluted with 17.8 grams of water. 0.0868 Grams of $(NH_4)ReO_4$ were dissolved in 2 cc of water/EDA mixture (50/50 by weight) and added to the silver solution. CsOH (50% solution in water) in an amount of 0.1743 grams was added to 60 grams of the above diluted silver solution and the resulting mixture was used for the carrier impregnation.

For Comparative Catalyst E:

129.7 Grams of silver stock solution containing 29.7% Ag was diluted with 14 grams of water and 6.3 grams of monoethanolamine. 0.0285 Grams of NH_4F were dissolved in 2 ml of water and added to the silver solution. CsOH (50% solution in water) in an amount of 0.0582 grams was added to 50 grams of the above diluted silver solution and the resulting mixture was used for the carrier impregnation.

For Catalyst F:

168.1 Grams of silver stock solution with a specific gravity of 1.546 was diluted with 10.9 grams of water. 0.1442 Grams of $(NH_4)ReO_4$, 0.0704 grams of $Li_2SO_4.H_2O$, 0.303 grams of $LiNO_3$ were dissolved in approximately 2.0 ml of ethylenediamine/H_2O (50/50 by weight) and added to the silver solution. CsOH (50% solution in water) in an amount of 0.1985 grams was added to 50 grams of the above diluted silver solution and the resulting mixture was used for the carrier impregnation.

For Comparative Catalyst G:

101 Grams of silver stock solution with a specific gravity of 1.558 was diluted with 12.9 grams of water. 0.0766 Grams of $(NH_4)ReO_4$, 0.0374 grams of $Li_2SO_4.H_2O$, 0.1616 grams of $LiNO_3$ were dissolved in approximately 2.0 grams of ethylenediamine/H_2O (50/50 by weight) and added to the silver solution. CsOH (50% solution in water) in an amount of 0.111 grams was added to 50 grams of the above diluted silver solution and the resulting mixture was used for the carrier impregnation.

Part C: Catalyst impregnation and curing

Catalyst A:

Approximately 30 g of carrier A (described above in Tables II and III) is placed under 25 mm 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 25 mm 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. If the impregnating solution is prepared without monoethanolamine, then the impregnated carrier is then cured by being continuously shaken in a 850 litre/hr. air stream flowing across a cross-sectional area of approximately 19.4-32.3 cm^2 at 240-270°C for 3-6 minutes. If significant monoethanolamine is present in the impregnating solution, then the impregnated carrier is cured by being continuously shaken in a 850 litre/hr. air stream at 250°C to 270°C for 4-8 minutes. The cured catalyst is then ready for testing.

The properties of Catalyst A are shown in Table IV below.

Catalyst B:

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 Catalyst B". The properties of Catalyst B are shown in Table IV below.

Catalyst C:

Catalyst C was prepared using a double impregnation technique. In this technique 120 g of Catalyst carrier B was impregnated with 240 g of silver stock solution with a specific gravity of 1.555. The impregnated carrier was dried/roasted to decompose silver salts to metallic silver. Water pore volume was determined after the first impregnation and was used to calculate the dopant concentrations. The second impregnation was carried out with the impregnating solution described in the Part B above under "For Catalyst C". The catalyst was cured in a manner similar to that described above. The properties of Catalyst C are shown in Table IV below.

Catalyst D:

Approximately 30 g of carrier A (described above in Tables II and III) is placed under 25 mm 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 D") is then introduced to submerge the carrier, and the vacuum is maintained at 25 mm 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. If the impregnating solution is prepared without monoethanolamine, then the impregnated carrier is then cured by being continuously shaken in a 850 litre/hr. air stream flowing across a cross-sectional area of approximately 19.4-32.3 cm^2 square inches at 240-270°C for 3-6 minutes. If significant monoethanolamine is present in the impregnating solution, then the

impregnated carrier is cured by being continuously shaken in a 850 litre/hr. air stream at 250°C to 270°C for 4-8 minutes. The cured catalyst is then ready for testing. The properties of Catalyst D are shown in Table IV below.

Comparative Catalyst E:

Comparative Catalyst E 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 Comparative Catalyst E". The properties of Comparative Catalyst E are shown in Table IV below.

Catalyst F:

Catalyst F was prepared in the same manner as Catalyst D, 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 Catalyst F". The properties of Catalyst F are shown in Table IV below.

Comparative Catalyst G:

Comparative Catalyst G was prepared in the same manner as Catalyst D, 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 G". The properties of Comparative Catalyst G are shown in Table IV below.

TABLE IV

CATALYST COMPOSITION

	Ag, wt%	Cs, ppm	Re, ppm
Catalyst A	14.5	596	None
Catalyst B	14.5	601	None
Catalyst C	26.6	500	None
Catalyst D	14.5	752	186
Comparative Catalyst E	14.5	285	None
Catalyst F	13.5	699	279
Comparative Catalyst G	13.2	493	279

The actual silver content of the catalyst can be determined by any of a number of standard, published procedures. 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 equivalent).

Part D: Standard Microreactor Catalyst Test Conditions/Procedure

A. For Catalysts A, B, C and Comparative Catalyst E:

1 to 3 Grams of crushed catalyst of 0.841-0.595 mm (20-30 mesh) are loaded into a 6.4 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 6800. The outlet gas pressure is 1550 kPa.

The gas mixture passed thorough the catalyst bed (in once-through operation) during the entire test run (including start-up) consists of 25% ethylene, 7% oxygen, 5% carbon dioxide, 1.25 to 5 ppmv ethyl chloride with the balance being nitrogen/argon.

The start-up procedure involved ramping the temperature from 180°C to 230°C in the following fashion: 1 hour at 180°C, 1 hour at 190°C, 1 hour at 200°C, 1 hour at 210°C, 1 hour at 220°C, 2 hours at 220°C, 2 hours at 225°C, 2 hours at 230°C, and then the temperature was adjusted to provide 1.5% ethylene oxide at the reactor outlet. Catalyst selectivity ($S_{1.5}$) and catalyst activity ($T_{1.5}$) were measured at those conditions.

To allow meaningful comparison of the performance of catalysts tested at different times, the Catalysts A, B, C and Comparative Catalyst E were tested simultaneously with a standard reference catalyst which was $S_{1.5}$ = 81.7% and $T_{1.5}$ = 235°C.

Catalysts A, B, C and Comparative Catalyst E prepared above were tested using the above procedure and the results are given in Table V below.

B. For Catalyst D:

Catalyst D was tested in a manner similar to that described for Catalysts A, B, C and Comparative Catalyst E above, except that start-up procedure is as follows. The initial reactor (heat medium) temperature is 225°C.

After 3 hours under nitrogen flow at this initial temperature, the temperature is increased to 235°C for 1 hour, followed by 245°C for 1 hour. The temperature was then adjusted to 1.5% ethylene oxide in the reactor outlet. The results are given in Table V below.

TABLE V

CATALYST PERFORMANCE

	$S_{1.5}$, %	$T_{1.5}$, °C
Catalyst A	82.0	226
Catalyst B	82.9	217
Catalyst C	82.0	220
Catalyst D	84.0	233
Comparative Catalyst E	81.2	230

As can be seen from Table V, the initial selectivities of Catalysts A, B, C and D are improved over the initial selectivity of Comparative Catalyst E. It can also be seen that the initial activities of Catalysts A, B and C are improved over that of Comparative Catalyst E.

C. For Catalyst F and Comparative Catalyst G:

3 to 5 Grams of crushed catalyst (14-20 mesh) are loaded into a ¼ 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 210 psig.

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, 1.5 to 5 ppmv ethyl chloride with the balance being nitrogen/argon.

Prior to being contacted with the reactant gases, the catalysts are typically pretreated with nitrogen gas at 225°C for 3 hours for all fresh catalysts and for 24 hours or longer for aged, but untested catalysts.

The initial reactor (heat medium) temperature is 225° C. After 1 hour at this initial temperature, the temperature is increased to 235°C, followed by 245°C for 1 hour. The temperature is then adjusted so as to achieve a constant oxygen conversion of 40% (T_{40}). The moderator level is varied for 4-24 hours at each level to determine the optimum moderator level and at T_{40} and S_{40} are usually obtained when the catalyst has been onstream for a total of about 24 hours and are provided in Table V below. 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_0} = 230°C.

Catalysts F and Comparative Catalyst G prepared above were tested using the above procedure and the results are given in Table VI below.

TABLE VI

CATALYST PERFORMANCE

	S_{40}, %	T_{40}, °C
Catalyst F	87.2	249
Comparative Catalyst G	86.5	262

As can be seen from Table VI, the initial selectivity and the initial activity of Catalyst F is improved over the initial selectivity and the initial activity of Comparative Catalyst G.

C L A I M S

1. A catalyst suitable for the vapour phase epoxidation of olefins having no allylic hydrogen, in particular ethylene, with oxygen, which catalyst comprises a catalytically effective amount of silver and a promoting amount of alkali metal deposited on a carrier having a crush strength of at least 2.3 kg and a settled packing density of at least 0.48 kg/litre which comprises first and second alpha alumina components with a first alpha alumina component in the form of particles having a median crystallite size of from 0.4 to 4 µm providing from 95% to 40% of the total weight of alpha alumina in the carrier and a second alpha alumina component generated in situ by a sol-gel process and providing the balance of the alpha alumina in the carrier.

2. The catalyst of claim 1 wherein, in the carrier, the first alpha alumina component comprises a first constituent and a second constituent in which the first constituent provides from 10% to 90% by weight of the first component in the form of particles with a median particle size of from 2.5 to 4 µm and an average crystallite size of from 1.5 to 2.5 µm, and the second constituent provides from 90% to 10% by weight of the first component in the form of particles with a median particle size of from 4 to 10 µm and an average crystallite size of from 0.4 to 0.8 µm.

3. The catalyst of claim 1 wherein, in the carrier, the second alpha alumina component is generated by a seeded sol-gel process.

4. The catalyst of claim 3 wherein, in the carrier, the sol-gel alumina is seeded with an effective amount of sub-µm sized particles of alpha alumina seed.

5. The catalyst of claim 1 wherein the carrier further comprises from 0.05% to 1% by weight, based on the weight of alumina in the carrier, of titania.

6. The catalyst of claim 1 wherein the carrier has a pore volume of from 0.3 to 0.6 ml/gram.

7. The catalyst of claim 1 wherein the carrier further comprises a ceramic bond material in an amount that is from 1% to 3% by weight of the alumina components, expressed as alpha alumina.

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

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

10. The catalyst of claim 1 wherein the catalyst additionally comprises a promoting amount of rhenium.

11. The catalyst of claim 10 wherein the catalyst additionally comprises a rhenium co-promoter selected from the group consisting of sulphur, molybdenum, tungsten, chromium and mixtures thereof.

12. A process for the preparation of the catalyst carrier of claim 11 which comprises the steps of:

a) forming a mixture comprising:

i) at least one alpha alumina component with a median particle size of from 3 to 8 µm,

ii) a hydrated precursor of alpha alumina in an amount sufficient to provide from 5% to 60% by weight of the total weight of alpha alumina in the catalyst carrier,

iii) from 5% to 40%, based on the weight of the alpha alumina, of a burnout material, and

iv) water in sufficient quantity to extrude the above

mixture;

b) extruding the mixture into the desired shapes; and

c) firing to convert the precursor of alpha alumina to alpha alumina so as to produce a catalyst carrier in which alpha alumina particles with a median particle size of from 3 to 8 µm are dispersed in a matrix of alpha alumina derived from the precursor material.

13. The process of claim 12 wherein, in the carrier, the precursor of alpha alumina comprises a boehmite.

14. The process of claim 12 wherein, in the carrier, the precursor of alpha alumina further comprises alumina trihydrate.

15. The process of claim 12 wherein the precursor of alpha alumina is seeded with sub-µm sized particles of alpha alumina in an amount that is from 0.2% 5% by weight based on the total alumina weight, measured as alpha alumina, in the catalyst carrier.

16. The process of claim 12 wherein from 0.05% to 1% by weight based on the total weight of alumina in the formulation expressed as alpha alumina, of titania is added to the mixture to be extruded.

17. The process of claim 12 wherein a ceramic bond material is added to the extrudable mixture in an amount that is from 1% to 3% of the weight of the alumina components, expressed as alpha alumina, in the mixture.

A B S T R A C T

EPOXIDATION CATALYST AND PROCESS

This invention relates to an ethylene oxide catalyst which contains silver and one or more alkali metal promoters supported an a carrier having a crush strength of at least 2.3 kg and a settled packing density of at least about 0.48 kg/litres which comprises first and second alpha alumina components with a first alpha alumina component in the form of particles having a median crystallite size of from 0.4 to 4 µm providing from 95% to 40% of the total weight of alpha alumina in the carrier and a second alpha alumina component generated in situ by a sol-gel process and providing the balance of the alpha alumina in the carrier. Titania is optionally added to the carrier.

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 is a measure of the activity of the catalyst employed. The value T_{40} indicates the temperature at 40 percent oxygen conversion in the reactor and the value T is expressed in °C. This temperature for any given catalyst is higher when the conversion of oxygen is higher. Moreover, this temperature is strongly dependent on the employed catalyst and the reaction conditions. 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-dichloroethane, vinyl chloride, ethyl chloride or chlorinated polyphenyl compounds, to the desirability of

REPLACEMENT SHEET
21 NOV 1997