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(54) Title: PROCESS FOR PREPARING EPOXIDATION CATALYSTS

(57) Abstract

This invention relates to a process for the preparation of a catalyst suitable for the epoxidation of olefins having no allylic hydrogen, in particular ethylene which process comprises depositing a promoting amount of a salt of a rare earth metal and a promoting amount of a salt of an alkaline earth metal and/or a salt of a Group VIII transition metal on a porous, refractory support, calcining the support, and thereafter depositing a catalytically effective amount of silver, a promoting amount of alkali metal, optionally a promoting amount of rhenium and optionally a promoting amount of a rhenium co-promoter selected from sulphur, molybdenum, tungsten, chromium, phosphorus, boron and mixtures thereof, on the support, and subsequently drying the support.

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PROCESS FOR PREPARING EPOXIDATION CATALYSTS

The invention relates to a process for the preparation of silver-containing catalysts suitable for epoxidation in particular for the preparation of ethylene oxide and to the use of the catalyst for the preparation of ethylene oxide.

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. 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 hydrogen.

U.S. Patent No. 4,459,372, issued July 10, 1984, discloses the use of rhenium metal in combination with a surface metallated (using Ti, Zr, Hf, V, Sb, Pb, Ta, Nb, Ge and/or Si) alumina or silica. U.S. Patent No. 4,005,049, issued January 25, 1977, teaches the preparation of a silver/transition metal catalyst useful in oxidation reactions. In this instance, the silver serves as both a catalyst and a support for the transition metal co-catalyst. In U.S. Patent No. 4,536,482, issued August 20, 1985, catalytically active metals such as Ag and Re are co-sputtered along with a co-sputtered support material on a particular support.

U.S. Patent No. 4,257,967, issued March 24, 1981, discloses a catalyst combination of reduced silver, a carbonate of a rare earth metal and yttrium, a salt of an alkali or alkaline earth metal and a catalyst carrier.

None of these references disclose pre-doping a catalyst support with a promoting amount of a salt of a rare earth metal and a promoting amount of a salt of an element selected from the group consisting of an alkaline earth metal, a Group VIII transition metal and mixtures thereof, prior to the addition of silver and alkali metal.

It has now been found that epoxidation catalysts pre-doped, pretreated or pre-impregnated with a promoting amount of a salt of a rare earth metal and a promoting amount of a salt of an element selected from the group consisting of an alkaline earth metal, a Group VIII transition metal and mixtures thereof, have improved selectivity stabilities when compared with those obtained with epoxidation catalysts which have not been pre-doped with a rare earth and an alkaline earth metal and/or a Group VIII transition metal.

The invention therefore relates to a process for the preparation of a catalyst suitable for the epoxidation of olefins having no allylic hydrogen, in particular ethylene, with molecular oxygen in the vapour phase which process comprises depositing a promoting amount of at least one salt of a rare earth metal and a promoting amount of a salt of an element selected from the group consisting of an alkaline earth metal, a Group VIII transition metal and mixtures thereof, on a porous, refractory support, calcining the support, and thereafter depositing a catalytically effective amount of silver, a promoting amount of alkali metal, optionally a promoting amount of rhenium and optionally a promoting amount of a rhenium co-promoter selected from sulphur, molybdenum, tungsten, chromium, phosphorus, boron and mixtures thereof, on the support, and subsequently drying the catalyst.

Figure 1 shows the selectivity decline in accelerated decline testing for Catalysts A (carrier pre-doped with lanthanum and cobalt), B (carrier pre-doped with cerium and magnesium), C (carrier pre-doped with neodymium and cobalt) and D (carrier not pre-doped) at 40 mole percent oxygen conversion, (S_{40}), over a time period expressed in days.

Generally, in the vapour phase reaction of ethylene with oxygen to produce ethylene oxide, the ethylene is present in at least a double amount (on a molar basis) compared with oxygen, but frequently is often much higher. Therefore, the conversion is 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 mole percent oxygen conversion in the reactor and T_{40} is expressed in °C. This temperature for any given catalyst is higher when the conversion of oxygen is higher. The selectivity (to ethylene oxide) indicates the molar amount of ethylene oxide in the reaction product compared with the total molar amount of ethylene converted. In this specification, the selectivity is indicated as S_{40}, which means the selectivity at 40 mole percent oxygen conversion. The selectivity of silver-based ethylene oxide catalysts can and will decrease over a period of time of usage. Therefore, from an economical and practical standpoint, it is not only the initial selectivity of a catalyst which is important, but also the rate at which the selectivity declines. In fact, significant improvement in lowering the decline rate of a catalyst can prove more economically attractive than a high initial selectivity. Thus, the rate at which a catalyst loses selectivity is a predominant factor influencing the efficiency of any particular catalyst, and lowering this decline rate can lead to significant savings in terms of minimizing waste of the ethylene starting material.

The catalysts of the instant invention comprise a catalytically effective amount of silver, a promoting amount of alkali metal, and optionally, a promoting amount of rhenium and/or a promoting amount of a rhenium co-promoter selected from sulphur, chromium, molybdenum, tungsten and mixtures thereof, supported on a porous, refractory support which has been pretreated with a promoting amount of a salt of a rare earth metal and a promoting amount of a salt of an element selected from the group consisting of an alkaline earth metal, a Group VIII transition metal and mixtures thereof.

In general, the catalysts of the present invention are prepared by impregnating porous refractory supports with rare earth compound(s), complex(es) and/or salt(s) and at least one of alkaline earth metal compound(s), complex(es) and/or salt(s) and Group VIII transition metal compound(s), complex(es) and/or salt(s) dissolved in a suitable solvent sufficient to cause deposition on the support of preferably from 0.05 to 10, more preferably from 0.05 to 2 percent by weight of the total catalyst, of rare earth, and preferably from 0.01 to 5, more preferably from 0.02 to 3 percent by weight of the total catalyst, of alkaline earth metal and/or Group VIII transition metal. The porous refractory support is then calcined and thereafter impregnated 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 25 more preferably from 5-20 percent by weight, basis the weight of the total catalyst, of silver. The impregnated support is subsequently 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. Optionally deposited on the support either prior to, coincidentally with, or subsequent to the deposition of the silver and/or alkali metal will be suitable rhenium ions or compound(s), complex(es) and/or salt(s) dissolved in an appropriate solvent, and/or suitable ions or salt(s), complex(es) and/or compound(s) of sulphur, molybdenum, tungsten, phosphorus, boron and/or chromium dissolved in an appropriate solvent.

The carrier or support employed in these catalysts in its broadest aspects can be any of the large number of conventional, porous refractory catalyst carriers or support materials which are considered relatively inert in the presence of ethylene oxidation feeds, products and reaction conditions. Such conventional materials are known to those skilled in the art and may be of natural or synthetic origin and preferably are of a macroporous structure, i.e., a structure having a surface area below 10 m^2/g and preferably below 3 m^2/g. Particularly suitable supports are those of aluminous composition, in particular those comprising alpha alumina. In the case of alpha alumina-containing supports, preference is given to those having a specific surface area as measured by the B.E.T. method of from 0.03 to 10, preferably from 0.05 to 5, more preferably from 0.1 to 3 m^2/g, and a water pore volume as measured by conventional water absorption techniques of from 0.1 to 0.75 ml/g by volume. The B.E.T. method for determining specific surface area is described in detail in Brunauer, S., Emmet, P. Y. and Teller, E., J. Am. Chem. Soc., 60, 309-16 (1938).

The support is preferably shaped into particles, chunks, pieces, pellets, rings, spheres, wagon wheels, and the like of a size suitable for use in fixed bed reactors.

The catalysts of the present invention are prepared by a technique in which a rare earth promoter in the form of soluble salts and/or compounds and an alkaline earth metal promoter in the form of soluble salts and/or compounds and/or a Group VIII transition metal promoter in the form of soluble salts and/or compounds are deposited on the support which is then subjected to partial drying or to a thermal treatment sufficient to allow deposition of the rare earth salts and the alkaline earth metal and/or Group VIII transition metal salts, and, while not wishing to be bound by any particular theory, presumed complexation with the anionic components on the surface of the catalyst. Thereafter, the alkali metal promoter(s), the rhenium promoter, if present, and the rhenium co-promoter, if present, in the form of soluble salts and/or compounds are deposited on the catalyst and/or support prior to, simultaneously with, or subsequent to the deposition of the silver and each other. The alkali metals may be deposited at one step of the process and the rhenium, if present, and/or the rhenium co-promoter, if present, at a different step or steps. The preferred method is to deposit silver, alkali metal, rhenium and rhenium co-promoter simultaneously on the support, that is, in a single impregnation step. The rare earth promoter and the alkaline earth and/or Group VIII transition metal promoters, however must be deposited on the support prior to all of the other catalyst components and the support must then be calcined to a degree sufficient to fix the rare earth and the alkaline earth and/or Group VIII transition promoters on the support before deposition of the other catalyst components. The pre-impregnation or pre-doping of the catalyst with a promoting amount of rare earth in combination with a promoting amount of an alkaline earth metal and/or Group VIII transition metal results in a catalyst having improved selectivity stability.

Although rare earth metals, alkaline earth metals and Group VIII transition metals exist in a pure metallic state, they are not suitable for use in that form. They are used as ions or compounds or rare earth metals, ions or compounds of alkaline earth metals and/or ions or compounds of Group VIII transition metals dissolved in a suitable solvent for impregnation purposes.

The promoting amounts of rare earth, alkaline earth metal and Group VIII transition metal utilized to pre-dope the catalyst carrier will depend on several variables, such as, for example, the surface area and pore structure and surface chemical properties of the carrier used.

Without intending to limit the scope of the invention, it is believed that the rare earth, the alkaline earth metal and the Group VIII transition metal are present on the catalyst in the form of oxides or oxygen-bound species, or surface compounds or surface complexes rather than as metals. For convenience, the amounts deposited on the support or present on the catalyst are expressed as the metal. More particularly, it is believed that the rare earth metal, the alkaline earth metal and the Group VIII transition metal compounds are probably in the form of mixed surface oxides or double surface oxides or complex surface oxides with the aluminum 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).

As used herein, the terms "rare earth metal" and "rare earth" and "lanthanide" refer to the rare earth metals or elements having atomic numbers 57 (lanthanum) through 71 (lutecium) in the Periodic Table of the Elements i.e., lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium.

In a preferred embodiment, the rare earth metal/s is/are selected from the group consisting of lanthanum, cerium, neodymium, samarium, gadolinium, dysprosium, erbium, ytterbium, and mixtures thereof, with lanthanum, cerium, neodymium, gadolinium, ytterbium, and mixtures thereof being particularly preferred.

In a preferred embodiment, the alkaline earth metal is selected from the group consisting of magnesium, calcium, strontium, barium and mixtures thereof, with magnesium, calcium and mixtures thereof being particularly preferred.

In a preferred embodiment, the Group VIII transition metal is selected from the group consisting of cobalt, iron, nickel, ruthenium, rhodium, palladium and mixtures thereof.

Promoting amounts of alkali metal or mixtures of alkali metal are deposited on a porous support which has been pretreated with a promoting amount of a salt of a rare earth metal and a salt of an element selected from the group consisting of an alkaline earth metal, a Group VIII transition metal and mixtures thereof, by impregnation using a suitable solution. 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 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, 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. It is believed that the alkali metal compounds are oxidic compounds, more particularly, in the form of mixed surface oxides or double surface oxides or complex surface oxides with the aluminum 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 chlorides or carbonates or residual species from the impregnating solution(s).

In a preferred embodiment, at least a major proportion (greater than 50%) of the alkali metals comprise the higher alkali metals, selected from the group consisting of potassium, rubidium, cesium and mixtures thereof.

A particularly preferred alkali metal promoter is cesium plus at least one additional alkali metal, preferably selected from sodium, lithium and mixtures thereof, with lithium being preferred.

In one embodiment, the pretreated or pre-doped carrier is also impregnated with rhenium ions, salt(s), compound(s), and/or complex(es). This may be done at the same time that the alkali metal promoter is added, or before or later; or at the same time that the silver is added, or before or later; or at the same time that the rhenium co-promoter, if present, is added, or before or later. Preferably, rhenium, if present, alkali metal, rhenium co-promoter, if present, and silver are in the same impregnating solution, although it is believed that their presence in different solutions will still provide suitable catalysts. When a rhenium promoter is utilized, the preferred amount of rhenium, calculated as the metal, deposited on or present on the carrier or catalyst ranges from 0.1 to 10, more preferably from 0.2 to 5 micromoles per gram of total catalyst, or, alternatively stated, from 19 to 1860, preferably from 37 to 930 parts per million by weight of total catalyst.

For purposes of convenience, the amount of rhenium present on the catalyst is expressed as the metal, irrespective of the form in which it is present.

Suitable rhenium compounds for use in the preparation of the instant catalysts are rhenium compounds that can be solubilized in an appropriate solvent. Preferably, the solvent is water-containing.

More preferably, the solvent is the same solvent used to deposit the silver and the alkali metal promoter. Examples of suitable rhenium compounds include the rhenium salts such as rhenium halides, rhenium oxyhalides, rhenates, perrhenates, oxides and acids of rhenium. A preferred compound for use in the impregnation solution is the perrhenate, preferably ammonium perrhenate. However, the alkali metal perrhenates, alkaline earth metal perrhenates, silver perrhenates, other perrhenates and rhenium heptoxide can also be suitably utilized.

In a preferred embodiment of the instant invention, the rhenium present on the catalyst is present in a form that is extractable in water.

U.S. Patent No. 4,766,105, teaches that if a rhenium co-promoter is added to an alkali metal/rhenium doped supported silver catalyst, an improvement in initial selectivity is obtained. While suitable catalysts can be prepared in the absence of both rhenium and a rhenium co-promoter, it is preferable that if the catalyst contains rhenium, the catalyst also contains a rhenium co-promoter. When a co-promoter is utilized, it is selected from the group consisting of sulphur, molybdenum, tungsten, chromium, phosphorus, boron and mixtures thereof. In a presently preferred embodiment, the co-promoter is applied to the catalyst in the oxyanionic form.

Preferred are sulphates, molybdates, tungstates, chromates, phosphates and borates. The anions can be supplied with various counter-ions. Preferred are ammonium, alkali metal, mixed alkali metal and hydrogen (i.e. acid form). The anions can be prepared by the reactive dissolution of various non-anionic materials such as the oxides such as SO_2, SO_3, MoO_3, WO_3, Cr_2O_3, P_2O_5, B_2O_3, etc., as well as other materials such as halides, oxyhalides, hydroxyhalides, hydroxides, sulphides, etc., of the metals.

The preferred amount of co-promoter compound present on or deposited on the support or catalyst ranges from 0.1 to 10, preferably from 0.2 to 5 micromoles, expressed as the element, per gram of total catalyst.

For purposes of convenience the amount of co-promoter present on the catalyst is expressed as the element irrespective of the form in which it is present.

Generally, the carrier is contacted with a rare earth salt, a rare earth compound or a rare earth complex and an alkaline earth metal and/or Group VIII transition metal salt, compound or complex which have been dissolved in aqueous or non-aqueous solutions, calcined and then contacted with a silver salt, a silver compound, or a silver complex which has been dissolved in an aqueous solution, so that the carrier is impregnated with said aqueous solution; thereafter the impregnated carrier is separated form the aqueous solution, e.g., by centrifugation or filtration and then dried. It is understood that the other dopants such as alkali metal promoter, rhenium promoter, if present, and rhenium co-promoter, if present, can be added to the silver-containing impregnation solution, if desired. 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.

As used herein, the term "calcined" refers to thermal treatment at a temperature sufficient to drive off volatile liquids and to chemically bind at least a portion of the rare earth and alkaline earth metal and/or Group VIII transition metal to the support. The calcination temperatures will typically be in the range of from 150 °C to 1500 °C, preferably between 200 °C and 1500 °C.

One method of preparing the silver containing catalyst can be found in U.S. Patent No. 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 No. 4,010,115, U.S. Patent No. 4,356,312, U.S. Patent No. 3,962,136, and U.S. Patent No. 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-promoter can be found in U.S. Patent No. 4,766,105.

The silver catalysts according to the present invention have been shown to have improved selectivity stabilities for ethylene oxide production in the direct oxidation of ethylene with molecular oxygen to ethylene oxide. 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 employing recycle operations or applying successive conversations in different reactors to increase the yields of ethylene oxide, and to any other special conditions which may be selected in processes for preparing ethylene oxide. Pressures in the range of from atmospheric to about 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 catalysts according to the present invention 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.

TABLE

*GHSV	1500-10,000
Inlet Pressure	1200-3000 kPa
Inlet Feed	
Ethylene	1-40%
O_2	3-12%
Ethane	0-3%
Argon and/or methane and/or nitrogen diluent	Balance
Chlorohydrocarbon Moderator	0.3-50 ppmv total
Coolant temperature	180-315 °C
Catalyst temperature	180-325 °C
O_2 conversion level	10-60%
EO Production (Work Rate)	32-400 kg EO/m^3 of catalyst/hr.

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

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

While the catalysts of the present invention are preferably used to convert ethylene to ethylene oxide, they can be also used to epoxidise other olefins having no allylic hydrogens, such as are broadly defined in U.S. Patent No. 4,897,498. Exemplary such olefins are butadiene, tertiary butyl ethylene, vinyl furan, methyl vinyl ketone, N-vinyl pyrrolidone, and the like. A presently preferred olefin for use in the practice of this process is butadiene, because of its ready availability, relative low cost, and the wide range of possible uses for the epoxide reaction product. U.S. Patent No. 5,081,096, issued January 14, 1992, discloses a silver-based, 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 process is carried out by contacting the olefin to be oxidized with molecular oxygen and an organic halide under oxidation conditions, i.e. in the presence of sufficient quantities of an oxygen-containing gas to provide a molar ratio of olefin to oxygen in the range of 0.01 up to 20, and in the presence of 0.1 up 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.

The process can be carried out in either batch or continuous mode. Continuous reaction is presently preferred since high reactor throughput and high purity product is obtained in this manner. The batch mode is satisfactorily employed when high volume of reactant throughput is not required, for example, for liquid phase reactions.

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 350 °C 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 about 20-25%, catalyst is ready for use.

The invention will be illustrated by the following illustrative embodiments.

Illustrative Embodiments

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

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

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

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

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

5) Add 630 g of high-purity oxalic acid dihydrate in approximately 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.

Part B: Catalyst pre-doping procedure:

For Catalyst A, in order to deposit 0.54 percent by weight, basis the total weight of the carrier, of lanthanum ions, and 0.23 percent by weight, basis the total weight of carrier, of cobalt ions, the following solution was made. 150 Grams of water was acidified with 9.5 grams of acetic acid. 5.0 Grams of $Co(CH_3COO)_2 \cdot 4H_2O$ and 8.69 grams of $La(NO_3)_3 \cdot 6H_2O$ were dissolved with stirring, followed by 9.0 grams of monoethanolamine. The volume of the solution thus prepared was adjusted to a total volume of 200 millilitres. Two hundred (200) grams of Catalyst carrier I (98.8 wt% alpha alumina, B.E.T. surface area 0.48 m^2/g, water pore volume 0.465 ml/g) is then vacuum impregnated at 3.33-6.66 kPa for three minutes. At the end of this time, the vacuum is released and the excess solution is decanted from the carrier. The carrier is then dried by continuous shaking in an 8500 litre/hr air stream at 270 °C for ten minutes. This drying step is followed by calcination in air; two hours at a temperature of 500 °C followed by four hours at a temperature of 1050 °C.

For Catalyst B, in order to deposit 0.27 percent by weight, basis the total weight of the carrier, of cerium ions, and 0.047 percent by weight, basis the total weight of carrier, of magnesium ions, the following solution is made. 2.56 Grams of $Mg(NO_3)_2 \cdot 6H_2O$, 5.48 grams of $(NH_4)_2Ce(NO_3)_6$ and 10.5 grams of acetic acid were dissolved in 150 millilitres of water, followed by the addition of 10.0 grams of monoethanolamine. The volume of the solution thus prepared was adjusted to a total volume of 200 millilitres. Two hundred and fifty (250) grams of Catalyst carrier I is then vacuum dried and calcined as described above.

For Catalyst C, in order to deposit 0.583 percent by weight, basis the total weight of the carrier, of neodymium ions, and 0.24 percent by weight, basis the total weight of carrier, of cobalt ions, the following solution is made. 7.5 Grams of $Co(CH_3COO)_2 \cdot 4H_2O$ and 10.18 grams of $Nd(CH_3COO) \cdot H_2O$ were dissolved in 250 millilitres of water, followed by the addition of 14.25 grams of acetic acid and 13.5 grams of monoethanolamine. The volume of the solution thus prepared was adjusted to a total volume of 300 millilitres. Four hundred (400) grams of Catalyst carrier I is then vacuum impregnated, dried air stream at 270 °C for ten minutes. This drying step is calcined as described above.

For Catalyst D, no pre-doping of Catalyst carrier I was carried out.

Part C: Preparation of impregnated catalysts:

Catalyst A (Pre-doped with lanthanum and cobalt)

For preparing impregnated Catalyst A, into a 10 ml beaker is added 0.124 g of NH_4ReO_4 and approximately 3 g of deionized water, and the mixture is allowed to dissolve with stirring. 0.059 g of $Li_2SO_4.H_2O$ is dissolved in 1 ml of water in a weighing dish, and then added to the perrhenate solution. 0.255 g of $LiNO_3$ is dissolved in 2 ml of water and added to the perrhenate solution. The perrhenate/lithium sulfate/lithium nitrate solution is allowed to stir, ensuring complete dissolution. This dopant solution is then added to 137 g of the above-prepared silver solution (specific gravity = 1.575 g/ml), and the resulting solution is diluted with water to a total weight of 153 g. One-third of this solution is used to prepare a catalyst. 0.0998 g of stock CsOH solution containing 45.5 wt% of cesium is added to a 51 g portion of the silver oxalate/dopant solution to prepare the final impregnation solution.

The final impregnation solution thus prepared is then used to impregnate a cesium pre-doped carrier in the manner described below.

Approximately 30 g of the cesium pre-doped carrier described above for Catalyst A are placed under 3.33 kPa for 3 minutes at room temperature. Approximately 50 g of doped impregnating solution is then introduced to submerge the carrier, and the vacuum is maintained at 3.33 kPa for an additional 3 minutes. At the end of this time, the vacuum is released, and 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 an 8500 litre/hr air stream flowing across a cross-sectional area of approximately 19-32 cm^2 at 250-270 °C for 5-6 minutes. The cured lanthanum and cobalt pre-doped catalyst (Catalyst A) is then ready for testing.

Catalyst B (Pre-doped cerium and magnesium)

Catalyst B was prepared in the same manner as Catalyst A, except that the catalyst carrier was pre-doped with cerium and magnesium instead of lanthanum and cobalt, and the amount of cesium was adjusted to 0.1116 grams of 45.5% cesium hydroxide solution.

Catalyst C (Pre-doped neodymium and cobalt)

Catalyst C was prepared in the same manner as Catalyst A, except that the catalyst carrier was pre-doped with neodymium and cobalt instead of lanthanum and cobalt, and the amount of cesium was adjusted to 0.1265 grams of 45.5% cesium hydroxide solution.

Catalyst D (No pre-dopants)

Catalyst D was prepared in the same manner as Catalyst A, except that the catalyst carrier was not pre-doped, and the amount of cesium was adjusted to 0.0952 grams of 45.5% cesium hydroxide solution.

The procedures set forth above for Catalysts A, B, C and D will yield catalysts on this carrier which contain approximately 13.2%w-14.5%w Ag with the following approximate dopant levels (expressed in parts per million by weight basis the weight of the total catalyst, i.e., ppmw, and percent by weight basis the weight of the total catalyst, i.e., % wt.) and which are approximately optimum in cesium for the given silver and rhenium, if present, and sulphur levels and support with regard to initial selectivity under the test conditions described below.

	Rare Earth Pre-Dopant, % wt.	Group VII Pre-Dopant, % wt.	Cs, ppmw	Re, ppmw	S, ppmw
Catalyst A	0.54 (La)	0.23 (Co)	470	280	48
Catalyst B	0.27 (Ce)	0.047 (Mg)	504	280	48
Catalyst C	0.583 (Nd)	0.24 (Co)	448	280	48
Catalyst D	None	None	430	280	48

Part D: Standard Microreactor Catalyst Test Conditions/Procedure

For Catalysts A, B, C and D:

3 to 5 grams of crushed catalyst (14-20 mesh, i.e. 1.41-0.84 mm) 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 ml of gas per ml of catalyst per hour. The inlet gas pressure is 1550 kPa.

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

The initial reactor (heat medium) temperature is 225 °C. The temperature is ramped at a rate of 10 °C per hour from 225 °C to 245 °C, and then adjusted so as to achieve a constant oxygen conversion level of 40%. Performance data at this conversion level are usually obtained when the catalyst has been on stream for a total of at least 1-2 days. Due to slight differences in feed gas composition, gas flow rates, and the calibration of analytical instruments used to determine the feed and product gas compositions, the measured selectivity and activity of a given catalyst may vary slightly from one test run to the next. To allow meaningful comparison of the performance of catalysts tested at different times, all catalysts described in this illustrative embodiment were tested simultaneously with a reference catalyst. All performance data reported in this illustrative embodiment are corrected relative to the average initial performance of the reference catalyst (S_{40} = 81.0%; T_{40} = 230 °C).

After obtaining initial performance values for selectivity at 40% conversion the catalysts are subjected to accelerated aging conditions. The oxygen conversion is brought to 85% or 285 °C, whichever first occurs. Once the temperature reaches 285 °C, there is no further increase in temperature and the catalyst is aged at 285 °C. Every ten days, the temperature is lowered and the data for 40% oxygen conversion is collected. The results can be seen in Figure 1.

As mentioned previously, selectivity decline is of tremendous economic importance when choosing a catalyst, and retarding this decline rate can lead to significant savings in costs. As can be seen in Figure 1, catalysts which are prepared using a pre-doped rare earth and Group VIII transition metal carrier, Catalysts A and C, and using a pre-doped rare earth and alkaline earth metal carrier, Catalyst B, decline less rapidly than catalysts prepared without using a pre-doped rare earth and a Group VIII transition metal carrier, Catalyst D, and are thus significantly advantaged.

CLAIMS

1. A process for preparing a catalyst suitable for the vapour phase epoxidation of olefins having no allylic hydrogen, in particular ethylene, with molecular oxygen which process comprises depositing a promoting amount of at least one salt of a rare earth metal and a promoting amount of a salt of a metal selected from the group consisting of an alkaline earth metal, a Group VIII transition metal and mixtures thereof, on a porous, refractory support, and thereafter depositing a catalytically effective amount of silver and a promoting amount of alkali metal on said support, optionally a promoting amount of rhenium and optionally a promoting amount of rhenium co-promoter selected from sulphur, molybdenum, tungsten, chromium, phosphorus, boron and mixtures thereof, and thereafter drying the support.

2. The process of claim 1 wherein the promoting amount of a salt of a rare earth metal is in the range of from 0.05 to 10 wt%, the promoting amount of a salt of a metal selected from the group consisting of an alkaline earth metal, a Group VIII transition metal and mixtures thereof, is in the range of from 0.01 to 5 wt%, the amount of silver is in the range of from 1 to 40 wt%, the amount of alkali metal promoter is in the range of from 10 to 1500 parts per million, the optional amount of rhenium promoter is in the range of from 0.1 to 10 micromoles, and the optional amount of rhenium co-promoter is in the range of from 0.1 to 10 micromoles, all expressed as the element, per gram of total catalyst.

3. The process of claim 1 wherein the rare earth metal is selected from the group consisting of lanthanum,

cerium, neodymium, samarium, gadolinium, dysprosium, erbium, ytterbium, and mixtures thereof.

4. The process of claim 1 wherein the alkaline earth metal is selected from the group consisting of magnesium, calcium, strontium, barium, and mixtures thereof.

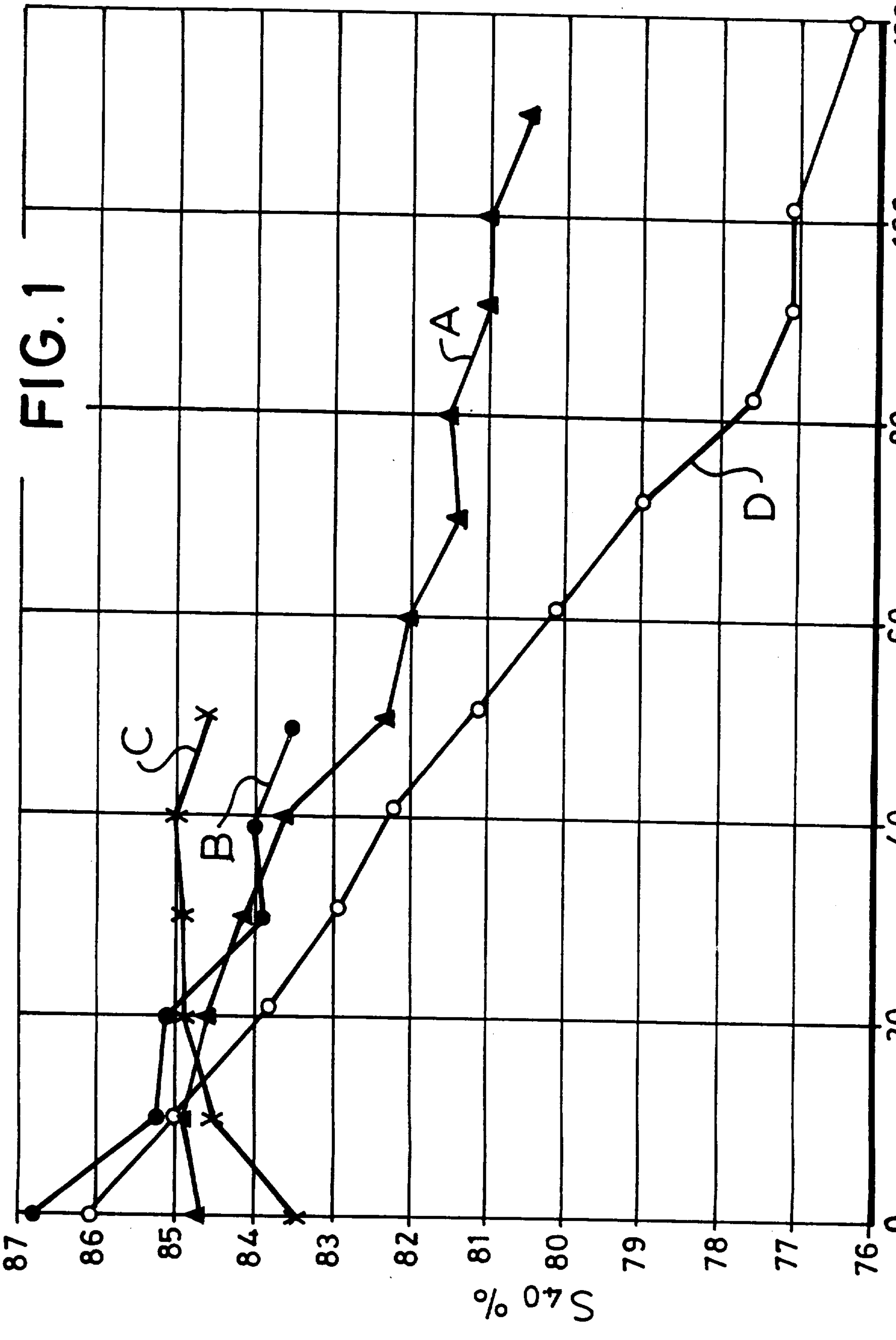
5. The process of claim 1 wherein the Group VIII transition metal is selected from the group consisting of cobalt, iron, nickel, ruthenium, rhodium, palladium and mixtures thereof.

6. The process of claim 1 wherein the support comprises alpha alumina, having a surface area in the range of from 0.05 m^2/g to 10 m^2/g.

7. The process of claim 1 wherein the alkali metal is selected from potassium, rubidium, cesium, and mixtures thereof.

8. The process of claim 7 wherein the alkali metal comprises cesium plus at least one additional alkali metal.

9. The process of claim 8 wherein the alkali metal is cesium plus lithium.



87
86
85
84
83
82
81
80
79
78
77
76
S_{40} %
0
20
40
60
80
100
120
DAYS
A
B
C
D

FIG. 1

INTERNATIONAL SEARCH REPORT

Inte onal Application No
PCT/EP 96/04298

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B01J23/68 B01J23/66 C07D301/10

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B01J C07D

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	EP,A,0 716 884 (SHELL INT RESEARCH) 19 June 1996 see the whole document ---	1-9
A	EP,A,0 624 398 (MITSUBISHI PETROCHEMICAL CO) 17 November 1994 see the whole document -----	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
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1

Date of the actual completion of the international search 29 November 1996	Date of mailing of the international search report 12. 12. 96
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+ 31-70) 340-3016	Authorized officer Dack, S

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte onal Application No
PCT/EP 96/04298

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-0716884	19-06-96	JP-A-	8224477	03-09-96
EP-A-0624398	17-11-94	CA-A-	2120591	15-10-94
		CN-A-	1098962	22-02-95
		JP-A-	6343864	20-12-94
		US-A-	5502020	26-03-96