Description

This invention relates to a silver catalyst to be used for the production of ethylene oxide by the catalytic gas-phase oxidation of ethylene with molecular oxygen and to a method for the manufacture of the silver catalyst.

For a satisfactory performance of the function of the silver catalyst which is used in the commercial production of ethylene oxide by the catalytic gas-phase oxidation of ethylene with molecular oxygen, it must exhibit high selectivity and high activity and enjoy a long catalyst life.

Various studies have been made to date for the purpose of improving the performance of the silver catalyst and consequently fulfilling the requirement, and efforts have been made to improve carriers, reaction promoters, silver compounds and the like. Numerous reports exist, including US-A- 3,207,700 and Japanese Patent Publications SHO 43(1968)-13,137, SHO 45(1970)-21,373, SHO 45(1970)-22,419 and SHO 45(1970)-11,217, Japanese Patent Laid-Open SHO 56(1981)-89,843, US-A- 2,766,261, 3,172,893, and 3,664,970. Most of these, however, concern pore distributions and specific surface areas of carriers.

In US-A- 2,125,333, there is a description to the effect that an alkali metal salt containing sodium or potassium and a metal salt thereof is used as an additive for the silver catalyst in the manufacture of ethylene oxide.

In US-A- 2,238,474, there is a description to the effect that sodium hydroxide improves the activity of the silver catalyst for the production of ethylene oxide and potassium hydroxide has an adverse effect upon the activity of the silver catalyst.

In US-A- 2,765,283, there is a description to the effect that the silver catalyst is improved by adding 1 to 2,000 ppm by weight of an inorganic chlorinated substance such as sodium chloride to the catalyst carrier before silver is deposited on the carrier.

In US-A- 2,799,687 there is a description to the effect that a halide such as sodium chloride or potassium chloride, used in an amount of 20 to 16,000 ppm, functions as an inhibitor and induces degradation of the activity of the silver catalyst.

In US-A- 4,007,135, there is disclosed a catalyst for the production of alkalene oxide, which catalyst contains copper, gold, zinc, cadmium, mercury, niobium, tantalum, molybdenum, tungsten, vanadium, or preferably chromium, calcium, magnesium, strontium, and/or more preferably barium, and preferably further an alkali metal, in an mount exceeding the amount naturally present as an impurity or cement in the carrier and sufficient to manifest the action of a promoter.

In US-A- 4,168,247, there is disclosed a catalyst for the production of alkylene oxide, which catalyst contains silver deposited on a porous heat-resistant carrier possessing a specific surface area in the range of 0.05 to 10 m^2/g and further contains sodium and at least one other alkali metal selected from the group consisting of potassium, rubidium, and cesium in a promoting amount in excess of the amount naturally present as an impurity or a binding agent in the carrier.

In US-A- 4,278,562, there is disclosure to the effect that a catalyst for the production of an alkylene oxide is obtained by depositing silver and optionally sodium or lithium in the subsequent treatment, depositing thereon the salts of such alkali metals as potassium, rubidium, and cesium in conjunction with an amine and/or ammonia.

In Japanese Patent Laid-Open SHO 55(1980)-145,677, there is disclosed a silver catalyst which, as a catalyst for the reaction of oxidation, has silver and, when necessary, further an alkali metal component or an alkaline earth metal component deposited on a non-acidic carrier containing alumina, silica, and titania in a total amount of not less than 99% by weight, containing metal of the Groups Va, VIa. VIII, Ib, and IIb of the Periodic Table of Elements in a total amount of less than 0.1% by weight, and assuming no acid colour on exposure to methyl red having a pKa value of +4.8.

In Japanese Patent Laid-Open SHO 56(1981)-105,750, there is disclosed a silver catalyst for the production of ethylene oxide, which silver catalyst is prepared by impregnating a carrier using a-alumina as a principal component thereof and having a sodium content of not more than 0.07% by weight and a specific surface area in the range of 1 to 5 m^2/g with an impregnation having 0.001 to 0.05 gram equivalent per kg of complete catalyst, of a complex of an alkali metal with boron, a complex of an alkali metal with molybdenum, and/or a complex of an alkali metal with tungsten contained in a decomposable silver solution formulated to give a deposition ratio of 5 to 25% by weight based on the complete catalyst, and then heating and reducing or thermally decomposing the product of impregnation.

In Japanese Patent Laid-Open SHO 57(1982)-107,241, there is disclosed a silver catalyst for the production of ethylene oxide, which catalyst incorporates therein, besides silver, sodium (Na) as a cationic component and chlorine (Cl) as an anionic component in amounts such that the atomic ratio of Cl/Na will be less than 1.

In US-A- 4,415,476, there is disclosed a silver catalyst for the production of ethylene oxide, which silver

catalyst contains, besides silver, at least sodium and cesium as cationic components and chlorine as an anionic component.

In US-A- 4,368,144, there is disclosed a silver catalyst for the production of ethylene oxide, which silver catalyst contains metallic silver particles deposited in a ratio of 5 to 25% by weight based on complete catalyst on an a-alumina carrier having a sodium content of not more than 0.07% by weight and a specific surface area in the range of 0.5 to 5 m^2/g and 0.001 to 0.05 gram equivalent of at least one alkali metal or alkali metal compound per kg of the complete catalyst and in excess of the amount naturally present in the carrier.

Japanese Patent Laid-Open SHO 63(1988)-116,743 discloses a silver catalyst for the production of ethylene oxide, containing at least sodium, potassium, rubidium, and/or cesium other than silver as cationic components, among other catalytic components, and using a carrier mainly comprising an α-alumina, having a surface area in the range of 0.6 to 2 m^2/g, a water absorption ratio in the range of 20 to 50%, a silica content in the range of 0.5 to 12% by weight, a silica content per surface area (% by weight/m^2/g) in the range of 0.5 to 12, preferably 1 to 8, and a sodium content in the range of 0.08 to 2% by weight.

Numerous silver catalysts have been proposed as described above. Most of them have their catalytic performance enhanced by incorporating in silver catalysts amounts of alkali falling in restricted ranges. Though these catalysts manifest satisfactory initial catalytic performance, they are deficient in terms of service life.

Concerning the carrier of the silver catalyst to be used for the production of ethylene oxide, many points remain yet to be clarified and many problems still await better solutions. For example, the component substances of the carrier, such physical properties of the carrier as specific surface area, pore diameter, pore distribution, pore volume, porosity, particle diameter, and shape, and the chemical properties owned by the such materials for the carrier as α-alumina, silicon carbide, silica, and zirconia have room for further improvements aimed at optimisation.

An object of this invention, therefore, is to provide a novel silver catalyst for the production of ethylene oxide, which silver catalyst combines such qualities as high selectivity, high activity, and long service life, and to provide a method for its production.

Another object of this invention is to provide a novel silver catalyst for the production ethylene oxide, which enjoys improved service life owing to the use of an α-alumina carrier possessing a specific surface area in the range of 0.75 to 5 m^2/g and an apparent porosity in the range of 45 to 70%, and a method for its production.

According to the invention, there is provided a catalyst for the production of ethylene oxide which comprises silver and cesium on an α-alumina carrier characterised in that the outer surface of the carrier and the surface of pores in the carrier are coated with amorphous silica, on which the metallic silver and cesium in finely divided form are supported, the silver representing 5 to 25% by weight, based on the amount of a finished catalyst, and the cesium representing 0.001 to 0.05 gram equivalent weight of cesium per kg of the finished catalyst.

The invention also provides a method for the production of such a silver catalyst comprising the steps of: impregnating the carrier with an aqueous solution containing colloidal silica; drying the impregnated carrier by heating; calcining the dried carrier thereby preparing an α-alumina carrier whose outer surface and the surface of whose pores are coated with amorphous silica; causing 5 to 25% by weight, based on the amount of a finished catalyst, of finely divided metallic silver and 0.001 to 0.05 gram equivalent weight of cesium per Kg of the finished catalyst to be carried by the carrier; activating the resultant composite thereby effecting deposition of the silver and cesium on the resultant porous inorganic refractory carrier, and subsequently subjecting the composite to a high temperature heat treatment in an inert gas at an elevated temperature in the range of 400° to 950°C.

By preparing an α-alumina carrier having its outer surface and the surface of its pores coated with amorphous silica and then causing 5 to 25% by weight, based on the amount of a finished catalyst, of finely divided metallic silver and 0.001 to 0.05 gram equivalent weight of cesium per kg of the finished catalyst to be carried on the α-alumina carrier, this invention obtains a novel silver catalyst for the production of ethylene oxide, which is capable of retaining high selectivity and high activity over a long time.

The present applicants' research into a carrier suitable for use in a silver catalyst for the production of ethylene oxide has revealed that when an α-alumina carrier having a specific surface area in the range of 0.075 to 5 m^2/g and an apparent porosity in the range of 45 to 70% and having its outer surface and the surface of its pores coated with amorphous silica is used (rather than a known carrier as previously used generally on a commercial scale), even though it has a relatively high specific surface area and has never been used on a commercial scale in the field because of the insufficient selectivity exhibited by a catalyst produced with such a carrier, together with a catalyst obtained by causing particularly cesium and/or a cesium compound to be carried as a reaction accelerator with silver and cesium and/or a cesium compound carried as an activating agent on the α-alumina carrier, and the resultant composite is subjected to an activating treatment cesium compound on the α-alumina carrier, then high temperature heat-treating the composite in an inert gas containing

oxygen in a concentration of not more than 3% by volume at an elevated temperature in the range of 400° to 950°C, the catalyst produced exhibits a high activity, a high selectivity, and a high durability never previously attained. The catalysts which are used in the production of ethylene oxide by the catalysts vapor-phase oxidation of ethylene with molecular oxygen are silver catalysts and, quite naturally, most of them are carried catalysts using a carrier. It is also known widely that the carriers used for these carried silver catalysts are porous particulate refractories.

The porous particulate refractory carrier, simple as it may be, may vary widely. The physical properties of the carrier such as specific area, pore distribution, pore volume, particle diameter, and shape, and the chemical properties owned by the component substances of carrier such as α-alumina, silica, silicon carbide, zirconia, and clay, greatly affect the produced catalysts.

The selection of a carrier having a specific set of properties, therefore, poses itself as a serious problem for persons engaged in the art. Among other properties, the specific surface area deserves particular attention because it bears also on pore diameter and affects the performance of a produced catalyst in large measure. From the standpoint of activity and durability, it is preferable for the catalyst to have a large specific surface area and, for that reason, it is preferable for the carrier to have a large specific surface area. For the carrier to have a large specific surface area, the alumina particles to be selected as the material for the carrier are required to have a small diameter. This fact necessarily signifies formation of pores of a minute diameter. However, this fact proves to be disadvantageous from the standpoint of dispersion and retention of gas and removal of heat of reaction. It also entails a disadvantage that the area of the exposed surface of the carrier is consequently large. These factors invariably contribute to impairing the selectivity. In the light of all of these facts, the statement that a large specific surface area is preferably does not always hold good but has limits of its own. Most carriers so far employed on a commercial scale have specific surface areas not exceeding 1 m^2/g, or even not exceeding 0.5 m^2/g. Exceptionally, some catalysts use carriers having specific surface areas exceeding 1 m^2/g. They, however, have lower selectivity than those using carriers of a lower specific surface area.

As a result of continuing a study in search of a solution to this disadvantage, the applicants have found a method of permitting the effective use of a carrier having a large specific surface area exceeding 0.75 m^2/g without sacrificing selectivity so allowing a catalyst to be produced with further improved activity and durability. Briefly, this method is accomplished by the use of an α-alumina carrier having its outer surface and the surface of its pores coated with amorphous silica. The method is particularly effective in a carrier which possesses a large specific surface area of not less than 0.75 m^2/g and also effective in an extended catalyst incorporating a cesium compound. It is a surprising fact that the disadvantages arising from the physical aspect of such a carrier is mitigated by the chemical quality of carrier, attributed to the coating of the outer surface of carrier and the surface of its pores with amorphous silica. The specific surface areas mentioned in the present specification represents values determined by the Brunauer-Emmett-Teller (hereinafter referred to as "BET") method.

In accordance with this invention, the outer surface of carrier and the surface of pores in the carrier delicately affect the performance of the produced catalyst and, in the case of a carrier possessing a specific surface area of not more than 0.5 m^2/g and heretofore used generally in the field, this adverse effect of the aspect of the surfaces decreased in proportion as the specific surface area decreases and gradually increases beyond the level of 0.5 m^2/g. It then increases conspicuously as the specific surfaces area exceeds 0.75 m^2/g. It has been now found that a carrier which possesses a specific surface area of not less than 0.75 m^2/g and which has failed to find utility because of the insufficient selectivity exhibited by a catalyst produced with the carrier (i.e. an α-alumina carrier using secondary alumina particles having a specific surface area in the range of 0.75 to 5 m^2/g, an apparent porosity in the range of 45 to 70%, and a particle diameter in the range of 50 to 100 microns), it is not only usable in this invention but excels in activity and selectivity.

As demonstrated clearly in the working examples set out below, an α-alumina carrier having a specific surface area of about 0.89 m^2/g is enabled by coating its outer surface and the surface of pores therein with amorphous silica, to show differences in performance manifested in the service life of the catalyst produced by the incorporation therein of life of the catalyst produced by the incorporation therein of cesium, though other properties of the carrier may be more or less responsible for the difference in quality. This is a surprising fact. The mechanism which underlies this unexpected improvement is still not fully understood. The presence of amorphous silica in an amount within the prescribed range on the carrier surfaces has a beneficial effect. The catalyst produced by causing the deposition of silver and cesium and/or a cesium compound on a porous inorganic refractory carrier, and then high temperature heat-treating the composite in an inert gas containing oxygen in a concentration of not more than 3% by volume at an elevated temperature in the range of 400° to 950°, exhibits an improvement of about 2% in selectivity as compared with a comparative catalyst which has not undergone this heat treatment. Further, it is reported that silica is strongly associated with the status of

pH. When all of these matters are taken into account, it is only logical to conclude that the presence of the amorphous silica on the outer surface of the carrier and the surface of pores in the carrier has a strong effect, as associated with the pH distribution within the carrier, on the deposition and distribution of silver and more of cesium. This fact is believed to bear upon the performance of the produced catalyst.

The amount of cesium and/or a cesium compound to be incorporated favorably in the catalyst of this invention is in the range of 0.001 to 0.05 gram equivalent weight, preferably 0.003 to 0.03 gram equivalent weight, and the most preferably in the range of more than 0.008 gram equivalent weight to 0.03 gram equivalent weight, per kg of finished catalyst.

The α-alumina carrier of this invention is required to have a specific area in the range of 0.75 to 5 m^2/g, preferably 0.8 to 2 m^2/g, to be used effectively in the present invention. An α-alumina carrier having a specific surface area of more than 5 m^2/g is impractical because it fails to produce a substantially satisfactory catalyst. In addition to the α-alumina and sodium component (mainly Na_2O), the carrier preferably contains such components in such amounts that are normal in the field of carriers.

The apparent porosity of the α-alumina carrier of this invention is preferable to be in the range of 45 to 70%, more preferably 50 to 60%. The specific pore volume of the α-alumina carrier of this invention preferably falls in the range of 0.1 to 0.8 cc/g, more preferably 0.2 to 0.5 cc/g. The α-alumina carrier of this invention comprises preferably not less than 90% by weight of a main α-alumina component having a particle diameter in the range of 3 to 20 mm, preferably 7 to 14 mm, and secondary alumina particles having a particle diameter in the range of 50 to 100 microns. The carrier to be used in the present invention is a particulate refractory carrier in the form of beads, pellets, or rings, whose average equivalent diameter is in the range of 3 to 20 mm, preferably 7 to 14 mm. The percentage composition of the components of the carrier and bears heavily on the performance of the produced catalyst. The selection of a carrier so shaped as to permit easy uniform deposition thereon of silver and cesium and/or a cesium compound during the course of production of a catalyst is a prerequisite for successful production of a catalyst excelling in selectivity.

To be used advantageously in the present invention, the α-alumina carrier is preferably produced by preparing an α-alumina carrier comprising more preferably not less than 90% by weight of an α-alumina component having a BET specific surface area in the range of 0.8 to 2 m^2/g, an apparent porosity in the range of 50 to 60%, a specific pore volume in the range of 0.2 to 0.5 cc/g, and particle diameter in the range of 3 to 20 mm, impregnating the α-alumina carrier with a liquid including colloidal silica having a particle diameter in the range of 5 to 50 millimicrons, preferably 6 to 20 millimicrons dispersed in water in an amount equaling the impregnated α-alumina carrier by heating, and calcining the dried composite at a temperature in the range of 700° to 1,500°C, preferably 1,000° to 1,400°C, for a period in the range of 1 to 10 hours, preferably 2 to 6 hours. As a result of the treatment of this procedure, the produced α-alumina carrier has its outer surface and the surface of pores therein coated with amorphous silica.

Preferably, the α-alumina carrier of this invention incorporates therein amorphous silica in a concentration in the range of 3×10^{-4} to 2×10^{-1} g, preferably 5×10^{-4} to 10^{-1} g, as Si per g of the carrier. The preparation of the catalyst is effected by a method which comprises impregnating the carrier described above with an aqueous solution or a solution in an organic solvent of a decomposable silver salt such as, for example, an aqueous silver nitrate solution, an ammonia complex of silver with an inorganic or organic acid, an amine complex of silver with an organic acid, or an aqueous silver lactate solution. The cesium and/or cesium compound may be deposited in advance on the carrier or deposited simultaneously with silver on the carrier by preliminary incorporation in the silver solution. Otherwise, it is may be deposited on the carrier on which silver has been already deposited after the step for decomposition and reduction of silver and the subsequent step for decomposition and reduction of silver and the subsequent step for decomposition and removal. Subsequently, the impregnated carrier is heated for decomposition or reduction of the decomposable silver salt. The product of this decomposition is then decomposed and removed by the use of a heated gas.

The salts of silver with inorganic and organic acids which are usable in this invention include silver nitrate, silver carbonate, silver sulphate, silver acetate, silver oxalate, silver lactate, silver succinate, and silver glucolate.

The amine which are usable for the formation of the amine complex include alkanolamines such as mono-, di-, and tri- ethanolamines, mono-, di-, and tri-n-propanolamines, mono-, di-, and tri-isopropanolamines, and alkylamines such as n-butylamine and isobutylamine.

Water is advantageously used as the solvent for the solution of a decomposable silver salt. The other solvents which are usable herein include lower aliphatic compounds of 2 to 6 carbon atoms having 1 to 3 alcoholic hydroxyl groups in the molecular unit, such as methanol, isopropanol, n-propanol, monoethylene glycol, diethylene glycol, triethylene glycol, trimethylene glycol, monopropylene glycol, methyl cellosolve, ethyl cellosolve, methyl carbitol, ethyl carbitol, and glycerol.

The cesium compounds which are usable herein include cesium oxalate, cesium carbonate, cesium acet-

ate, and other salts, and oxides and hydroxides.

It is important that the high temperature heat treatment should be carried out in an inert gas containing molecular oxygen in a concentrations of not more than 3% by volume, preferably not more than 1%. Typical effective inert gases are nitrogen, helium, argon, carbon dioxide and neon.

In the present invention, activation treatment means a heat treatment at a relatively low temperature, e.g. at least 150°C to less than 400°C in a molecular oxygen containing gas such as air for decomposing and dispersing an organic compound after precipitating and depositing the used silver compound and cesium compound in a conventional method for production of silver catalyst.

As concerns the preparation of the silver catalyst using the α-alumina catalyst contemplated by this invention, a silver catalyst to be used in the production of ethylene oxide by the catalytic vapor-phase oxidation of ethylene with molecular oxygen can be obtained by adopting a method which comprises preparing an α-alumina carrier of the invention, impregnating this α-alumina carrier with a solution of a decomposable silver such as an amine complex of silver with an organic acid, heating the impregnated α-alumina carrier to a temperature in the range of 100°C to 300°C thereby reducing or thermally decomposing the silver salt effecting deposition of silver and cesium and/or a cesium compound on the porous inorganic refractory carrier, and finally high temperature heat-treating the resultant composite in an inert gas containing oxygen in a concentration of not more than 3% by volume at an elevated temperature in the range of 400°C to 950°C, preferably 500° to 800°C.

In the silver catalyst of this invention silver can be deposited on the surface of the carrier in the form of a fine powder in an amount in the range of 5 to 25% by weight, preferably 5 to 20% by weight, based on the amount of a finished catalyst. The cesium or the cesium compound may be deposited simultaneously with the silver or deposited separately either before or after the deposition of the silver. For any of these manners of deposition, the cesium or the cesium compound is added in the form of an aqueous solution or an alcohol solution to the silver solution in a concentration in the range of 0.001 to 0.05 gram equivalent weight, preferably 0.003 to 0.03 gram equivalent weight, per kg of finished catalyst.

Reaction conditions heretofore known in the art are all usable in the production of ethylene oxide by the oxidation of ethylene with molecular oxygen in the presence of the silver catalyst of this invention. The reaction conditions generally employed in the production of ethylene oxide on a commercial scale can be used advantageously. Specifically, the ethylene content of the feed gas is in the range of 0.5 to 40% by volume, preferably 2 to 20% by volume, the oxygen content thereof in the range of 3 to 10% by volume, preferably 4 to 8% by volume, the carbon dioxide gas content in the range of 5 to 30% by volume, preferably 6 to 12% by volume, and the balance of such inert gases as nitrogen, argon, and steam, lower hydrocarbons such as methane and ethane, and halides such as ethylene dichloride and diphenyl chloride as reaction depressants. The spatial velocity of the feed gas is in the range of 1,000 to 30,000 hr^{-1} (STP), preferably 1,000 to 10,000 hr^{-1} (STP) and the pressure is in the range of 2 to 40 kg/cm^2 G, preferably 10 to 30 kg/cm^2 G.

Now, the present invention will be described more specifically below with reference to working examples and controls. It should be noted, however, that this invention is not limited to these examples.

The magnitudes of conversion and the selectivity reported in the working examples and controls were calculated in accordance with the following formulas.

$$\text{Conversion} = (\%)\ \frac{\text{Mol number of reacted ethylene}}{\text{Mol number of ethylene in feed gas}} \times 100$$

$$\text{Selectivity}(\%) = \frac{\text{Mol number of ethylene converted into ethylene oxide}}{\text{Mol number of reacted ethylene}} \times 100$$

[Procedure for production of Carrier A]

An Al_2O_3 (98.9% by weight in purity) carrier (produced by Norton Company and marketed under trademark designation of "Carrier SA-5102") having a BET specific surface area of 0.89 m 2/g, an apparent porosity of 52.8%, and a specific pore volume of 0.28 cc/g was impregnated with a liquid having colloidal silica 2 to 50 millimicrons in particle diameter dispersed in water in an amount equaling the water content of carrier. The impregnated carrier was concentrated and dried by heating and calcined at 1,000°C for four hours. Consequently, there was obtained an α-alumina carrier having a BET specific surface area of 0.89 m^2/g, an apparent porosity of 52.8%, and a pre volume of 0.28 cc/g and having the surface of pores in the carrier of Al_2O_3 (98.4% by weight) coated with amorphous silica. This α-alumina carrier was labelled as Carrier A. The amount of amorphous silica carried on Carrier A was found by the following method to be 5×10^{-3} g of Si per g of carrier.

[Method for determination of amount of amorphous silica on the outer surface of the carrier (Carrier A) and the surface of pores in the carrier]

10g of the carrier was crushed to a size of 8 to 10 mesh, immersed for one hour in 20 ml of an aqueous 46% by weight hydrofluoric acid solution, and filtered. The filtrate was tested for Si ion content with an atomic absorption analyzer.

Example 1

An impregnating solution was prepared by preparing a slurry containing 830 g of silver oxalate and 200 ml of water, adding this slurry to 700 ml of ethanolamine, stirring the resultant mixture thoroughly for solution of solids, thoroughly stirring the resultant solution and 100 ml of water added thereto, and then stirring the resultant solution with a solution of 14.2g of cesium nitrate in 200 ml of water.

In this impregnating solution, 4,000 ml of the α-alumina carrier A, heated in advance to about 100°C was left standing for impregnation. The impregnated carrier was concentrated and dried by heating, further heated in an air bath at 120°C for three hours, and then activated in a current of air at 280°C for 48 hours.

The catalyst thus obtained was packed in a closed container of stainless steel adapted to receive an inert gas, swept with nitrogen gas, and heat-treated in an electric oven at a catalyst bed temperature of 600°C for three hours, to obtain a finished catalyst. The total cesium content of the finished catalyst was found to be 11 x 10^{-3} gram equivalent weight/kg of catalyst.

[Method for determination of total cesium content of finished catalyst]

A sample, about 20 g, was pulverised and rolled (with a pressure of 20 kg/cm^2) to prepare a test sheet. A catalyst of known cesium content was similarly treated to prepare a standard test sheet. The test sheet was evaluated by the use of a calculation graph obtained from a record data of the standard sample with a fluorescent X-ray spectral analyzer. The finished catalyst was consequently found to have a total cesium content of 11 x 10^{-3} gram equivalent weight/kg of catalyst.

The finished catalyst thus obtained was packed in an externally heated double-pipe length. To the packed bed of the finished catalyst, a mixed gas containing 20% by volume of ethylene, 7% by volume of oxygen, 7% by volume or carbon dioxide gas, and the balance of methane, nitrogen, argon, and ethane and 1 ppm of ethylene dichloride was introduced to induce a reaction under the conditions of reaction pressure of 24 Kg/cm^2 G. The results of 10 days reaction and those of one year's reaction were as shown in Table 1.

Example 2

A reaction was performed by following the procedure of Example 1, except that the heat treatment was carried out under the conditions shown in Table 1. The results of 10 days' reaction and those of one year's reaction were as shown in Table 1.

Examples 3 and 4

A reaction was performed by following the procedure of Example 1, except that carrier indicated in Table 1 were used instead. The results of 10 days' reactions and those of one year's reactions were as shown in Table 1.

Controls 1 and 2

A reaction was performed by following the procedure of Example 1, except that the high temperature heat treatment was carried out under the conditions indicated in Table 1. The results of 10 days' reaction were as shown in Table 1.

Control 3

A reaction was performed by following the procedure of Example 1, except that the carrier (produced by Norton Company and marketed under trademark designation of "Carrier SA-5102") was used in its unmodified form. The results of 10 days' reaction were as shown in Table 1.

Control 4

A reaction was performed by following the procedure of Example 1, except that the carrier (produced by Norton Company and marketed under trademark designation of "Carrier SA-5102") was used in its unmodified form and the cesium content was changed as shown in Table 1 and the heat treatment was omitted. The results of 10 days' reaction and those of one year's reaction were as shown in Table 1.

Control 5

A reaction was performed by following the procedure of Example 1, except that the cesium content was changed as shown in Table 1 and the high temperature heat treatment was omitted. The results of 10 days' reaction and those of one year's reaction were as shown in Table 1.

Control 6

A reaction was performed by following the procedure of Example 1, except that the high temperature heat treatment was carried out in air instead of nitrogen atmosphere. The results of 10 days' reaction and those of one year's reaction were as shown in Table 1.

Table 1

	Example				Control					
	1	2	3	4	1	2	3	4	5	6
<Properties of carrier>										
Specific surface area (m^2/g)	0.89	0.89	0.89	0.89	0.89	0.89	0.89	0.89	0.89	0.89
Apparent Porosity (%)	52.8	52.8	52.8	52.8	52.8	52.8	52.8	52.8	52.8	52.8
Specific pore volume (cc/g)	0.28	0.28	0.28	0.28	0.28	0.28	0.28	0.28	0.28	0.28
<Composition>										
Al_2O_3 (% by weight)	98.4	98.4	98.9	89.9	98.4	98.4	98.9	98.9	98.4	98.4
Amount of amorphous silica in finished catalyst (g as Si/g of carrier)	$5x10^{-3}$	$5x10^{-3}$	$5x10^{-4}$	$1x10^{-1}$	$5x10^{-3}$	$5x10^{-3}$	$1.5x10^{-4}$	$1.5x10^{-4}$	$5x10^{-3}$	$5x10^{-3}$
Ratio of deposition of silver in finished catalyst (% by weight)	9	9	9	9	9	9	9	9	9	9
Amount of cesium in finished catalyst (gram equivalent weight/kg of catalyst)	$11x10^{-3}$	$22x10^{-3}$	$11x10^{-3}$	$11x10^{-3}$	$11x10^{-3}$	$11x10^{-3}$	$11x10^{-3}$	$3x10^{-3}$	$3x10^{-3}$	$11x10^{-3}$
Temperature of heat treatment (°C)	600	700	600	600	-	300	600	-	-	500
Time of heat treatment (hours)	3	3	3	3	-	3	3	-	-	3
Atmosphere of heat treatment	N_2	N_2	N_2	N_2	N_2	N_2	N_2	N_2	N_2	air
<Reaction conditions>										
(after 10 days)										
Reaction temperature (°C)	233	233	233	233	No reaction	No reaction	No reaction	230	230	245
Conversion (%)	10	10	10	10				10	10	10
Selectivity (%)	81	81	80.5	80.5				78.5	79.0	79.0
(after 1 year)										
Reaction temperature (°C)	235	235	235	235	-	-	-	235	235	235
Conversion (%)	10	10	10	10				10	10	10
Selectivity (%)	80.5	80.5	79.8	80.0				76.5	77.0	77.0

Claims

1. A catalyst for the production of ethylene oxide which comprises silver and cesium on an α-alumina carrier characterised in that the outer surface of the carrier and the surface of pores in the carrier are coated with amorphous silica, on which the metallic silver and cesium in finely divided form are supported, the silver representing 5 to 25% by weight, based on the amount of a finished catalyst, and the cesium representing 0.001 to 0.05 gram equivalent weight of cesium per kg of the finished catalyst.

2. A catalyst as claimed in Claim 1, characterised in that the α-alumina carrier contains the amorphous silica in an amount in the range of 3×10^{-4} to 2×10^{-1} g as Si per g of carrier.

3. A catalyst as claimed in Claim 1 or Claim 2, characterised in that the α-alumina carrier possesses an apparent porosity in the range of 45 to 70%.

4. A catalyst as claimed in any preceding claim, characterised in that the amount of cesium to be carried is in the range of 0.003 to 0.03 gram equivalent weight per Kg of the finished catalyst.

5. A catalyst as claimed in any preceding claim, characterised in that the α-alumina carrier contains the said amorphous silica in an amount in the range of 5×10^{-4} to 1×10^{-1} as Si per g of carrier.

6. A catalyst as claimed in any preceding claim, characterised in that the alumina carrier possesses a BET specific surface area in the range of 0.75 to 5 m^2/g, a specific porosity in the range of 0.1 to 0.8 cc/g, and a particle diameter in the range of 3 to 20mm.

7. A method for the production of a catalyst as claimed in any preceding claim, characterised by the steps of: impregnating the carrier with an aqueous solution containing colloidal silica; drying the impregnated carrier by heating; calcining the dried carrier thereby preparing an α-alumina carrier whose outer surface and the surface of whose pores are coated with amorphous silica; causing 5 to 25% by weight, based on the amount of a finished catalyst, of finely divided metallic silver and 0.001 to 0.05 gram equivalent weight of cesium per Kg of the finished catalyst to be carried by the carrier; activating the resultant composite thereby effecting deposition of the silver and cesium on the resultant porous inorganic refractory carrier, and subsequently subjecting the composite to a high temperature heat treatment in an inert gas at an elevated temperature in the range of 400° to 950°C.

8. A method as claimed in Claim 7, characterised in that the inert gas contains oxygen in a concentration of not more than 3% by volume.

9. A method as claimed in Claim 7 or 8, characterised in that coating the carrier with the amorphous silica is accomplished by dispersing colloidal silica having a particle diameter in the range of 5 to 50 millimicrons in water of an amount equaling the water content of carrier, and impregnating the carrier with the resultant dispersion, then drying and calcing the impregnated carrier.

Patentansprüche

1. Katalysator zur Herstellung von Ethylenoxid, der auf einem α-Aluminiumoxidträger Silber und Cäsium aufweist, dadurch gekennzeichnet, daß die äußere Oberfläche des Trägers und die Oberfläche der Poren im Träger mit amorphem Siliziumdioxid beschichtet sind, auf welchem das metallische Silber und Cäsium in fein verteilter Form aufgetragen sind, das Silber 5 bis 25 Gew.-%, bezogen auf die Menge des fertigen Katalysators, und das Cäsium 0,001 bis 0,05 Gramm Äquivalentgewicht des Cäsiums pro kg des fertigen Katalysators darstellen.

2. Katalysator gemäß Anspruch 1, dadurch gekennzeichnet, daß der α-Aluminiumoxidträger das amorphe Siliziumdioxid in einer Menge im Bereich von 3×10^{-4} bis 2×10^{-1} g als Silizium pro g des Trägers enthält.

3. Katalysator gemäß Anspruch 1 oder 2, dadurch gekennzeichnet, daß der α-Aluminiumoxidträger eine scheinbare Porösität im Bereich von 45 bis 70 % besitzt.

* C L M S *

4. Katalysator gemäß einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß die Menge des aufgetragenen Cäsiums im Bereich von 0,003 bis 0,03 Gramm Äquivalentgewicht pro kg des fertigen Katalysators liegt.

5. Katalysator gemäß einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß der α-Aluminiumoxidträger dieses amorphe Siliziumdioxid in einer Menge im Bereich von 5×10^{-4} bis 1×10^{-1} g als Silizium pro g des Trägers enthält.

6. Katalysator gemäß einem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß der Aluminiumoxidträger einen BET spezifischen Oberflächenbereich im Bereich von 0,75 bis 5 m^2/g, eine spezifische Porösität im Bereich von 0,1 bis 0,8 cm^3/g und einen Teilchendurchmesser im Bereich von 3 bis 20 mm besitzt.

7. Verfahren zur Herstellung eines Katalysators gemäß einem der vorhergehenden Ansprüche, gekennzeichnet durch die Schritte, daß man den Träger mit einer wässerigen Lösung, die kolloidales Siliziumdioxid enthält, imprägniert, den imprägnierten Träger durch Erhitzen trocknet, den getrockneten Träger kalziniert, wodurch ein α-Aluminiumoxidträger hergestellt wird, dessen äußere Oberfläche und Porenoberfläche mit amorphem Siliziumdioxid beschichtet sind, 5 bis 25 Gew.-%, bezogen auf die Menge des fertigen Katalysators, fein verteiltes, metallisches Silber und 0,001 bis 0,05 Gramm Äquivalentgewicht des Cäsiums pro kg des fertigen Katalysators mittels des Träger tragen läßt, den erhaltenen Verbundstoff aktiviert, wodurch Silber und Cäsium auf dem resultierenden, porösen, anorganischen, feuerfesten Träger abgelagert wird, und anschließend den Verbundstoff einer Hochtemperatur-Hitzebehandlung in einem Inertgas bei einer erhöhten Temperatur im Bereich von 400° bis 950°C unterwirft.

8. Verfahren gemäß Anspruch 7, dadurch gekennzeichnet, daß das Inertgas Sauerstoff in einer Konzentration von nicht mehr als 3 Volumen-% enthält.

9. Verfahren gemäß Anspruch 7 oder 8, dadurch gekennzeichnet, daß man den Träger mit dem amorphen Siliziumdioxid dadurch beschichtet, daß kolloidales Siliziumdioxid, welches einen Teilchendurchmesser im Bereich von 5 bis 50 Millimikron aufweist, in einer Wassermenge dispergiert wird, die dem Wassergehalt des Trägers entspricht, und den Träger mit der resultierenden Dispersion imprägniert, dann trocknet und den imprägnierten Träger kalziniert.

Revendications

1. Catalyseur pour la production d'oxyde d'éthylène, qui comprend de l'argent et du césium sur un support d'alumine-α, caractérisé en ce que la surface externe du support et la surface des pores du support sont enduites avec de la silice amorphe, sur laquelle l'argent et le césium métalliques sont placés sous une forme finement divisée, l'argent représentant 5 à 25% en poids sur base de la quantité de catalyseur fini et le césium représentant 0,001 à 0,05 g de poids équivalent de césium par kg du catalyseur fini.

2. Catalyseur suivant la revendication 1, caractérisé en ce que le support alumine-α contient de la silice amorphe en une quantité dans l'intervalle de 3×10^{-4} à 2×10^{-1} g de Si par g de support.

3. Catalyseur suivant la revendication 1 ou la revendication 2, caractérisé en ce que le support alumine-α possède une porosité apparente dans l'intervalle de 45 à 70%.

4. Catalyseur suivant l'une quelconque des revendications précédentes, caractérisé en ce que la quantité de césium à porter se situe dans l'intervalle de 0,003 à 0,03 g de poids équivalent par kg de catalyseur fini.

5. Catalyseur suivant l'une quelconque des revendications précédentes, caractérisé en ce que le support alumine-α contient de la silice amorphe en une quantité dans l'intervalle de 5×10^{-4} à 1×10^{-1} de Si par gramme de support.

6. Catalyseur suivant l'une quelconque des revendications précédentes, caractérisé en ce que le support alumine possède une surface spécifique BET dans l'intervalle de 0,75 à 5 m^2 par g, une porosité spécifique dans l'intervalle de 0,1 à 0,8 cm^3 par g et un diamètre particulaire dans l'intervalle de 3 à 20 mm.

* C L M S *

7. Procédé de production d'un catalyseur suivant l'une quelconque des revendications précédentes, caractérisé par les étapes de :

imprégnation du support par une solution aqueuse contenant de la silice colloïdale;

séchage du support imprégné par chauffage;

calcination du support séché pour préparer un support d'alumine-a dont la surface externe et la surface des pores sont enduites par de la silice amorphe;

transport par le support de 5 à 25% en poids, sur base de la quantité de catalyseur fini, d'argent métallique finement divisé et de 0,001 à 0,05 g d'équivalent en poids de césium par kg de catalyseur fini;

activation du composite résultant pour effectuer le dépôt de l'argent et du césium sur le support réfractaire inorganique poreux résultant, et ensuite

exposition du composite à un traitement par la chaleur à température élevée dans un gaz inerte à une température élevée dans l'intervalle de 400° à 950°C.

8. Procédé suivant la revendication 7, caractérisé en ce que le gaz inerte contient de l'oxygène à une concentration qui n'est pas supérieure à 3% en volume.

9. Procédé suivant la revendication 7 ou 8, caractérisé en ce que le revêtement du support par la silice amorphe est réalisé par dispersion de la silice colloïdale ayant un diamètre particulaire dans l'intervalle de 5 à 50 nm, dans de l'eau en une quantité équivalente à la teneur en eau du support et imprégnation du support avec la dispersion résultante, puis séchage et calcination du support imprégné.

* C L M S *