

Description

The invention relates to a catalyst carrier as well as to a composition and a process for making same.

Catalysts for the production of ethylene oxide from ethylene and molecular oxygen generally comprise silver supported on a carrier formed substantially of alpha alumina. 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. See, for example, U.S. 4,766,105, issued August 23, 1988. 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 are incorporated in to an alpha alumina carrier.

US-A-3,725,307 relates to a silver-supported catalyst used in the production of the ethylene oxide by the vapor phase oxidation of ethylene. The catalyst disclosed in US-A-3,725,307 has a selectivity in the range of 70%. The carrier of this catalyst contains a large amount of silicon oxide (11.65%).

The invention provides a catalyst carrier according to independent claim 1, a carrier composition suitable for preparing a catalyst carrier according to independent claim 5, and methods for making catalyst carriers according to independent claims 11 and 13. Further advantageous features, aspects, and details of the invention are evident from the dependent claims, the description and embodiments and tables.

The invention provides a novel alpha alumina carrier useful in conjunction with silver-containing catalysts in the preparation of ethylene oxide.

The invention provides an alpha alumina based carrier comprising at least about 85% by weight of alpha alumina, from about 0.05 to about 6% by wt. (measured as the oxide) of a calcium or magnesium oxide which is defined to include mixed oxides such as the preferred silicate; from 0.05 to about 5% by weight, (measured as silica) of a silicon oxide, including mixed oxides such as the silicates, and from zero to about 10% by wt. (measured as the oxide) of a zirconium oxide.

Preferred carrier compositions comprise the calcium, magnesium 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 calcium or magnesium oxide upon heating, with the amount of the oxide formed being in stoichiometric excess over the silica so as to leave essentially no residual base-soluble silica in the final composition.

The alkaline earth metal component of the catalyst is chosen between calcium and magnesium with the former being 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 about 1350 °C to about 1500 °C.

The novel carrier of the invention may be prepared from high purity alpha alumina powder, a calcium or magnesium oxide-providing compound, a silica-providing compound, an optional zirconia-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 about 98.5% and less than about 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 about 0.5 to about 5 μm and more preferably from about 1 to about 4 μm. The average crystallite size, which can be from about 0.1 to about 5 μm and more preferably from about 2 to about 4 μm, 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 calcium or magnesium component of the carrier composition of the invention this can be present in an amount that represents from 0.05 to about 6% by weight (measured as the oxide, MO_x) of the carrier weight but preferably the amount present is from about 0.05 to about 5.0% and especially from about 0.05 to about 4.0% by weight. Calcium or magnesium amounts present of 0.05 to 2% weight are also preferred. Where a silicate is formed in situ, the weights of the components used should be selected with these

limitations in mind and so as to avoid the presence of base-soluble silica in the finished composition.

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

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

The zirconia component, while optional, is preferably present in an amount that is from about 0.01 to about 10.0%, such as from about 0.3 to about 5.0% and especially from about 0.05 to about 2.0% by
 15 weight based on the carrier weight. Where the zirconia is generated in situ, the amount used should be selected to give a final proportion within these parameters.

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

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 with essentially no base soluble
 25 silica. 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
 30 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 binding agents can also serve as burnout agents. The burnout agents are provided in an amount and size distribution to provide a final carrier having a water pore volume preferably ranging from about 0.2 to 0.6 cm³/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
 40 suitable are the carbon based materials that can also serve as burnout agents, including celluloses and substituted celluloses such as methylcellulose, ethylcellulose and carboxyethylcellulose, stearates such as organic stearate esters, e.g. methyl or ethyl stearate, waxes, polyolefin oxides and the like. Preferred binding agents are 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
 45 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
 50 heated in the absence of calcium silicate.

After the components of the carrier are mixed together, say by milling, 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 would convert to steam during calcination and destroy the physical integrity of the extrudate shapes. Typically the drying and calcination are combined in one step by suitable program-
 55 ming of the time and temperature. Calcining is carried out 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 over 1300°C and preferably ranging from about 1350°C to about 1500°C. Times at these

maximum temperatures can range from about 0.5 to about 200 minutes.

The calcined carriers will typically have pore volumes (water) ranging from about 0.2 to about 0.6, and more preferably from about 0.3 to about 0.5 cm³/g, and surface areas ranging from about 0.15 to about 3.0, and preferably from about 0.3 to about 2.0 m²/g.

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

The carriers described above are particularly suited for preparing ethylene oxide catalysts which have high initial selectivities and long lives (enhanced stability).

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

Illustrative Embodiments

Carrier Preparation

Carrier A:

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

Table 2

Median Particle Size	3.0-3.4 μ m
Average Crystallite Size	1.8-2.2 μ m
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*	5.0%

* Polyolefin oxide

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 .79cm x .79cm (5/16 x 5/16 inch) 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	8.48Kg (18.7 lbs.)
Surface Area	0.56 m ² /g.
Total Pore Volume (Hg)	0.43 cm ³ /g.
Median Pore Diameter	4.6μm

Leachable Cations (in 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	3.0-4.0 μm
Average Crystallite size	1.6-1.8	1.0-1.4 μm
Soda Content	0.02-0.06%	0.02-0.06% by 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 same manner described above for carrier A except that no zirconia or calcium silicate were added. This comparative carrier was denoted as Com-A. Its properties are provided in Table 4 below.

Table 4

Carrier	Pore Vol. cm ³ /g	Surface Area m ² /g (water)	Firing Temp. Degrees °C
Com-A	0.46	0.52	1371
A	0.41	0.54	1388
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
X	0.42	0.41	1400
Z	0.41	0.44	1371
AA	0.40	0.46	1371

Table 5

Carr.	Alumina	Compound A*	Compound B*	Compound C*
Com-A	#10			
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)	CaAlSiO ₆ (0.20)	
I	#10	ZrO ₂ (1.0)	Ca(NO ₃) ₂ (0.28)	SiO ₂ (0.10)
J	#10	ZrO ₂ (1.0)	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 ₃ Al 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)	
X	#11	ZrO ₂ (1.0)	Mullite (0.07)	Ca(NO ₃) ₂ (0.22)
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 perrenate, lithium sulfate and lithium nitrate in amounts sufficient to provide in the impregnated carrier (basis dry weight of carrier) 13.2 %wt silver, 440 ppm cesium, 1.5 micromoles/g of ammonium perrenate, 1.5 micromoles/g of lithium sulfate and 4 micromoles/g of lithium nitrate. Approximately 30 g of the carrier were placed under 25 mm vacuum for 3 minutes at room temperature. Approximately 50 g of the impregnating solution were 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 8.4 cu.m./hr (300 cu.ft./hr.) air stream at 250 °C for 5 minutes. The cured catalyst, denoted as C-A', 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 to 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 20 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 Table 4 and 5 were used to prepare the catalysts listed in Table 6. C-A and C-A' refer to a catalyst prepared with carrier A, C-B and C-B' refer to a catalyst prepared with carrier B, etc.

Table 6

Catalyst	Ag Wt%	Cs ppm	NH ₄ ReO ₄ μ mol/g	Li ₂ SO ₄ μ mol/g	LiNO ₃ μ mol/gC-
C-Com-A	13.2	501	1.5	1.5	4
C-A	13.5	463	1.5	1.5	4
C-A'	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'	13.2	481	1.5	0	4
C-M	13.2	415	1.5	1.5	4
C-M'	13.2	382	1.5	0	4
C-N	14.5	620	1.5	1.5	4
C-N'	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-X	13.3	500	1.5	1.5	4

The Process

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

Three to five grams of crushed catalyst (14 filaments warp direction, 20 filaments shute direction per 2.54cm (14-20 mesh) are loaded into a .58cm (0.23 inch) diameter stainless steel U-shaped tube. The U tube is immersed in a molten metal bath (heat medium) and the ends are connected to a gas flow system. The weight of catalyst used and the inlet gas flow rate are adjusted to achieve a gas hourly space velocity of 3300 cc of gas per cc of catalyst per hour. The inlet gas pressure is 14.49 bar guage (210 psig).

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, 5-7% carbon dioxide, 54.5% nitrogen, and 0.5 to 5 ppmv ethyl chloride.

The initial reactor (heat medium) temperature is 180°C. After one hour at this initial temperature, the temperature is increased to 190°C for one hour, followed by 200°C (1hour), 220°C (1 hour), 227°C (2 hours), 235°C (2 hours), and 242°C (2 hours). The temperature is then adjusted so as to achieve a constant oxygen conversion level of 40% (T₄₀). 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 T₄₀ 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 performance 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 $T_{40} = 230^\circ\text{C}$.

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

Table 7

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Catalyst	$S_{40},\%$	$T_{40},^\circ\text{C}$
C-Com-A	85.1	261
C-A	85.8	258
C-A'	86.0	258
C-B	86.3	261
C-C	85.8	256
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	87.4	258
C-L	87.1	250
C-L'	87.3	252
C-M	86.8	260
C-M'	86.0	252
C-N	87.0	257
C-N'	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-X	85.9	254

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Claims

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1. A catalyst carrier based on alpha alumina comprising at least about 85% by weight of alpha alumina, from 0.05 to about 6% by weight (measured as the oxide) of calcium or magnesium oxide; from 0.05 to about 5% by weight, (measured as silica) of a silicon oxide, and from zero to about 10% by weight (measured as the oxide) of a zirconium oxide.
2. The catalyst carrier of claim 1 wherein the calcium or magnesium oxide includes mixed oxides.
3. The catalyst carrier of claim 2, wherein the calcium or magnesium oxide includes silicates.
4. The catalyst carrier according to one of claims 1 to 3 wherein the silicon oxide includes mixed oxides.
5. The catalyst carrier of claim 4, wherein the silicon oxide includes silicates.
6. The catalyst carrier of one of the preceding claims obtainable by calcinating an extruded mixture.
7. A carrier composition for preparing catalyst carriers according to one of the preceding claims, said composition comprising at least 85% by weight of alpha alumina, from 0.05 to about 6% by weight

To allow meaningful comparison of the performance of catalysts tested at different times, all catalysts described in this illustrative embodiment were tested simultaneously with a standard reference catalyst. 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 $T_{40} = 230^\circ\text{C}$.

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

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C-A	85.8	258
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C-B	86.3	261
C-C	85.8	256
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	87.4	258
C-L	87.1	250
C-L'	87.3	252
C-M	86.8	260
C-M'	86.0	252
C-N	87.0	257
C-N'	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-X	85.9	254

Claims

1. A catalyst carrier based on alpha alumina comprising at least about 85% by weight of alpha alumina, from 0.05 to about 6% by weight (measured as the oxide) of calcium or magnesium oxide; from 0.05 to about 5% by weight, (measured as silica) of a silicon oxide, and from zero to about 10% by weight (measured as the oxide) of a zirconium oxide.
2. The catalyst carrier of claim 1 wherein the calcium or magnesium oxide includes mixed oxides.
3. The catalyst carrier of claim 2, wherein the calcium or magnesium oxide includes silicates.
4. The catalyst carrier according to one of claims 1 to 3 wherein the silicon oxide includes mixed oxides.
5. The catalyst carrier of claim 4, wherein the silicon oxide includes silicates.
6. The catalyst carrier of one of the preceding claims obtainable by calcinating an extruded mixture.
7. A carrier composition for preparing catalyst carriers according to one of the preceding claims, said composition comprising at least 85% by weight of alpha alumina, from 0.05 to about 6% by weight



(measured as the oxide, MO,) of a calcium or magnesium oxide, from 0.05 to about 5% by weight (measured as silica) of a silicon oxide, and from zero to about 10% by weight (measured as the dioxide) of zirconium in the form of an oxide.

- 5 8. A carrier composition for preparing catalyst carriers comprising at least 85% by weight of alpha alumina, from 0.05 to about 6% by weight (measured as the oxide, MO,) of a calcium or magnesium oxide, from 0.05 to about 5% by weight (measured as silica) of a silicon oxide, and from zero to about 10% by weight (measured as the dioxide) of zirconium in the form of an oxide.
- 10 9. A carrier composition according to one of claims 7 or 8, wherein the catalyst is a silver-based ethylene oxide catalysts.
- 10 10. The carrier composition according to one of claims 7 to 9 comprising at least 85 percent by weight of alpha alumina, from 0.05 to 6% by weight of a calcium or magnesium silicate and from 0.01 to about 15 10 percent by weight of zirconia.
- 20 11. The carrier composition according to one of claims 7 to 10 comprising at least 95 percent by weight of alpha alumina, from 0.05 to 4 percent by weight of calcium silicate and from 0.3 to 5 percent by weight of zirconia.
- 20 12. The carrier composition according to one of claims 7 to 11 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.
- 25 13. A carrier composition according to one of claims 7 to 14 which is free of base-soluble silica.
- 25 14. A carrier composition according to one of claims 7 to 14 in which the alumina has a soda content of less than 0.06% by weight.
- 30 15. A process for preparing a carrier for use as a catalyst carrier which comprises:
 - 30 (a) mixing:
 - (i) an alpha alumina powder having a purity of greater than about 98 percent and having an average crystallite size between 0.1 and 5 μ m,
 - (ii) calcium or magnesium oxide or compound which is decomposable to or forms oxide upon calcination,
 - 35 (iii) a silicon oxide or compound which is decomposable to or forms an oxide upon calcination and
 - (iv) optionally a zirconium oxide or compound which is decomposable to or forms an oxide upon calcination,
 - 40 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, a calcium or magnesium oxide in an amount ranging from 0.05 to 6% by weight, silicon oxide in an amount ranging from 0.05 to 5% by weight, and zirconium oxide in an amount ranging from zero to 10% by weight;
 - 45 (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 ranging from 0.3 to 2 square meters per gram and a water pore volume ranging from 0.2 to 0.6 cubic centimeters per gram.
- 50 16. A process according to claim 15 for preparing a carrier for use as a catalyst carrier according to one of claims 1 to 6.
- 50 17. A process according to one of claims 15 or 16, wherein the catalyst is a silver-based, rhenium promoted ethylene oxide catalyst.
- 55 18. The process according to one of claims 15 to 17 in which the amounts of the components are selected to give a carrier composition comprising at least 90% by weight of alumina, from 0.05 to 5% by weight of a calcium or magnesium oxide, from 0.05 to 4% by weight of a silicon oxide and from 0.3 to 5% by weight of zirconia, the relative proportions being selected so that there is no base-soluble silica in the final carrier composition.



19. The process according to one of claims 15 to 18 in which the calcium or magnesium compound and the silicon oxide are selected such that, after calcination, they are present in the form of a single compound.
- 5 20. A process for preparing a carrier for use as a catalyst carrier which comprises:
 (a) mixing high purity alpha alumina powder, a calcium or magnesium oxide - providing compound, a silica providing compound and, optionally, a zirconia providing compound with water and a binder/burnout agent, in amounts sufficient to provide in the finished carrier alpha alumina in an amount greater than about 95 percent by weight, calcium silicate in an amount ranging from 0.05 to about 4
 10 percent by weight, and zirconium oxide in an amount ranging from 0.3 to about 5 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 ranging from 0.3 to 2 square meters per gram and a water pore volume ranging from 0.2 to 0.6 cubic centimeters per gram.
- 15 21. A process according to claim 20 for preparing a carrier for use as a catalyst carrier according to one of claims 1 to 6.
- 20 22. A process for preparing a carrier according to one of claims 20 or 21, wherein the catalyst is a silver-based, rhenium promoted ethylene oxide catalyst.

Patentansprüche

- 25 1. Katalysatorträger auf der Basis von Alpha-Aluminiumoxid mit mindestens etwa 85 Gew.% Alpha-Aluminiumoxid, 0,05 bis etwa 6 Gew.% (gemessen als das Oxid) Calcium- oder Magnesiumoxid; 0,05 bis etwa 5 Gew.% (gemessen als Siliciumdioxid) eines Siliciumoxids und null bis etwa 10 Gew.% (gemessen als das Oxid) eines Zirkoniumoxids.
- 30 2. Katalysatorträger gemäß Anspruch 1, bei dem das Calcium- oder Magnesiumoxid gemischte Oxide enthält.
3. Katalysatorträger gemäß Anspruch 2, bei dem das Calcium- oder Magnesiumoxid Silicate enthält.
- 35 4. Katalysatorträger gemäß einem der Ansprüche 1 bis 3, bei dem das Siliciumoxid gemischte Oxide enthält.
5. Katalysatorträger gemäß Anspruch 4, bei dem das Siliciumoxid Silicate enthält.
- 40 6. Katalysatorträger gemäß einem der vorhergehenden Ansprüche, erhältlich durch Kalzinierung einer extrudierten Mischung.
7. Trägerzusammensetzung zur Herstellung von Katalysatorträgern gemäß einem der vorhergehenden Ansprüche, wobei die Zusammensetzung mindestens 85 Gew.% Alpha-Aluminiumoxid, 0,05 bis etwa 6 Gew.% (gemessen als das Oxid, MO₂) eines Calcium- oder Magnesiumoxids, 0,05 bis etwa 5 Gew.% (gemessen als Siliciumdioxid) eines Siliciumoxids und null bis etwa 10 Gew.% (gemessen als das Dioxid) Zirkonium in der Form eines Oxids enthält.
- 45 8. Trägerzusammensetzung zur Herstellung von Katalysatorträgern mit mindestens 85 Gew.% Alpha-Aluminiumoxid, 0,05 bis etwa 6 Gew.% (gemessen als das Oxid, MO₂) eines Calcium- oder Magnesiumoxids, 0,05 bis etwa 5 Gew.% (gemessen als Siliciumdioxid) eines Siliciumoxids und null bis etwa 10 Gew.% (gemessen als das Dioxid) Zirkonium in der Form eines Oxids.
- 50 9. Trägerzusammensetzung gemäß einem der Ansprüche 7 oder 8, bei der der Katalysator ein Ethylen-oxiddkatalysator auf der Basis von Silber ist.
- 55 10. Trägerzusammensetzung gemäß einem der Ansprüche 7 bis 9 mit mindestens 85 Gew.% Alpha-Aluminiumoxid, 0,05 bis 6 Gew.% eines Calcium- oder Magnesiumsilicats und 0,01 bis etwa 10 Gew.% Zirkoniumoxid.



11. Trägerzusammensetzung gemäß einem der Ansprüche 7 bis 10 mit mindestens 95 Gew.% Alpha-Aluminiumoxid, 0,05 bis 4 Gew.% Calciumsilicat und 0,3 bis 5 Gew.% Zirkoniumoxid.
12. Trägerzusammensetzung gemäß einem der Ansprüche 7 bis 11 mit einem Oberflächenbereich von 0,15 bis 3 Quadratmeter pro Gramm und einem Wasserporenvolumen von 0,2 bis 0,6 Kubikzentimeter pro Gramm.
13. Trägerzusammensetzung gemäß einem der Ansprüche 7 bis 12, die frei von basenlöslichem Siliciumdioxid ist.
14. Trägerzusammensetzung gemäß einem der Ansprüche 7 bis 13, bei der das Aluminiumoxid einen Sodagehalt von weniger als 0,06 Gew.% aufweist.
15. Verfahren zur Herstellung eines Trägers zur Verwendung als Katalysatorträger, das folgendes umfaßt:
- (a) Mischen:
- (i) eines Alpha-Aluminiumoxid-Pulvers mit einer Reinheit von über etwa 98 Prozent und mit einer durchschnittlichen Kristallitgröße zwischen 0,1 und 5 μm ,
- (ii) Calcium- oder Magnesiumoxid oder einer Verbindung, welche durch Kalzination zu Oxid abbaubar ist oder Oxid bildet,
- (iii) eines Siliciumoxids oder einer Verbindung, welche durch Kalzination zu Oxid abbaubar ist oder ein Oxid bildet, und
- (iv) wahlweise eines Zirkoniumoxids oder einer Verbindung, welche durch Kalzination zu Oxid abbaubar ist oder ein Oxid bildet,
- mit Wasser und einem Binde-/Ausbrennmittel in Mengen, welche ausreichen, um in dem fertigen Träger Alpha-Aluminiumoxid in einer Menge über etwa 85 Gew.%, ein Calcium- oder Magnesiumoxid in einer Menge von 0,05 bis 6 Gew.%, Siliciumoxid in einer Menge von 0,05 bis 5 Gew.% und Zirkoniumoxid in einer Menge von null bis 10 Gew.% bereitzustellen;
- (b) Extrudieren der entstandenen Mischung aus Schritt (a) zur Bildung von Pellets; und
- (c) Kalzinieren der Pellets bei einer Temperatur über 1300 °C über eine Zeit, welche ausreicht, einen Träger mit einer Oberfläche von 0,3 bis 2 Quadratmeter pro Gramm und einem Wasserporenvolumen von 0,2 bis 0,6 Kubikzentimeter pro Gramm bereitzustellen.
16. Verfahren gemäß Anspruch 15 zur Herstellung eines Trägers zur Verwendung als Katalysatorträger gemäß einem der Ansprüche 1 bis 6.
17. Verfahren gemäß einem der Ansprüche 15 oder 16, bei dem der Katalysator ein durch Rhenium verbesserter Ethylenoxiddkatalysator auf der Basis von Silber ist.
18. Verfahren gemäß einem der Ansprüche 15 bis 17, bei dem die Mengen der Bestandteile so ausgewählt werden, daß eine Trägerzusammensetzung mit mindestens 90 Gew.% Aluminiumoxid, 0,05 bis 5 Gew.% eines Calcium- oder Magnesiumoxids, 0,05 bis 4 Gew.% eines Siliciumoxids und 0,3 bis 5 Gew.% Zirkoniumoxid zur Verfügung gestellt wird, wobei die relativen Verhältnisse so ausgewählt werden, daß in der Endträgerzusammensetzung kein basenlösliches Siliciumdioxid vorhanden ist.
19. Verfahren gemäß einem der Ansprüche 15 bis 18, bei dem die Calcium- oder Magnesiumverbindung und das Siliciumoxid so ausgewählt werden, daß diese nach dem Kalzinieren in Form einer einzigen Verbindung vorliegen.
20. Verfahren zur Herstellung eines Trägers zur Verwendung als Katalysatorträger, das folgendes umfaßt:
- (a) Mischen von Alpha-Aluminiumoxid-Pulver hoher Reinheit, einer Calcium- oder Magnesiumoxid bereitstellenden Verbindung, einer Siliciumdioxid bereitstellenden Verbindung und wahlweise einer Zirkoniumoxid bereitstellenden Verbindung mit Wasser und einem Binde-/Ausbrennmittel in Mengen, welche ausreichen, um in dem fertigen Träger Alpha-Aluminiumoxid in einer Menge von über etwa 95 Gew.%, Calciumsilicat in einer Menge von 0,05 bis 4 Gew.%, und Zirkoniumoxid in einer Menge von 0,3 bis etwa 5 Gew.% bereitzustellen;
- (b) Extrudieren der entstandenen Mischung aus Schritt (a) zur Bildung von Pellets; und
- (c) Kalzinieren der Pellets bei einer Temperatur über 1300 °C über eine Zeit, welche ausreicht, einen Träger mit einer Oberfläche von 0,3 bis 2 Quadratmeter pro Gramm und einem Wasserporenvolu-



men von 0,2 bis 0,6 Kubikzentimeter pro Gramm bereitzustellen.

21. Verfahren gemäß Anspruch 20 zur Herstellung eines Trägers zur Verwendung als Katalysatorträger gemäß einem der Ansprüche 1 bis 6.

22. Verfahren zur Herstellung eines Trägers gemäß einem der Ansprüche 20 oder 21, bei dem der Katalysator ein durch Rhenium verbesserter Ethylenoxiddkatalysator auf der Basis von Silber ist.

Revendications

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1. Support de catalyseur à base d'alpha-alumine constitué d'au moins environ 85% en poids d'alpha-alumine ; de 0,05 à environ 6% en poids (mesuré sur la base de l'oxyde) d'oxyde de calcium ou de magnésium ; de 0,05 à environ 5% en poids (mesuré sur la base de la silice) d'un oxyde de silicium et de 0 à environ 10% en poids (mesuré sur la base de l'oxyde) d'un oxyde de zirconium.

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2. Support de catalyseur selon la revendication 1, dans lequel l'oxyde de calcium ou de magnésium comprend des oxydes mixtes.

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3. Support de catalyseur selon la revendication 2, dans lequel l'oxyde de calcium ou de magnésium comprend des silicates.

4. Support de catalyseur selon l'une des revendications 1 à 3, dans lequel l'oxyde de silicium comprend des oxydes mixtes.

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5. Support de catalyseur selon la revendication 4, dans lequel l'oxyde de silicium comprend des silicates.

6. Support de catalyseur selon l'une des revendications précédentes, pouvant être obtenu par calcination d'un mélange extrudé.

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7. Composition de support pour préparer des supports de catalyseurs selon l'une des revendications précédentes, ladite composition étant constituée d'au moins 85% en poids d'alpha-alumine ; de 0,05 à environ 6% en poids (mesuré sur la base de l'oxyde, MO) d'un oxyde de calcium ou de magnésium ; de 0,05 à environ 5% en poids (mesuré sur la base de la silice) d'un oxyde de silicium ; et de 0 à environ 10% en poids (mesuré sur la base du dioxyde) de zirconium sous forme d'oxyde.

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8. Composition de support pour préparer des supports de catalyseurs, ladite composition étant constituée d'au moins 85% en poids d'alpha-alumine ; de 0,05 à environ 6% en poids (mesuré sur la base de l'oxyde, MO) d'un oxyde de calcium ou de magnésium ; de 0,05 à environ 5% en poids (mesuré sur la base de la silice) d'un oxyde de silicium ; et de 0 à environ 10% en poids (mesuré sur la base du dioxyde) de zirconium sous forme d'oxyde.

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9. Composition de support selon l'une des revendications 7 ou 8, dans laquelle le catalyseur est un catalyseur d'oxyde d'éthylène à base d'argent.

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10. Composition de support selon l'une des revendications 7 à 9, constituée d'au moins 85% en poids d'alpha-alumine ; de 0,05 à 6% en poids d'un silicate de calcium ou de magnésium ; et de 0,01 à environ 10% en poids de zircone.

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11. Composition de support selon l'une des revendications 7 à 10, comprenant au moins 95% en poids d'alpha-alumine ; de 0,05 à 4% en poids de silicate de calcium ; et de 0,3 à 5% en poids de zircone.

12. Composition de support selon l'une des revendications 7 à 11, ayant une aire superficielle allant de 0,15 à 3 m²/g et un volume de pores dans l'eau allant de 0,2 à 0,6 cm³/g.

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13. Composition de support selon l'une des revendications 7 à 12, qui est exempte de silice soluble dans une base.



14. Composition de support selon l'une des revendications 7 à 12, dans laquelle l'alumine a une teneur en carbonate neutre de sodium inférieure à 0,06% en poids.
15. Procédé de préparation d'un support destiné à être utilisé comme support de catalyseur, lequel procédé consiste à :
- (a) mélanger :
- (i) une poudre d'alpha-alumine ayant une pureté supérieure à environ 98% et une taille moyenne de cristallites comprise entre 0,1 et 5 μm ,
- (ii) un oxyde de calcium ou de magnésium ou un composé qui est décomposable en, ou forme, un oxyde de calcium ou de magnésium par calcination,
- (iii) un oxyde de silicium ou un composé qui est décomposable en, ou forme, un oxyde de silicium par calcination, et
- (iv) éventuellement un oxyde de zirconium ou un composé qui est décomposable en, ou forme, un oxyde de zirconium par calcination,
- avec de l'eau et un agent liant/d'échauffement en quantité suffisante pour que le support fini contienne de l'alpha-alumine en une quantité supérieure à environ 85% en poids, un oxyde de calcium ou de magnésium en une quantité allant de 0,05 à 6% en poids, un oxyde de silicium en une quantité allant de 0,05 à 5% en poids et un oxyde de zirconium en une quantité allant de 0 à 10% en poids ;
- (b) extruder le mélange résultant de l'étape (a) pour former des pastilles ; et
- (c) calciner les pastilles à une température supérieure à 1300°C, pendant une période de temps suffisante pour produire un support ayant une surface allant de 0,3 à 2 m^2/g et un volume de pores dans l'eau qui va de 0,2 à 0,6 cm^3/g .
16. Procédé selon la revendication 15 pour préparer un support destiné à être utilisé comme support de catalyseur selon l'une des revendications 1 à 6.
17. Procédé selon l'une des revendications 15 ou 16, dans lequel le catalyseur est un catalyseur d'oxyde d'éthylène à base d'argent, activé par du rhénium.
18. Procédé selon l'une des revendications 15 à 17, dans lequel les quantités des composants sont sélectionnées pour obtenir une composition de support constituée d'au moins 90% en poids d'alumine ; de 0,05 à 5% en poids d'un oxyde de calcium ou de magnésium ; de 0,05 à 4% en poids d'un oxyde de silicium ; et de 0,3 à 5% en poids de zircone, les proportions relatives étant choisies de sorte que la composition finale du support est exempte de silice soluble dans une base.
19. Procédé selon l'une des revendications 15 à 18, dans lequel le composé du calcium ou du magnésium et l'oxyde de silicium sont choisis de telle sorte que, après calcination, ils sont présents sous forme d'un composé unique.
20. Procédé de préparation d'un support destiné à être utilisé comme support de catalyseur, consistant à :
- (a) mélanger de la poudre d'alpha-alumine de haute pureté, un composé apportant de l'oxyde de calcium ou de magnésium, un composé apportant de la silice, éventuellement un composé apportant de la zircone, avec de l'eau et un agent liant/d'échauffement, dans des quantités suffisantes pour que le support fini contienne de l'alpha-alumine en une quantité supérieure à environ 95% en poids, du silicate de calcium en une quantité allant de 0,05 à environ 4% en poids, et de l'oxyde de zirconium en une quantité allant de 0,3 à environ 5% en poids ;
- (b) extruder le mélange résultant de l'étape (a) pour former des pastilles ; et
- (c) calciner les pastilles à une température supérieure à 1300°C, pendant une période de temps suffisante pour produire un support ayant une surface qui va de 0,3 à 2 m^2/g et un volume de pores dans l'eau qui va de 0,2 à 0,6 cm^3/g .
21. Procédé selon la revendication 20 pour préparer un support destiné à être utilisé comme support de catalyseur selon l'une des revendications 1 à 6.
22. Procédé de préparation d'un support selon l'une des revendications 20 ou 21, dans lequel le catalyseur est un catalyseur d'oxyde d'éthylène à base d'argent, activé par du rhénium.

