Description

The invention relates to silver-containing catalysts suitable for the preparation of ethylene oxide and to the use of the catalysts for the preparation of ethylene oxide. The catalysts are prepared using a unique alpha alumina carrier.

Catalysts for the production of ethylene oxide from ethylene and molecular oxygen generally comprising silver supported on a carrier formed substantially of alpha alumina are known from the European application EP-A-266015, corresponding to US-A-4766105, issued August 23, 1988. Such catalysts are typically promoted with alkali metals. Other co-promoters, such as rhenium, or rhenium along with sulfur, molybdenum, tungsten and chromium can also be utilized. While much research has been focused on promoters, more recently, work has been focused on the alumina supports and ways to modify them to produce improved catalysts.

European Patent Application 247,414, published December 2, 1987, discloses the addition of silica to an alpha alumina carrier. U.S. Patent No. 4,428,863, issued January 31, 1984, discloses the addition of barium aluminate or barium silicate to alumina carriers during their manufacture. In U.S. Patent No. 4,728,634, issued March 1, 1988, silicon dioxide and an alkali metal salt are mixed with water and an aluminum compound and calcined to produce a silica- and alkali metal-containing alpha alumina support. In U.S. Patent No. 4,874,739, October 17, 1989, a tin compound and an alkali metal compound is incorporated into an alpha alumina carrier.

The invention relates to ethylene oxide catalysts comprising silver, alkali metal promoters, rhenium promoters and optionally rhenium co-promoters selected from sulfur, molybdenum, tungsten, chromium and mixtures thereof supported on a carrier, characterized in that the carrier comprises at least 85, preferably at least 90 percent by weight of alpha alumina, from 0.01 to 6 percent by weight (measured as the oxide) of an added alkaline earth metal in the form of an oxide, from 0.01 to 5 percent by weight (measured as the dioxide) of added silicon in the form of an oxide and from zero to 10, preferably from 0.1 to 10 percent by weight (measured as the dioxide) of zirconium in the form of an oxide. Preferably the alkaline earth metal is calcium and/or magnesium.

The carrier is prepared by mixing a powdered alpha alumina having a purity of greater than about 98 percent, an average particle size ranging from 0.5 to 5 micrometer (microns) and an average crystallite size ranging from about 0.1 to about 5 micrometer (microns), an alkaline earth metal compound, a silicon compound and an optional zirconium compound, water, binder and/or burnout material to prepare a mixture which is extruded and calcined at a maximum temperature greater than about 1300 °C and preferably ranging from 1350 °C to 1500 °C.

The catalysts of the instant invention have an excellent initial activity and an improved stability over time.

The catalysts of the instant invention comprise a catalytically effective amount of silver, a promoting amount of alkali metal, a promoting amount of rhenium and optionally a promoting amount of a co-promoter selected from sulfur, chromium, molybdenum. tungsten and mixtures thereof, supported on a novel alpha alumina support. Descriptions of the carrier, the catalyst prepared with the carrier and the use of the catalyst are provided in detail below.

The novel carrier used to prepare the catalysts of the instant invention may, in general terms, be prepared from high purity alpha alumina powder, an alkaline earth metal oxide-providing compound, a silicon oxide-providing compound, an optional zirconium oxide-providing compound and conventional binders/burnout agents.

The alpha alumina used in the carrier preparation generally has a purity greater than about 98%, preferably greater than 98.5% and less than 0.06% by weight, such as from 0.02 to 0.06% by weight, of soda impurities. The alumina has the form of a fine powder, preferably one having an average particle size of from 0.5 to 100 microns. Smaller sizes such as from about 0.5 to about 5 microns and more preferably from about 1 to about 4 microns are particularly suitable. The average size may be determined by measuring the maximum dimension of a number of particles and taking the average thereof. The average crystallite size, which can be from 0.1 to 5 micrometer (microns) and more preferably from 2 to 4 micrometer (microns), is determined by measuring the maximum dimension of a number of crystallites and taking the average thereof. The alpha alumina will be present in the calcined carrier in an amount greater than about 85%, preferably 90%, and more preferably 95% by weight of the total carrier.

The alkaline earth metal component of the carrier can be present in an amount that represents from 0.01 to 6% by weight (measured as the oxide, MO) of the carrier weight but preferably the amount present is from 0.03 to 5.0% and especially from 0.05 to 2.0% by weight.

The alkaline earth metal compounds that may be used to prepare the carriers are oxides or compounds which are decomposable to or which form oxides upon calcination. Examples include carbonates, nitrates and carboxylates. Suitable compounds include the alkaline earth oxides themselves, as well as the mixed oxides such as the alkaline earth metal silicates, aluminates, aluminosilicates, zirconates and the like. The preferred compounds are calcium nitrate, calcium oxide and calcium silicate ($CaSiO_3$).

The silicon compounds used to prepare the carriers are oxides or compounds which are decomposable to or which form oxides upon calcination. Suitable compounds include silicon dioxide itself, as well as the mixed oxides such as the alkaline earth metal silicates, zirconium silicates, aluminosilicates including zeolites, hydrolyzable silicon compounds, polysiloxanes and the like. The amount of silicon component used should be such as to provide, in the final carrier composition, from 0.01 to 5.0%, preferably from 0.03 to 4.0% and most conveniently from 0.05 to 3.0% by weight (measured as silica).

The zirconium component, while optional, is preferably present in an amount that is from 0.1 to 10.0%, preferably from 0.3 to 5.0% and especially from 0.5 to 2.0% by weight based on the carrier weight. Where zirconia is generated in situ, the amount used should be selected to give a final proportion within these parameters.

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

Preferred carrier compositions comprise the alkaline earth metal-and the silicon-containing compounds in the form of a single compound, an alkaline earth metal silicate, which may be added as an original component or generated in situ by the reaction of silica or silica generating compounds with compounds that decompose to the alkaline earth metal oxide upon heating, with the amount of the oxide formed being in stoichiometric equivalent to or excess over the silica.

While the alkaline earth metal component of the catalyst can be chosen from magnesium, calcium, strontium and barium, the preferred embodiments are calcium and magnesium with calcium the most preferred. In the further description of this invention reference will frequently be made to the calcium form for the sake of simplicity.

The preferred carriers may be prepared by mixing a powdered alpha alumina, calcium silicate and zirconia with water and a binder and/or burnout material to prepare a mixture which is then extruded and calcined at a temperature ranging from 1350 °C to 1500 °C.

The alpha alumina powder is most preferably combined with calcium silicate itself but, as indicated above, it is also possible to use a calcium oxide-generating compound and silica or a silica-generating compound in such proportions that on heating calcium silicate is produced. These components are mixed with zirconia or a zirconia-generating compound, (where present), a burnout/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 ranging from 0.2 to 0.6, preferably 0.3 to 0.5 ml/g (cc/g). 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 the various components of the carrier prior to calcination to form an extrudable paste, i.e., the so-called low temperature binding agent. The binding agent also facilitates the extrusion process by adding lubricity. Typical binding agents include alumina gels, particularly in combination with a peptizing agent such as nitric or acetic acid. Also suitable are the carbon based materials that can also serve as burnout agents, such as the celluloses and substituted celluloses such as methylcellulose, ethylcellulose and carboxyethylcellulose, stearates such as organic stearate esters, e.g. methyl or ethyl stearate, waxes, polyolefin oxides and the like. Preferred binding agents are polyolefin oxides.

The use of calcium silicate, whether prepared directly or in situ with the constraints described above, allows the use of bonds containing, overall, a lower amount of silica than is present in conventional bonds. It also permits the avoidance of an excess of silicon dioxide which typically contains deleterious amounts of sodium, iron and/or potassium impurities, especially when present in clays, bentonite and the like.

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

When reference is made to oxide(s) of alkaline earth metal(s), silicon or zirconium which are present in the finished carrier and/or catalyst, it is understood that the oxide may be an oxide of only one metal or may be a complex oxide made up of the indicated metal and one or more of the other metals as well as alumina and/or catalyst promoters, such as, alkali metals.

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. 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, say less than about 2%, the extruded material is calcined under conditions sufficient to remove burnout agents 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 about 1300 °C and preferably ranging from 1350 °C to 1500 °C. Times at these maximum temperatures typically range from 0.1 to 10 hours, 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 (cc/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 height are usually found acceptable.

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

The catalysts of the instant invention comprise a catalytically effective amount of silver, a promoting amount of alkali metal, a promoting amount of rhenium and optionally a promoting amount of a co-promoter selected from sulfur, chromium, molybdenum, tungsten and mixtures thereof, supported on a novel alpha alumina support. In a preferred embodiment the alkali metal promoter is a higher alkali metal of potassium, rubidium, cesium or mixtures thereof. In a particularly preferred embodiment the alkali metal is cesium. Cesium in combination with lithium also provides very desirable advantages and is a preferred combination. Other promoters may be present such as co-promoters selected from sulfur, molybdenum, tungsten, chromium and mixtures thereof. Sulfate is a particularly preferred co-promoter. These catalysts and their preparation are particularly described in U.S. Patent No. 4,761,394, issued August 1988, U.S. Patent No. 4,766,105, issued August 23, 1988 and U.S. Patent No. 4,820,675, issued April 11, 1989.

The amount of silver present on the catalyst will typically range from 1 to 25, preferably from 5 to 20 percent by weight of the total catalyst. The amount of alkali metal promoter preferably present on the catalyst generally lies between 10 and 3000, preferably between 20 and 2000 and more preferably between 50 and 1500 parts by weight (basis metal) per million parts by weight of total catalyst. The amount of rhenium promoter preferably present on the catalyst generally lies between 0.1 to 10, more preferably between 0.2 to 5 micromoles (basis metal) per gram of total catalyst. The rhenium co-promoter, when present,
preferably will be present on the catalyst in an amount between 0 to 15, preferably between 0.1 to 15 micromoles (basis metal) per gram of total catalyst.

Methods for preparing the instant catalysts are conventional and are described in the above referenced patents. In general, the carrier is mixed with an aqueous solution of a silver complex, preferably in the presence of a solubilizing agent such as ethylenediamine, so that the carrier is impregnated with this solution, after which the carrier is separated from the solution and subsequently dried. The impregnated carrier is then heated to a temperature of between 100 °C and 400 °C for a period necessary for the silver complex to decompose and form a finely distributed layer of metallic silver which adheres to the carrier surfaces. The promoters may also be dissolved in the silver-containing solution to provide the desired amounts or they may be applied separately or together to the carrier by an impregnation step separate from the silver impregnation step. Preferably, silver and promoters are all combined in one impregnation step.

In commercial operation, ethylene and oxygen are converted to ethylene oxide in an ethylene oxide reactor which comprises a large fixed tube sheet heat exchanger containing several thousand tubes filled with catalyst. A coolant is used on the shell side of the reactor to remove the heat of reaction. Coolant temperatures are frequently utilized as an indication of catalyst activity, high coolant temperatures cor-

responding to lower catalyst activities.

In the reaction of ethylene with oxygen to produce ethylene oxide, the ethylene is present in at least a double molecular quantity, but the quantity of ethylene employed is generally much higher. The conversion is therefore conveniently calculated according to the quantity of converted oxygen in the reaction and one speaks of oxygen conversion. This oxygen conversion is dependent on the temperature of the reaction and is a measure of the activity of the catalyst. For example, the value T_{40} refers to the temperature at 40 mol% conversion of the oxygen fed to the reactor, T being the reactor temperature, or more preferably the coolant temperature, which latter is directly related to the former. The temperatures are generally higher for a higher conversion and are dependent on the catalyst employed and the reaction conditions. Selectivity is an indication of catalyst efficiency and indicates the mol% of ethylene in the feed which is converted to ethylene oxide in the product. The selectivity is indicated as, for example, S_{40}, which refers to the selectivity at 40 mol% oxygen conversion.

The conditions for carrying out an ethylene 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, presence of moderating agents to control the catalytic action, for example, 1-2-dichloroethane, vinyl chloride , ethyl chloride or chlorinated polyphenyl compounds, the desirability of employing recycle operations or applying successive conversions in different reactors to increase the yields of ethylene oxide, and any other special conditions which may be selected in processes for preparing ethylene oxide. Pressures in the range of from atmospheric to 3500 KPa (35 bar) are generally employed. Higher pressures are, however, by no means excluded. Molecular oxygen employed as reactant can be obtained from conventional sources. The suitable oxygen charge may consist essentially of 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 oxidation 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 1

GHSV*	1500 - 10,000
Inlet pressure	103 - 276 KPa
Inlet Feed	
Ethylene	1 - 40%
O_2	3 - 12%
CO_2	2 - 40%
Ethane	0 - 3%
Argon and/or methane and/or nitrogen diluent chloro-hydrocarbon moderator	0.3 - 20 ppmv total
Coolant temperature	180 - 315 °C
Catalyst temperature	180 - 325 °C
O_2 conversion level	10 - 60%
EO production (work rate)	0.91-7.26 Kg (2 - 16 lbs) EO/cu. ft. catalyst/hr.

* Liters of gas at standard temperature and pressure passing over the one liter 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.

Example 1

Carrier Preparation

Carrier A:

An alpha alumina powder (alumina #10) having the properties listed in Table 2 below was used to prepare the carrier.

Table 2

Properties for Alumina #10	
Median Particle Size	3.0-3.4 micrometer (microns)
Average Crystallite Size	1.8-2.2 micrometer (microns)
Soda Content	0.02-0.06% by wt.

This powder was used to prepare a formulation of the following ceramic components:

Alpha Alumina	98.8%
Zirconia	1.0%
Calcium Silicate	0.2%

Based on the weight of this formulation, the following were added in the indicated proportions:

Burn-out (walnut shell flour)	25.0%
Boric Acid	0.1%
Extrusion Aid(polyolefin oxide)	5.0%

After the above had been mixed for 45 seconds, enough water was added to give an extrudable mixture, (about 30% in practice), and mixing was continued for a further 4 minutes. At this point 5% (based on the weight of the ceramic components), of vaseline was added and mixing was continued for a further 3 minutes.

This material was extruded in the form of 7.94 mm x 7.94 mm (5/16 in. x 5/16 in.) hollow cylinders and dried to less than 2% moisture. These were then fired in a tunnel kiln to a maximum temperature of 1390 °C for about 4 hours.

After processing in this manner the carrier had the following properties:

Water Absorption	40.8%
Crush Strength	8.5 kg
Surface Area	0.54 m^2/g
Total Pore Volume (Hg)	0.43 ml/g (cc/g)
Median Pore Diameter	4.6 micrometer (microns)
Leachable Components (in 10% nitric acid) in ppm:	
Na	141
K	55
Ca	802
Al	573
SiO_2	1600

Additional carriers were prepared in a manner similar to the method described above with the exception that different starting materials were used. The properties of the different starting aluminas are shown in Table 3 below.

Table 3

Properties for Aluminas Nos. 11 and 49		
	#11	#49
Median Particle Size	3.0-3.6 μm (microns)	3.0-4.0 μm (microns)
Average Crystallite Size	1.6-1.8 μm (microns)	1.0-1.4 μm (microns) Soda
Content	0.02-0.06% wt.	0.02-0.06% wt.

The water pore volumes, surface areas and firing temperatures are shown in Table 4 and the other starting materials and their amounts are shown in Table 5 below.

A comparative carrier was made with alumina # 10 in the manner described above for carrier A except that no zirconia or calcium silicate were added. This comparative carrier is denoted as Comp-A. Its properties are provided in Table 4 below.

Table 4

Carrier	Water P.V., ml (cc)/g	SA,m^2/g	Firing Temp, °C
Comp-A	0.46	0.52	1371
A	0.41	0.54	1390
B	0.42	0.52	1371
C	0.39	0.49	1371
D	0.34	0.60	1371
E	0.26	0.16	1371
F	0.30	0.34	1371
G	0.27	0.25	1371
H	0.35	0.57	1454
I	0.43	0.60	1400
J	0.44	0.51	1393
K	0.37	0.50	1371
L	0.42	0.59	1371
M	0.38	0.51	1371
N	0.44	0.73	1371
O	0.42	0.74	1371
P	0.50	0.66	1413
Q	0.47	0.68	1413
R	0.51	0.81	1413
S	0.43	0.45	1413
T	0.43	0.38	1413
U	0.54	1.09	1413
V	0.55	0.66	1413
W	0.54	0.98	1413
X	0.42	0.41	1400
Y	0.47	0.60	1400
Z	0.41	0.44	1371
AA	0.40	0.46	1371

Table 5

Carrier	Alumina	Compound A*	Compound B*	Compound C*
Comp-A	#10	-0-	-0-	-0-
A	#10	ZrO_2 (1.0)	$CaSiO_3$ (0.20)	
B	#10	ZrO_2 (1.0)	$CaSiO_3$ (0.10)	
C	#10	ZrO_2 (1.0)	$CaSiO_3$ (0.40)	
D	#10		$CaSiO_3$ (0.40)	
E	#10		$CaSiO_3$ (0.20)	
F	#10	ZrO_2 (1.0)	$CaSiO_3$ (2.00)	
G	#10	ZrO_2 (1.0)	$CaSiO_3$ (4.00)	
H	#10	ZrO_2 (1.0)	$CaAl_2SiO_5$ (0.20)	
I	#10	ZrO_2 (1.0)	$Ca(NO_3)_2$ (0.28)	SiO_2 (0.10)
J	#10	ZrO_2 (0.8)	$Ba(NO_3)_2$ (0.47)	$ZrSiO_4$ (0.31)
K	#10	ZrO_2 (1.0)	$CaSiO_3$ (0.20)	$Ca(NO_3)_2$ (0.29)
L	#10	ZrO_2 (1.0)	$MgSiO_3$ (0.20)	
M	#10	ZrO_2 (1.0)	$MgSiO_3$ (2.20)	
N	#10	ZrO_2 (1.0)	$Mg_3Al_2(SiO_4)_3$ (0.20)	
O	#10	ZrO_2 (1.0)	$SrSiO_3$ (2.20)	
P	#49	ZrO_2 (1.0)	$CaSiO_3$ (0.30)	
Q	#49	ZrO_2 (1.0)	$CaSiO_3$ (0.30)	$Ca(NO_3)_2$ (0.29)
R	#49	$ZrSiO_4$ (0.46)	$Ca(NO_3)_2$ (0.44)	
S	#49	$ZrSiO_4$ (0.46)	$Ca(NO_3)_2$ (0.73)	
T	#49	$ZrSiO_4$ (0.46)	$Ca(NO_3)_2$ (1.02)	
U	#49	$ZrSiO_4$ (0.46)	$Ba(NO_3)_2$ (0.70)	
V	#49	$ZrSiO_4$ (0.46)	$Ba(NO_3)_2$ (1.17)	
W	#49	$ZrSiO_4$ (0.46)	$Ba(NO_3)_2$(1.63)	
X	#11	ZrO_2 (1.0)	mullite (0.07)	$Ca(NO_3)_2$(0.22)
Y	#11	ZrO_2 (1.0)	mullite (0.07)	$Ba(NO_3)_2$(0.13)
Z	#10	ZrO_2 (5.0)	$CaSiO_3$ (0.20)	
AA	#10	ZrO_2 (10.0)	$CaSiO_3$ (0.20)	

* Weight percent basis alumina.

Catalyst Preparation

Carrier A described above is a preferred carrier and was used to prepare an ethylene oxide catalyst. Into a solution of water and ethylenediamine were dissolved silver oxalate, cesium hydroxide, ammonium perrhenate, lithium sulfate and lithium nitrate in amounts sufficient to provide in the impregnated carrier (basis dry weight of carrier) 13.5 %wt silver, 437 ppm cesium, 1.5 micromoles/g of ammonium perrhenate, 1.5 micromoles/g of lithium sulfate and 12 micromoles/g of lithium nitrate. Approximately 30 g of the carrier was placed under 25 mm vacuum for 3 minutes at room temperature. Approximately 50 g of the impregnating solution was then introduced to submerge the carrier, and the vacuum was maintained at 25 mm for an additional 3 minutes. At the end of this time, the vacuum was released, and the excess impregnating solution was removed from the carrier by centrifugation for 2 minutes at 500 rpm. The impregnated carrier was then cured by being continuously shaken in a 279 l/hr (300 cu.ft./hr) air stream at 250 °C for 5 minutes. The cured catalyst, denoted as C-A[1] , is ready for testing.

The actual silver content of the catalyst can be determined by any of a number of standard, published procedures. The actual level of rhenium on the catalysts prepared by the above process can be determined by extraction with 20 mM aqueous sodium hydroxide solution, followed by spectrophotometric determination of the rhenium in the extract. The actual level of cesium on the catalyst can be determined by employing a stock cesium hydroxide solution, which has been labeled 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 the other alkali metals, is measured by extraction from the catalyst by boiling 10 grams of whole catalyst in 25 milliliters 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). It should be noted that the cesium content of the catalyst as determined by the water leaching technique may be lower than the cesium content of the catalyst as determined by the radiotracer technique.

The carriers listed in Tables 4 and 5 were used to prepare the catalysts listed in Table 6. C-A and C-A[1] refer to catalysts prepared with carrier A, C-B refer to catalysts prepared with carrier B, etc. C-Comp-A is the catalyst made from carrier Comp-A.

Table 6

Catalyst	Ag wt%	Cs ppm	NH_4ReO_4 µmol/g	Li_2SO_4 µmol/g	$LiNO_3$ µmol/g
C-Comp-A	13.2	501	1.5	1.5	4
C-A	13.5	463	1.5	1.5	4
C-A[1]	13.5	437	1.5	1.5	12
C-B	13.2	506	1.5	1.5	4
C-C	13.2	480	1.5	1.5	4
C-D	13.2	470	1.5	1.5	4
C-E	10.0	274	0.75	0.75	4
C-F	12.0	277	1.0	1.0	4
C-G	12.0	306	1.0	1.0	4
C-H	13.4	589	1.5	1.5	4
C-I	13.2	665	2.0	2.0	4
C-J	14.5	468	1.5	1.5	4
C-K	13.2	442	1.5	1.5	4
C-L	13.2	540	1.5	1.5	4
C-L[1]	13.2	481	1.5	0	4
C-M	13.2	415	1.5	1.5	4
C-M[1]	13.2	382	1.5	0	4
C-N	14.5	620	1.5	1.5	4
C-N[1]	14.5	573	1.5	0	4
C-O	14.5	547	1.5	1.5	4
C-P	14.5	599	2.0	2.0	4
C-Q	14.5	572	1.5	1.5	4
C-R	14.5	795	2.0	2.0	4
C-S	13.2	510	1.5	1.5	4
C-T	13.2	520	1.5	1.5	4
C-U	14.5	887	2.0	2.0	4
C-V	14.5	750	2.0	2.0	4
C-W	14.5	786	2.0	2.0	4
C-X	13.3	500	1.5	1.5	4
C-Y	14.5	620	1.5	1.5	4

The Process

The following describes the standard microreactor catalyst test conditions and procedures used to test the catalysts for the production of ethylene oxide from ethylene and oxygen.

Three to five grams of crushed catalyst 1.19-0.84 mm (14-20 mesh) are loaded into a 5.84 mm (0.23 inch) internal 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 catalyst used and the inlet gas flow rate are adjusted to achieve a gas hourly space velocity of 3300 ml (cc) of gas per cc 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 startup) consists of 30% ethylene, 8.5% oxygen, 5 to 7% carbon dioxide, 0.5% argon, balance nitrogen, and 0.5 to 5 ppmv ethyl chloride.

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 for 1 hour, followed by 245 °C for 1 hour. The temperature is then adjusted so as to achieve a constant oxygen conversion level of 40% (T_{40}) . The moderator level is varied and run for 4-24 hours at each level to determine the optimum moderator level for maximum selectivity. Performance data at the optimum moderator level and at T_{40} are usually obtained when the catalyst has been onstream for a total of about 24 hours and are provided in the examples given 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 performances of catalysts tested at different times, all catalysts described in this illustrative embodiment were tested simultaneously with a standard reference catalyst. All performance data reported in this illustrative embodiment are corrected to conform to the average initial performance of the reference catalyst which was S_{40} = 81.0% and T_{40} = 230 °C.

The catalysts prepared above were tested using the above procedure and the results are given in the table below.

Table 7

Catalyst	S_{40},%	T_{40}, °C
C-Comp-A	85.1	261
C-A	85.8	258
C-A[1]	86.0	258
C-B	86.3	261
C-C	86.0	255
C-D	86.5	259
C-E	83.8	266
C-F	85.6	259
C-G	85.0	276
C-H	85.9	267
C-I	85.2	263
C-J	84.2	262
C-K	87.0	258
C-L	87.1	250
C-L[1]	87.3	252
C-M	86.8	260
C-M[1]	86.0	252
C-N	87.0	257
C-N[1]	85.2	257
C-O	87.1	265
C-P	84.3	247
C-Q	85.5	252
C-R	86.6	260
C-S	83.8	250
C-T	85.7	264
C-U	82.9	254
C-V	83.5	260
C-W	81.9	252
C-X	85.6	254
C-Y	85.3	258

EXAMPLE 2

The performance of the preferred catalyst according to the invention over time was compared in a commercial ethylene oxide process to that of a comparative catalyst, having the same active components

on a slightly different carrier.

The catalyst according to the invention was that, referred to in Table 6 as C-A[1].

The comparative catalyst, hereinafter to be designated C-Comp-B, had 13.2 wt% of silver, 1.5 µmol/g of NH_4ReO_4, 1.5 µmol of Li_2SO_4, 2 µmol/g of $LiNO_3$, and CsOH added to give 415 ppm of Cs, on an alumina-based carrier comprising 54.5 wt% of Al, 0.039 wt% of $Ca(OH)_2$, 0.092 wt% of SiO_2 and no Zr, and having a Water Absorption of 36.0%, a Crush Strength of 7 kg, a Surface Area of 0.45 m^2/g, a Total Pore Volume of 58%, and a Median Pore Diameter of 3.6 µm (micron).

Both catalysts were continuously used in a commercial ethylene oxide production plant and followed for a period of 338 days (C-A[1]) and 312 days (C-Comp-B). During this period, the following average reaction conditions were maintained for the respective catalysts:

- Inlet Flow Gas Rate 3100 and 3400 ml (cc) of gas per cc of catalyst per hour;
- Inlet Gas Pressure 1550 and 1550 kPa;
- Gas feed containing, in wt%, 29.7 and 30.4 of ethylene, 7.9 and 7.4 of oxygen, 3.6 and 4.0 of carbon dioxide, 0.2 and 0.2 of ethane, balance methane, and 0.5 ppmv ethyl chloride.

The selectivity at 40 mol% oxygen conversion (S_{40}) and the activity measured by coolant temperature at 40 mol% oxygen conversion (T_{40} °C) were determined repeatedly during the operation and the results are given in Figure 1 and 2, respectively.

From the results it is clear, that the catalyst according to the invention is much more stable during operation under commercial plant conditions.

Claims

1. An ethylene oxide catalyst for the vapor phase production of ethylene oxide from ethylene and oxygen comprising a catalytically effective amount of silver, a promoting amount of alkali metal and a promoting amount of rhenium supported on a carrier characterised in that the carrier comprises at least 85 percent by weight of alpha alumina, from 0.05 to 6 percent by weight (measured as the oxide, MO) of an alkaline earth metal in the form of an oxide, from 0.01 to 5 percent by weight (measured as the dioxide) of silicon in the form of an oxide and from zero to 10 percent by weight (measured as the dioxide) of zirconium in the form of an oxide.

2. The catalyst of claim 1 wherein the carrier has a water pore volume between 0.2 and 0.6 ml/g (cc/g) and a surface area between 0.15 and 3 m^2/g.

3. The catalyst of claim 2 wherein the carrier has a water pore volume between 0.3 and 0.5 ml/g (cc/g) and a surface area between 0.3 and 2 m^2/g.

4. The catalyst of claim 1 wherein, in 100 weight percent of the carrier, the alpha alumina is present in an amount greater than about 90 weight percent, the alkaline earth metal oxide ranges from 0.05 to 5 weight percent, the silicon oxide ranges from 0.03 to 4 weight percent and the zirconium oxide ranges from 0.3 to 5 weight percent.

5. The catalyst of claim 4 wherein, in the carrier, the alpha alumina is present in an amount greater than about 95 weight percent, the alkaline earth metal oxide ranges from 0.05 to 4 weight percent, the silicon oxide ranges from 0.05 to 3 weight percent and the zirconium oxide ranges from 0.5 to 2 weight percent.

6. The catalyst of claim 5 wherein, in the carrier, the alkaline earth metal oxide is selected from the group consisting of calcium oxide, magnesium oxide and mixtures thereof and is present in an amount ranging from 0.05 to 2% by weight.

7. The catalyst of claim 1 wherein the alpha alumina has a soda content of less than about 0.06% weight.

8. The catalyst of claim 1 wherein the catalyst additionally comprises a rhenium co-promoter selected from the group consisting of sulfur, molybdenum, tungsten, chromium and mixtures thereof supported on the carrier.

9. The catalyst of claim 1 wherein the silver ranges from 1 to 25 percent by weight of the total catalyst, the alkali metal ranges from 10 to 3000 parts per million by weight of the total catalyst and the rhenium

on a slightly different carrier.

The catalyst according to the invention was that, referred to in Table 6 as C-A[1].

The comparative catalyst, hereinafter to be designated C-Comp-B, had 13.2 wt% of silver, 1.5 µmol/g of NH_4ReO_4, 1.5 µmol of Li_2SO_4, 2 µmol/g of $LiNO_3$, and CsOH added to give 415 ppm of Cs, on an alumina-based carrier comprising 54.5 wt% of Al, 0.039 wt% of $Ca(OH)_2$, 0.092 wt% of SiO_2 and no Zr, and having a Water Absorption of 36.0%, a Crush Strength of 7 kg, a Surface Area of 0.45 m^2/g, a Total Pore Volume of 58%, and a Median Pore Diameter of 3.6 µm (micron).

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The selectivity at 40 mol% oxygen conversion (S_{40}) and the activity measured by coolant temperature at 40 mol% oxygen conversion (T_{40} °C) were determined repeatedly during the operation and the results are given in Figure 1 and 2, respectively.

From the results it is clear, that the catalyst according to the invention is much more stable during operation under commercial plant conditions.

Claims

1. An ethylene oxide catalyst for the vapor phase production of ethylene oxide from ethylene and oxygen comprising a catalytically effective amount of silver, a promoting amount of alkali metal and a promoting amount of rhenium supported on a carrier characterised in that the carrier comprises at least 85 percent by weight of alpha alumina, from 0.05 to 6 percent by weight (measured as the oxide, MO) of an alkaline earth metal in the form of an oxide, from 0.01 to 5 percent by weight (measured as the dioxide) of silicon in the form of an oxide and from zero to 10 percent by weight (measured as the dioxide) of zirconium in the form of an oxide.

2. The catalyst of claim 1 wherein the carrier has a water pore volume between 0.2 and 0.6 ml/g (cc/g) and a surface area between 0.15 and 3 m^2/g.

3. The catalyst of claim 2 wherein the carrier has a water pore volume between 0.3 and 0.5 ml/g (cc/g) and a surface area between 0.3 and 2 m^2/g.

4. The catalyst of claim 1 wherein, in 100 weight percent of the carrier, the alpha alumina is present in an amount greater than about 90 weight percent, the alkaline earth metal oxide ranges from 0.05 to 5 weight percent, the silicon oxide ranges from 0.03 to 4 weight percent and the zirconium oxide ranges from 0.3 to 5 weight percent.

5. The catalyst of claim 4 wherein, in the carrier, the alpha alumina is present in an amount greater than about 95 weight percent, the alkaline earth metal oxide ranges from 0.05 to 4 weight percent, the silicon oxide ranges from 0.05 to 3 weight percent and the zirconium oxide ranges from 0.5 to 2 weight percent.

6. The catalyst of claim 5 wherein, in the carrier, the alkaline earth metal oxide is selected from the group consisting of calcium oxide, magnesium oxide and mixtures thereof and is present in an amount ranging from 0.05 to 2% by weight.

7. The catalyst of claim 1 wherein the alpha alumina has a soda content of less than about 0.06% weight.

8. The catalyst of claim 1 wherein the catalyst additionally comprises a rhenium co-promoter selected from the group consisting of sulfur, molybdenum, tungsten, chromium and mixtures thereof supported on the carrier.

9. The catalyst of claim 1 wherein the silver ranges from 1 to 25 percent by weight of the total catalyst, the alkali metal ranges from 10 to 3000 parts per million by weight of the total catalyst and the rhenium

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ranges from 0.1 to 10 micromoles per gram of catalyst.

10. The catalyst of claim 9 wherein the catalyst additionally comprises a rhenium co-promoter selected from the group consisting of sulfur, molybdenum, tungsten, chromium and mixtures thereof supported on the carrier in an amount ranging from about 0.1 to about 15 micromoles per gram of catalyst.

11. A process for the preparation of an ethylene oxide catalyst according to claim 1 which comprises:
(a) mixing:
(i) an alpha alumina powder having a purity of greater than about 98 percent, an average crystallite size between about 0.1 and about 5 μm (microns),
(ii) an alkaline earth metal oxide or compound which is decomposable to or forms an oxide upon calcination,
(iii) a silicon oxide or compound which is decomposable to or forms an oxide upon calcination and
(iv) an optional zirconium oxide or compound which is decomposable to or forms an oxide upon calcination;
with water and a binder/burnout agent in amounts sufficient to provide in the finished carrier alpha alumina in an amount greater than about 85 percent by weight, alkaline earth metal oxide in an amount ranging from 0.01 to 6 percent by weight, silicon oxide in an amount ranging from 0.01 to 5 percent by weight and zirconium oxide in an amount ranging from zero to 10 percent by weight,
(b) extruding the resulting mixture of step (a) to form pellets and
(c) calcining the pellets at a temperature greater than 1300 °C for a time sufficient to produce a carrier having a surface area ranging from 0.15 to 3 square meters per gram and a water pore volume ranging from 0.2 to 0.6 cubic centimeters per gram;
(d) adding the appropriate amount of silver, alkali metal and rhenium to the support.

12. A process according to claim 11, wherein the alpha alumina powder has a purity of greater than about 98.5 percent, an average crystallite size between 2 and 4 micrometer (microns) and a soda content of less than about 0.06% weight;

13. A process according to claim 11 or 12, wherein rhenium co-promoter selected from the group consisting of sulfur, molybdenum, tungsten, chromium and mixtures thereof is added to the carrier.

14. A process for the production of ethylene oxide by contacting ethylene in the vapor phase with an oxygen-containing gas at ethylene oxide forming conditions at a temperature ranging between 180 °C and 330 °C with the catalyst of any one of claims 1-10.

Patentansprüche

1. Ein Ethylenoxidkatalysator für die Dampfphasenherstellung von Ethylenoxid aus Ethylen und Sauerstoff, umfassend eine katalytisch wirksame Menge an Silber, eine als Promotor wirkende Menge an Alkalimetall und eine als Promotor wirksame Menge an Rhenium auf einem Träger, dadurch gekennzeichnet, daß der Träger mindestens 85 Gewichtsprozent alpha-Aluminiumoxid, 0,05 bis 6 Gewichtsprozent (gemessen als Oxid ,MO) eines Erdalkalimetalls in Form eines Oxids, 0,01 bis 5 Gewichtsprozent (gemessen als Dioxid) Silicium in Form eines Oxids und 0 bis 10 Gewichtsprozent (gemessen als Dioxid) an Zirkon in Form eines Oxids enthält.

2. Der Katalysator von Anspruch 1, in welchem der Träger ein Wasserporenvolumen von 0,2 bis 0,6 ml/g (cm^3/g) und eine Oberflächenausdehnung von 0,15 bis 3 m^2/g aufweist.

3. Der Katalysator von Anspruch 2, in welchem der Träger ein Wasserporenvolumen von 0,2 bis 0,5 ml/g (cm^3/g) und eine Oberflächenausdehnung von 0,3 bis 2 m^2/g aufweist.

4. Der Katalysator von Anspruch 1, in welchem bezogen auf 100 Gewichtsprozent des Trägers, das alpha-Aluminiumoxid in einer Menge vorliegt, die größer ist als ca. 90 Gewichtsprozent, das Erdalkalimetalloxid in einer Menge im Bereich von 0,05 bis 5 Gewichtsprozent, das Siliciumoxid in einer Menge von 0,03 bis 4 Gewichtsprozent und das Zirkonoxid in einer Menge von 0,3 bis 5 Gewichtsprozent vorliegt.

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5. Der Katalysator von Anspruch 4, in welchem das alpha-Aluminiumoxid im Träger in einer Menge von mehr als 95 Gewichtsprozent, das Erdalkalimetalloxid in einer Menge von 0,05 bis 4 Gewichtsprozent, das Siliciumoxid in einer Menge von 0,05 bis 3 Gewichtsprozent und das Zirkonoxid in einer Menge von 0,5 bis 2 Gewichtsprozent vorliegt.

6. Der Katalysator von Anspruch 5, in welchem das Erdalkalimetalloxid im Träger ausgewählt ist aus der Gruppe, bestehend aus Calciumoxid, Magnesiumoxid und Mischungen davon, und in einer Menge von 0,05 bis 2 Gewichtsprozent vorliegt.

7. Der Katalysator von Anspruch 1, in welchem das alpha-Aluminiumoxid einen Sodagehalt von weniger als ca. 0,06 Gewichtsprozent aufweist.

8. Der Katalysator von Anspruch 1, wobei der Katalysator zusätzlich einen Rhenium-Copromotor, ausgewählt aus der Gruppe, bestehend aus Schwefel, Molybdän, Wolfram, Chrom und Mischungen davon, auf einem Träger enthält.

9. Der Katalysator von Anspruch 1, in welchem die Menge an Silber im Bereich von 1 bis 25 Gewichtsprozent, bezogen auf den Gesamtkatalysator liegt, die Menge an Alkalimetall im Bereich von 10 bis 3000 Gewichtsteilen p.M., bezogen auf den Gesamtkatalysator, und die Menge an Rhenium im Bereich von 0,1 bis 10 µM je g Katalysator liegt.

10. Der Katalysator von Anspruch 9, wobei der Katalysator zusätzlich einen Rhenium-Copromotor, ausgewählt aus der Gruppe, bestehend aus Schwefel, Molybdän, Wolfram, Chrom und Mischungen davon, auf einem Träger in einer Menge von ca. 0,1 bis ca. 15 µM je g Katalysator enthält.

11. Ein Verfahren zur Herstellung eines Ethylenoxidkatalysators nach Anspruch 1, welches umfaßt:
    a) das Vermischen von:
    (i) einem alpha-Aluminiumoxidpulver mit einer Reinheit von mehr als 98%, einer durchschnittlichen Kristallitgröße von ca. 0,1 bis ca. 5 µm,
    (ii) einem Erdalkalimetalloxid oder einer Verbindung, die beim Calcinieren zu einem Oxid abbaubar ist oder ein Oxid bildet,
    (iii) eines Siliciumoxids oder einer Verbindung, die beim Calcinieren zu einem Oxid abbaubar ist oder ein Oxid bildet, und
    (iv) eines gegebenenfalls vorhandenen Zirkonoxids oder einer Verbindung, die beim Calcinieren zu einem Oxid abbaubar ist oder ein Oxid bildet;
    mit Wasser und einem Binde/Ausbrenn-Material in Mengen, die ausreichen,damit im endgültigen Träger alpha-Aluminiumoxid in einer Menge von mehr als ca. 85 Gewichtsprozent, Erdalkalimetalloxid in einer Menge von 0,01 bis 6 Gewichtsprozent, Siliciumoxid in einer Menge von 0,01 bis 5 Gewichtsprozent und Zirkonoxid in einer Menge von 0 bis 10 Gewichtsprozent vorliegt,
    b) das Extrudieren der resultierenden Mischung von Stufe a) unter Bildung von Kügelchen und
    c) das Calcinieren der Kügelchen bei einer Temperatur von mehr als 1300 °C über einen ausreichenden Zeitraum, um einen Träger herzustellen, der eine Oberflächenausdehnung im Bereich von 0,15 bis 3 m^2 je g und ein Wasserporenvolumen im Bereich von 0,2 bis 0,6 cm^3 je g aufweist;
    d) das Zugeben der geeigneten Menge an Silber, an Alkalimetall und Rhenium zum Träger.

12. Ein Verfahren nach Anspruch 11, in welchem das alpha-Aluminiumoxidpulver eine Reinheit von mehr als ca. 98,5%, eine durchschnittliche Kriztallitgröße zwischen 2 und 4 µm und einen Sodagehalt von weniger als ca. 0,06 Gewichtsprozent aufweist.

13. Ein Verfahren nach Anspruch 11 oder 12, in welchem der Rhenium-Copromotor, ausgewählt aus der Gruppe, bestehend aus Schwefel, Molybdän, Wolfram, Chrom und Mischungen davon zu dem Träger zugegeben wird.

14. Ein Verfahren sur Herstellung von Ethylenoxid durch Kontaktieren des Ethylens in der Dampfphase mit einem sauerstoffhaltigen Gas bei den zum Bilden von Ethylenoxid erforderlichen Bedingungen bei einer Temperatur im Bereich von 180 °C bis 330 °C mit dem Katalysator nach einem der Ansprüche 1 bis 10.

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Revendications

1. Un catalyseur pour l'oxyde d'éthylène destiné à la préparation en phase vapeur d'oxyde d'éthylène à partir d'éthylène et d'oxygène, comportant une quantité efficace du point de vue catalytique d'argent, une quantité promotrice de métal alcalin et une quantité promotrice de rhénium supporté sur un support, caractérisé en ce que le support comporte au moins 85% en poids d'alpha alumine, de 0,05 à 6% (mesuré en tant qu'oxyde, MO) d'un métal alcalino-terreux sous la forme d'un oxyde, de 0,01 à 5% en poids, (mesuré en tant que dioxyde) de silicium sous la forme d'un oxyde et de 0 à 10% en poids (mesuré en tant que dioxyde) de zirconium sous la forme d'un oxyde.

2. Le catalyseur de la revendication 1, dans lequel le support présente un volume des pores dans l'eau entre 0,2 et 0,6 ml/g (cm^3/g) et une surface spécifique entre 0,15 et 3 m^2/g.

3. Le catalyseur de la revendication 2, dans lequel le support présente un volume des pores dans l'eau entre 0,3 et 0,5 ml/g (cm^3/g) et une surface spécifique entre 0,3 et 2 m^2/g.

4. Le catalyseur de la revendication 1, dans lequel dans 100% en poids du support, l'alumine alpha est présente en une quantité plus importante qu'environ 90% en poids, l'oxyde de métal alcalino terreux se situe dans la gamme de 0,5 à 5% en poids, l'oxyde de silicium se situe dans la gamme de 0,03 à 4% en poids et l'oxyde de zirconium se situe dans la gamme de 0,3 à 5% en poids.

5. Le catalyseur de la revendication 4, dans lequel, dans le support l'alumine alpha est présente en une quantité plus importante qu'environ 95% en poids, l'oxyde de métal alcalino-terreux se situe de 0,05 à 4% en poids, l'oxyde de silicium se situe dans la gamme de 0,05 à 3% en poids et l'oxyde de zirconium se situe dans la gamme de 0,5 à 2% en poids.

6. Le catalyseur de la revendication 5, dans lequel, dans le support, l'oxyde de métal alcalino-terreux est choisi dans le groupe constitué de l'oxyde de calcium, de l'oxyde de magnésium et de mélanges de ceux-ci et est présent en une quantité se situant dans la gamme de 0,05 à 2% en poids.

7. Le catalyseur de la revendication 1, dans lequel l'alpha alumine a une teneur en soude inférieure à environ 0,06% en poids.

8. Le catalyseur de la revendication 1, dans lequel le catalyseur comporte en outre un co-promoteur du rhénium choisi dans le groupe constitué du soufre, du molybdène, du tungstène, du chrome et des mélanges de ceux-ci supporté sur le support.

9. Le catalyseur de la revendication 1, dans lequel l'argent se situe dans la gamme de 1 à 25% en poids du catalyseur total, le métal alcalin se situe dans la gamme de 10 à 3000 parties par million en poids du catalyseur total et le rhénium se situe dans la gamme de 0,1 à 10 micromoles par gramme de catalyseur.

10. Le catalyseur selon la revendication 9, dans lequel le catalyseur comporte en outre un co-promoteur de rhénium choisi dans le groupe constitué du soufre, du molybdène, du tungstène, du chrome et des mélanges de ceux-ci supporté sur le support en une quantité se situant d'environ 0,1 à environ 15 micromoles par gramme de catalyseur.

11. Un procédé pour la préparation d'un catalyseur pour l'oxyde d'éthylène selon la revendication 1, qui comporte:
    (a) le mélange :
    (i) d'une poudre d'alumine alpha présentant une pureté supérieure d'environ 98%, une dimension moyenne des cristallites entre environ 0,1 et environ 5 µm (microns),
    (ii) d'un oxyde d'un métal alcalino-terreux ou d'un composé qui est susceptible d'être décomposé en ou de former un oxyde après calcination,
    (iii) d'un oxyde de silicium ou d'un composé qui est susceptible d'être décomposé en ou de former un oxyde après calcination et
    (iv) d'un oxyde de zirconium éventuel ou d'un composé qui est susceptible d'être décomposé ou de former un oxyde après calcination ;

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avec de l'eau ou un agent liant/agent de combustion en des quantités suffisantes pour procurer dans le support fini l'alumine alpha en une quantité supérieure à environ 85% en poids, un oxyde de métal alcalino-terreux en une quantité se situant dans la gamme de 0,01 à 6% en poids, de l'oxyde de silicium en une quantité se situant entre 0,01 à 5% en poids et de l'oxyde de zirconium en une quantité se situant de 0 à 10% en poids,
(b) l'extrusion du mélange résultant obtenu à l'étape (a) pour former des comprimés et
(c) la calcination des comprimés à une température supérieure à 1300 °C pendant un temps suffisant pour obtenir un support présentant une surface spécifique se situant dans la gamme de 0,15 à 3 m^2/g et un volume des pores dans l'eau se situant dans la gamme de 0,2 à 0,6 cm^3/g ;
(d) l'addition de la quantité appropriée d'argent, de métal alcalin et de rhénium au support.

12. Un procédé selon la revendication 11, dans lequel la poudre d'alumine alpha présente une pureté supérieure à environ 98,5%, une dimension moyenne des cristallites entre 2 et 4 micromètres (microns) et une teneur en soude inférieure à environ 0,06% en poids.

13. Un procédé selon la revendication 11 ou 12, dans lequel le co-promoteur du rhénium qui est choisi dans le groupe constitué du soufre, du molybdène, du tungstène, du chrome et de mélanges de ceux-ci est ajouté au support.

14. Un procédé pour la préparation d'oxyde d'éthylène en mettant en contact l'éthylène en phase vapeur avec un gaz renfermant de l'oxygène sous des conditions de formation d'oxyde d'éthylène à une température se situant entre 180 °C et 330 °C avec le catalyseur de l'une quelconque des revendications 1 à 10.

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