(12) PATENT **(11)** Application No. **AU 199957469 B2**
(19) AUSTRALIAN PATENT OFFICE **(10)** Patent No. **750895**

(54) Title
Process for removing ionizable species from catalyst surface to improve catalytic properties

(51)7 International Patent Classification(s)
B01J 023/50 **C07D 301/10**
B01J 037/06

(21) Application No: **199957469** (22) Application Date: **1999.09.09**

(87) WIPO No: **WO00/15333**

(30) Priority Data

(31) Number	(32) Date	(33) Country
60/100194	**1998.09.14**	**US**

(43) Publication Date : **2000.04.03**
(43) Publication Journal Date : **2000.05.25**
(44) Accepted Journal Date : **2002.08.01**

(71) Applicant(s)
Shell Internationale Research Maatschappij B.V.

(72) Inventor(s)
John Robert Lockemeyer

(74) Agent/Attorney
DAVIES COLLISON CAVE,1 Little Collins Street,MELBOURNE VIC 3000

(56) Related Art
GB 568978
US 4797279
US 4212772

57469/99

PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 :		(11) International Publication Number:	WO 00/15333
B01J 23/50, 37/06, C07D 301/10	A1	(43) International Publication Date:	23 March 2000 (23.03.00)

(21) International Application Number: PCT/EP99/06721

(22) International Filing Date: 9 September 1999 (09.09.99)

(30) Priority Data:
60/100,194 14 September 1998 (14.09.98) US

(71) Applicant: SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V. [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR The Hague (NL).

(72) Inventor: LOCKEMEYER, John, Robert; 3403 Stoney Mist Drive, Sugar Land, TX 77479 (US).

(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, ~~UG~~, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: PROCESS FOR REMOVING IONIZABLE SPECIES FROM CATALYST SURFACE TO IMPROVE CATALYTIC PROPERTIES

(57) Abstract

This invention relates to a process for the preparation of a catalyst having improved properties, said process comprising selecting a carrier, lowering the concentration of ionizable species present on the surface of the carrier, and depositing a catalytically effective amount of one or more catalytically reactive metals on the carrier. The invention further relates to catalysts made from the process and to the use of such catalysts in alkene epoxidation processes. In the examples the lowering of the concentration of ionizable species is obtained by washing the alpha alumina carrier with boiling water. Then the dried carrier is impregnated with a promotor and silver.

PROCESS FOR REMOVING IONIZABLE SPECIES FROM CATALYST SURFACE TO IMPROVE CATALYTIC PROPERTIES

Field of the Invention

The invention relates to a process for the preparation of catalyst with improved catalytic properties.

Background of the Invention

The presence of certain species contained in the carriers of catalysts can be detrimental to the catalytic metal deposition thereon and/or catalyst performance and it is commonly believed that the concentration of these detrimental species must be controlled throughout the bulk of carrier. One way of controlling the amount of impurities through the bulk, although expensive, is by the use of purer raw materials. For example, US Patent No. 4,797,270 discloses water washing to reduce the sodium content of an alumina powder. The pH of the wash water may need to be adjusted for extraction of other metals and Japanese patent JP56164013 discloses the use of a low pH (acid) to extract uranium and thorium from a calcined α-alumina raw material.

Several procedures in the art teach that washing after deposition of the catalytic metal is helpful. US Patent Nos. 4,361,504 and 4,366,092 suggest that ethylene oxide catalyst be water washed after the deposition of silver or silver/gold on the carrier. EP-A 211521 discloses washing of a catalyst with hot water to remove basic materials left on the catalyst from a silver impregnation process or the physical deposition of alkali metals. US Patent No. 4,367,167 discloses a process for preparing a supported catalyst wherein an impregnated support is immersed in an inert water immiscible organic solvent containing a dissolved aliphatic amine.

US Patent No. 4,810,689 discloses depositing a silver compound, decomposing the silver compound to silver in the presence of an alkali metal compound, removing organic deposits by washing and introducing fresh alkali metal by impregnation during or after the washing stage.

GB patent specification No. 568,978 discloses a process for preparing alumina of high stability and resistance to disintegration, comprising precipitating hydrous alumina, subjecting the precipitate to hot aging at above 125 °F to stabilize the alumina, washing the alumina, grinding, forming into pieces and heat treating the formed pieces at between 1000 and 1600 °F whereby said pieces, when they are pellets 4 mm in diameter, have a knife edge hardness of at least 3500 grams.

US Patent No. 4,994,587 discloses a process for the epoxidation of alkene comprising contacting the alkene and an oxygen-containing gas in the presence of at least one efficiency-enhancing gaseous member of a redox-half reaction pair, selected from the group of NO, NO_2, N_2O_3 and N_2O_4, and a solid catalyst, the catalyst comprising silver and at least one efficiently-enhancing nitrate salt of a member of a redox-half reaction pair, on a solid alpha-alumina support having less than about 50 ppm and preferably less than 20 ppm by weight of leachable sodium. This document further connects the requirement to relatively low sodium to the specified redox reaction pair, stating that in other instances the presence of leachable sodium in a silver catalyst tends to improve the efficiency of the system under epoxidation conditions generally used.

U.S. Patent Nos. 4,186,106 and 4,125,480 disclose washing with an inert liquid after deposition of the catalytic metal and before deposition of a promoter material.

U.S. Patent No. 4,908,343 teaches that it may be desirable to remove cations which are exchangeable with the alkali and alkaline earth metals contained in the impregnating solution, to allow for ease of repeatability in the use and reuse of the impregnating solution. No methods are taught for such removal; however, it is commonly known in the art that acids are highly effective cation removal solutions.

The prior art remains concerned with the total amount of impurities; i.e., impurities throughout the bulk. Unfortunately, the impurity removal techniques taught typically attack the carrier itself. It has now been found that the metal deposition and/or catalytic properties of a catalyst may be greatly improved by controlling the purity of the surface of the carrier rather than the purity of the carrier bulk, such that the total amounts of impurities may actually be high as long as the surface amounts of impurities are maintained at a low level.

Summary of the Invention

According to one embodiment of the invention, there is provided a process for improving the properties of a carrier for a catalyst by a treatment which is performed on one or more of the materials from which the carrier is formed and/or on the complete carrier and which is effective in lowering the concentration of one or more ionizable silicates present on the surface of the complete carrier, the lowering being expressed as the lowering of the relative concentration of Si atoms, as measured by X-ray Photoelectron Spectroscopy (XPS) performed on the untreated and treated carrier.

The concentration, as measured by XPS, of Si on the surface of the carrier is generally lowered by at least 5 percent. More preferably the concentration of Si is lowered by at least 10%.

Optionally the concentration lowering treatment is followed by a drying step.

There is further provided a process for preparing a catalyst, especially an olefin epoxidation catalyst, by depositing a catalytically effective amount of one or more catalytically reactive metals and optionally one or more promoter materials on a carrier prepared by a process as defined above.

There is yet further provided a process for the vapor phase catalytic epoxidation of an alkene with an oxygen containing gas, using a catalyst prepared by a process as defined above.

Description of the Preferred Embodiments

It has been found that carriers which have been treated to reduce ionizable silicates which are present on the surface of the carrier provide catalysts with improved catalytic properties, when compared with the performance of catalysts made from carriers which have not been so treated. The process is believed to work to improve the properties of most catalysts, no matter how impure the bulk carrier material, compared to a catalyst made with an untreated carrier. Further, the process will work for organic or inorganic carriers.

The process is effective in improving at least one of the catalytic properties of a catalyst wherein a catalytically reactive metal is deposited or impregnated upon a carrier which contains ionizable species on its surface. "Improvement in catalytic properties" as used herein means the properties of the catalyst are improved as compared to a catalyst made from the same carrier which has not been treated to lower surface ionizable species. Catalytic properties include catalyst activity, selectivity, activity and/or selectivity performance over time, operability (resistance to runaway), conversion and work rate.

The process requires that the concentration of ionizable silicates present on the surface of the carrier be reduced. As used herein, the "surface" of the carrier is that area of the carrier which may be measured by the standard method of Brunauer, Emmett and Teller (BET). Specifically, the surface of the carrier is the site at which reaction takes place. An "ionizable" silicate is a silicate which is capable of being rendered ionic, where the term "ionic" or "ion" refers to an electrically charged chemical moiety.

The solubilization rate of silicates may be measured by inductively coupled plasma (ICP) techniques and the amount of silicon species on a surface may be measured by x-ray photoelectron spectroscopy (XPS). In defining the present invention the amounts of silicon, present on the surface of the carrier, as measured by XPS, before and after treatment according to the invention, have been chosen as an indicator for the amounts of ionizable silicates. Another measurement technique is to measure the change in electrical conductivity of the treatment solution.

Carriers are commonly inorganic materials such as, for example, alumina-, silica-, or titania-based compounds, or combinations thereof, such as alumina-silica carriers. Carriers may also be made from carbon-based materials such as, for example, charcoal, activated carbon, or fullerenes.

Ionizable species typically present on the inorganic type carriers include sodium, potassium, aluminates, soluble silicate, calcium, magnesium, aluminosilicate, cesium, lithium, and combinations thereof. Of particular concern are the ionizable anionic species present on the surface, and in the present invention particularly ionizable silicates. Lowering the undesirable ionizable silicates concentration may be accomplished by any means (i) which is effective in rendering the ionizable silicates ionic and removing them, or (ii) which renders the ionizable silicates insoluble, or (iii) which renders the ionizable silicates immobile; however, use of aggressive media is discouraged as these media tend to dissolve the carrier, extract too much material from the bulk, and generate acidic or basic sites in the pores. Acids, besides being aggressive media, will remove the cations on a carrier but are fairly ineffectual in removing the undesirable anions, such as silicates. Effective means of lowering concentration include washing the carrier; ion exchange; volatilizing, precipitating, or sequestering the impurities; causing a reaction to make the ionizable silicates on the surface insoluble; and combinations thereof. Examples of wash and ion exchange solutions include aqueous and/or organic solvent-based solutions which may also contain tetraethylammonium hydroxide, ammonium acetate, lithium carbonate, barium acetate, strontium acetate, crown ether, methanol, ethanol, dimethylformamide, and mixtures thereof.

The formed carrier may be treated, or the materials used to form the carrier may be treated before the carrier is manufactured. When the carrier materials are treated before the carrier is formed, still further improvement may be seen by also treating the surface of the formed carrier. The carrier may be dried following the ionizable silicates reduction treatment.

To make a catalyst from the carrier, the carrier is typically impregnated with metal compound(s), complex(es) and/or salt(s) dissolved in a suitable solvent sufficient to deposit or impregnate a catalytically effective amount of metal on the carrier. As used herein, "catalytically effective amount" means an amount of metal that provides a measurable catalytic effect. For example, a catalytically effective amount of metal when referring to an olefin epoxidation catalyst is that amount of metal which provides a measurable conversion of olefin and oxygen to alkylene oxide.

Further improvement in the catalyst properties are seen when the metal deposition is effected by contacting the carrier with an impregnation solution whose hydrogen ion activity has been lowered. "Hydrogen ion activity" as used herein is the hydrogen ion activity as measured by the potential of a hydrogen ion selective electrode. As used herein, a solution with "lowered" hydrogen ion activity refers to a solution whose hydrogen activity has been altered by the addition of a base, such that the hydrogen ion activity of the altered solution is lowered compared to the hydrogen ion activity of the same solution in an unaltered state. The base selected to alter the solution may be chosen from any base or compound with a pKb lower than the original impregnation solution. It is particularly desirable to choose a base which does not alter the formulation of the impregnation solution; i.e., which does not alter the desired metals concentration present in the impregnation solution and deposited on the carrier. Organic bases will not alter the impregnation solution metals concentrations, examples of which are tetraalkylammonium hydroxides and 1,8-bis-(dimethylamino)-naphthalene. If changing the metals concentration of the impregnation solution is not a concern, metal hydroxides may be used.

When the impregnation solution is at least partially aqueous, an indication of the change in the hydrogen activity may be measured with a pH meter, with the understanding that the measurement obtained is not pH by a true, aqueous definition. '"Measured pH"' as used herein shall mean such a non-aqueous system pH measurement using a standard pH probe. Even small changes in the "measured pH" from the initial impregnation solution to that with added base are effective and improvements in catalytic properties continue as the "measured pH" change increases with base addition. High base additions do not seem to adversely affect catalyst performance; however, high additions of hydroxides have been seen to cause sludging of the impregnation solution, creating manufacturing difficulties. When the base addition is too low, the hydrogen ion activity will not be affected. The hydrogen ion activity lowering procedure is also quite effective when used by itself; i.e., when no ionizable species concentrations are lowered prior to impregnation.

The impregnated carrier, also known as a catalyst precursor, can be dried in the presence of an atmosphere which also reduces the catalytic metal. Drying methods known in the art include steam drying, drying in an atmosphere with a controlled oxygen concentration, drying in a reducing atmosphere, air drying, and staged drying using a suitable ramped or staged temperature curve.

By way of example, the process will be described in more detail for a catalyst suitable for the vapor phase production of epoxides, also known as an epoxidation catalyst.

First, a carrier is selected. In the case of an epoxidation catalyst the carrier is typically an inorganic material, such as for example, an alumina-based carrier such as α-alumina.

In the case of α-alumina-containing carriers, preference is given to those having a specific surface area as measured by the B.E.T. method of from 0.03 to 10 m^2/g, preferably from 0.05 to about 5 m^2/g, more preferably from 0.1 to 3 m^2/g, and a water pore volume as measured by conventional water absorption techniques of from 0.1 to 0.75 ml/g by volume. The B.E.T. method for determining specific surface area is described in detail in Brunauer, S., Emmett, P. Y. and Teller, E., J. Am. Chem. Soc., 60, 309-16 (1938).

Certain types of α-alumina containing carriers are particularly preferred. These α-alumina carriers have relatively uniform pore diameters and are more fully characterized by having B.E.T. specific surface areas of from 0.1 to about 3 m^2/g, preferably from 0.1 to about 2 m^2/g, and water pore volumes of from 0.10 ml/g to about 0.55 ml/g. Manufacturers of such carriers include Norton Chemical Process Products Corporation and United Catalysts, Inc. (UCI).

The concentration of undesirable ionizable species present on the surface of the carrier are reduced to create a "cleansed" carrier. Or, alternatively, the concentration of ionizable species in the materials used to make the carrier may be reduced prior to formation of the carrier. If the carrier raw materials are treated, the formed carrier may be retreated for further improvement.

Ionizable species present on an α-alumina carrier, for example, typically include sodium, potassium, aluminates, soluble silicates, calcium, magnesium, aluminosilicates, and combinations thereof. It has been found that silicates, and certain other anions, are particularly undesirable ionizable species in an epoxidation catalyst.

After the concentration of the surface ionizable species are lowered, the carrier is optionally dried. When aqueous or organic solvent washing is used, drying or some similar method is recommended to displace the wash solution from the carrier pores. The carrier is now ready for a catalytically reactive metal to be deposited or impregnated thereon.

The carrier having the controlled solubilization rate is impregnated with metal ions or compound(s), complex(es) and/or salt(s) dissolved in a suitable solvent sufficient to cause the desired deposition on the carrier. When silver is the deposition material, a typical deposition is from 1 to 40 wt%, preferably from 1 to 30 wt% of silver, basis the weight of the total catalyst. The impregnated carrier is subsequently separated from the solution and the deposited metal(s) compound is reduced to metallic silver.

One or more promoters may be deposited either prior to, coincidentally with, or subsequent to the deposition of the metal. Promoters for epoxidation catalysts are typically selected from sulfur, phosphorus, boron, fluorine, Group IA through Group VIII metals, rare earth metals, and combinations thereof. The promoter material is typically compound(s) and/or salt(s) of the promoter dissolved in a suitable solvent.

For olefin epoxidation oxide catalysts, Group IA metals are typically selected from potassium, rubidium, cesium, lithium, sodium, and combinations thereof; with potassium and/or cesium and/or rubidium being preferred. Even more preferred is a combination of cesium plus at least one additional Group IA metal, such as cesium plus potassium, cesium plus rubidium, or cesium plus lithium. Group IIA metals are typically selected from magnesium, calcium, strontium, barium, and combinations thereof, Group VIII transition metals are typically selected from cobalt, iron, nickel, ruthenium, rhodium, palladium, and combinations thereof; and rare earth metals are typically selected from lanthanum, cerium, neodymium, samarium, gadolinium, dysprosium, erbium, ytterbium, and mixtures thereof. Non-limiting examples of other promoters include perrhenate, sulfate, molybdate, tungstate, chromate, phosphate, borate, sulfate anion, fluoride anoin, oxyanions of Group IIIB to VIB, oxyanions of an element selected from Groups III through VIIB, alkali(ne) metal salts with anions of halides, and oxyanions selected from Groups IIIA to VIIA and IIIB through VIIB. The amount of Group IA metal promoter is typically in the range of from 10 ppm to 1500 ppm, expressed as the metal, by weight of the total catalyst, and the Group VIIb metal is less than 3600 ppm, expressed as the metal, by weight of the total catalyst.

For further improvement in catalytic properties, the hydrogen ion activity of the impregnation solution is optionally lowered, such as by the addition of a base. The typical impregnation solution for an epoxidation catalyst begins quite basic, so a strong base is used to further lower the hydrogen ion activity. Examples of strong bases include, alkyl ammonium hydroxides such as tetraethylammonium hydroxide, lithium hydroxide and cesium hydroxide. In order to maintain the desired impregnation solution formulation and metal loading, a organic base is preferred. Base additions in these systems typically result in a "measured pH" change ranging up to about 2, realising that the "measured pH" is not a true pH since the impregnation system is not aqueous.

If an excess of impregnation solution is used, the impregnated carrier is subsequently separated from the solution before the deposited metal compound is reduced. Promoters, components which work effectively to provide an improvement in one or more of the catalytic properties of the catalyst when compared to a catalyst not containing such components, may also be deposited on the carrier either prior to, coincidentally with, or subsequent to the deposition of the catalytically reactive metal.

The resulting epoxidation catalysts just described are used for the vapor phase production of epoxides, such as in the production of ethylene oxide from ethylene and an oxygen containing gas. In this epoxidation process on or more nitrogen oxides (NO_x) may also be added to the feedstock to boost catalyst conversion performance.

Other embodiments of the invention provide catalysts made by the processes just described.

Having generally described the invention, a further understanding may be obtained by reference to the following examples.

Examples

Carriers

Table I shows the carriers used for the Examples.

TABLE I

Carrier	A	B	C	D	E
B.E.T. Surface Area (m^2/g)[(a)]	0.84	0.97	0.78	0.76	0.87
Water Absorption (%)	39.7	46.2	37.6	32.5	43.4
Crush Strength (kg)[(b)]	6.53	8.07	12.29	10.93	5.44
Total Pore Volume (ml/g)[(c)]	0.408	0.460	0.390	0.430	
Median Pore Diameter (microns)[(c)]	1.8	2.7	1.3	4.6	
SiO_2 (%w)	0.5	0.8	0.1	0.5	0.5
Bulk Acid-Leachable Na (ppmw)	438	752	186	1907	339
Bulk Acid-Leachable K (ppmw)	85	438	109	71	37
Bulk Acid-Leachable Ca (ppmw)	207	508	526	293	123
Bulk Acid-Leachable Al (ppmw)	744	1553	657	1978	499
Bulk Acid-Leachable SiO_2 (ppmw)	808	1879	1560	> 2000	600
alpha-Alumina (% w)	Bal.	Bal.	Bal.	Bal.	Bal.

[a] Method of Brunauer, Emmett and Teller, loc. cit.

[b] Flat Plate Crush Strength, single pellet.

[c] Determined by mercury intrusion to 3.8×10^8 Pa using Micromeritics Autopore 9200 or 9210 (130° contact angle, 0.473 N/m surface tension of Hg).

Carrier Water-Washing Procedures for Examples 1, 2, 3, 4, 5, 7, 8, 10, 11, 13

Carrier washing was carried out by immersing 100 grams of carrier in 300 grams of boiling de-ionized water for 15 minutes. The carrier was then removed and placed in a fresh 300 grams of boiling water for another 15 minutes. This procedure was repeated once more for a total of three immersions, at which point the carrier was separated from the water and dried in a well ventilated oven at 150 °C for 18 hours. The dried carrier was then used for preparation of a catalyst by the procedures outlined in the following Examples.

Impregnation Solution

A silver-amine-oxalate stock solution was prepared by the following procedure:

415 g of reagent-grade sodium hydroxide were dissolved in 2340 ml de-ionized water and the temperature was adjusted to 50 °C.

1699 g high purity "Spectropure" silver nitrate were dissolved in 2100 ml de-ionized water and the temperature was adjusted to 50 °C.

The sodium hydroxide solution was added slowly to the silver nitrate solution, with stirring, while maintaining a solution temperature of 50 °C. The mixture was stirred for 15 minutes, then the temperature was lowered to 40 °C.

Water was removed from the precipitate created in the mixing step and the conductivity of the water, which contained sodium and nitrate ions, was measured. An amount of fresh deionized water equal to the amount removed was added back to the silver solution. The solution was stirred for 15 minutes at 40 °C. The process was repeated until the conductivity of the water removed was less than 90 µmho/cm. 1500 ml fresh deionized water was then added.

630 g of high-purity oxalic acid dihydrate were added in approximately 100 g increments. The temperature was keep at 40 °C and the pH was kept above 7.8.

Water was removed from the mixture to leave a highly concentrated silver-containing slurry. The silver oxalate slurry was cooled to 30 °C.

699 g of 92 %w ethylenediamine (8% de-ionized water) was added while maintaining a temperature no greater than 30 °C. The resulting solution contained approximately 27-33 %w silver.

Enough 45 %w aqueous CsOH and water was added to this solution to give a finished catalyst having 14.5 %w silver and a desired cesium loading (see Examples).

Sodium and Silicate Measurement Procedures

The XPS analayses were performed in a VG ESCALAB mkII X-ray photoelectron spectrometer. Non-monochromatized Al kα (1484.6 eV) X-rays were used as the excitation source. The electron kinetic energy analyzer was a 150 degree spherical sector analyzer equipped with a three channeltron detection system. All spectra were obtained in the constant analyzer pass energy mode with the pass energy set at 50 eV. Prior to analysis, samples were lightly crushed in a mortar and mounted onto a sample stub using double-sided tape. The analysis region was roughly 3 mm x 5 mm. The Al2s peak was used for charge correction and was corrected to 118.5 eV. Linear baselines were used for measuring the peak heights of the Al2s, Si2s, and Na1s lines, and a horizontal baseline starting at a bonding energy of 105.5 eV was used for measuring the height of the Si2p line due to an interference with an aluminum Auger line. Peak intensities were converted to relative molar values using the following empirically derived sensitivity factors:

Al2s 0.22, Si2p 0.32, Si2s 0.24 and Na1s 1.72

and the following relationship:

$$\text{Relative number of atoms} = \frac{(\text{peak intensity/sensitivity factor}) \cdot 100}{(\text{Al2s intensity}/0.22)}$$

The results of the XPS measurements are given in Table II. The numbers reported for XPS measurements are the number of atoms detected relative to 100 aluminum atoms. The XPS silicon values reported are the average of the Si2p and Si2s values.

TABLE II. Na and Si XPS for Selected α-Alumina Carriers

Carrier	XPS Na Un-washed Carrier (atom %)	XPS Na Washed Carrier (atom %)	Change in Na Unwashed to Washed (%)	XPS Si Un-washed Carrier (atom %)	XPS Si Washed Carrier (atom %)	Change in Si Un-washed to Washed (%)
A	6.1	2.7	55.7	13.4	11.5	14.2
B	6.0	2.7	55.0	14.0	11.2	20.0
C	3.8	0.8	78.9	11.3	10.1	10.6
D	11.2	5.8	47.9	10.4	9.7	5.9
E	8.5	3.3	61.2	12.5	10.6	15.2

pH Measurement Procedures

Silver solution pH measurements were done using a Metrohm model 744 pH meter, employing a model 6.0220.100 combination electrode and a Pt 100 model 6.1110.100 resistance thermometer for temperature compensation. The meter was calibrated with commercially available buffer solutions before each use. In a typical measurement, a 50 ml aliquot of the doped silver solution to be used for a catalyst impregnation was filtered into a 100 ml glass beaker through a 2 micrometer filter attached in-line to a plastic syringe. The pH probe was lowered into the magnetically stirred solution, and the reading obtained after 3 minutes was recorded as the equilibrated pH. The probe was cleaned between each measurement with deionized water, and checked for calibration. Special care was taken to prevent accumulation of AgCl solids on the electrode membrane. Such accumulation was removed by soaking the probe in ammonium hydroxide solution, as recommended by the manufacturer.

Example 1

A catalyst pre-cursor was prepared from Carrier A by first subjecting the carrier to carrier washing. Following the wash, approximately 30 grams of washed Carrier A were placed under a 3.33 kPa vacuum for 1 minute at ambient temperature. Approximately 50 grams of the impregnating solution was then introduced to submerse the carrier, and the vacuum was maintained at 3.33 kPa for an additional 3 minutes. The cesium target was 450 ppm/gram finished catalyst. The vacuum was then released and the excess impregnating solution was removed from the catalyst pre-cursor by centrifugation at 500 rpm for two minutes. The catalyst pre-cursor was then dried while being shaken at 240 °C for 4 minutes in a stream of air flowing at 11.3 m^3/hr.

Example 1a (Comparative)

Carrier A was impregnated as described in Example 1; however, the carrier was not subjected to carrier washing. The cesium target was 400 ppm/gram finished catalyst.

Example 2

Carrier B was subjected to carrier washing and impregnation as described in Example 1. The cesium target was 450 ppm/gram finished catalyst.

Example 2a (Comparative)

Carrier B was impregnated as described in Example 1; however, the carrier was not subjected to carrier washing. The cesium target was 400 ppm/gram finished catalyst.

Example 3

Carrier C was subjected to carrier washing and impregnation as described in Example 1. The cesium target was 300 ppm/gram finished catalyst.

Example 3a (Comparative)

Carrier C was impregnated as described in Example 1; however, the carrier was not subjected to carrier washing. The cesium target was 360 ppm/gram finished catalyst.

Example 4

Carrier D was subjected to carrier washing and impregnation as described in Example 1. The cesium target was 400 ppm/gram finished catalyst.

Example 4a (Comparative)

Carrier D was impregnated as described in Example 1; however, the carrier was not subjected to carrier washing. The cesium target was 400 ppm/gram finished catalyst.

Example 5

Carrier A was subjected to carrier washing and impregnation as described in Example 1. The cesium target was 450 ppm/gram finished catalyst. In addition, 35 %w aqueous tetraethylammonium hydroxide (TEAH) was added to the stock impregnation solution at a target of 117.8 micromoles OH^-/ml Ag solution, to lower the hydrogen ion activity to a "measured pH" of 13.2.

Example 6

100 g of Carrier A were immersed in 300 ml of boiling 5% TEAH for 15 min, then immersed six times in 300 ml of boiling de-ionized water for 15 minutes each. The carrier was then removed and dried in a well ventilated oven at 150 °C for 18 hours. The carrier was then impregnated with a cesium target of 400 ppm/gram finished

catalyst. In addition, 35 %w TEAH was added to the stock impregnation solution at a target of 117.8 micromoles OH^-/ml Ag, to lower the hydrogen ion activity to a "measured pH" of 13.6.

Example 7

Carrier A was subjected to carrier washing and impregnation as described in Example 1. The cesium target was 720 ppm/gram finished catalyst. In addition, TEAH was dissolved in water and added to the stock solution at a target of 117.8 micromoles OH^-/ml Ag, to lower the hydrogen activity to a "measured pH" of 13.2, and NH_4ReO_4 was dissolved in water and added to the stock solution to provide 1.5 micromoles Re/gram finished catalyst.

Example 8

Carrier A was subjected to carrier washing and impregnation as described in Example 1. The cesium target was 450 ppm/gram finished catalyst. In addition, LiOH was dissolved in water and added to the stock impregnation solution to lower the hydrogen ion activity to a "measured pH" of 13.2.

Example 8a (Comparative)

Carrier A was impregnated as described in Example 5; however, the carrier was not subjected to carrier washing. The cesium target was 400 ppm/gram finished catalyst.

Example 9

300 g of Carrier A were immersed in 900 ml of a boiling 0.1 M solution of ammonium acetate for 15 min, then immersed in 300 ml of de-ionized water at 25 °C for 15 minutes, followed by immersion three times in 300 ml of boiling de-ionized water for 15 minutes each. The carrier was then removed and dried in a well ventilated oven at 150 °C for 18 hours. The carrier was then

impregnated as described in Example 1. The cesium target was 450 ppm/gram finished catalyst. In addition, LiOH was dissolved in water and added to the stock impregnation solution to lower the hydrogen ion activity to a "measured pH" of 13.2.

Example 10

The α-alumina source material for Carrier A was washed with de-ionized water at 25 °C, then homogenized with the same ingredients used to form Carrier A before extruding, drying, and firing in a muffle furnace. The resulting carrier was designated Carrier E. A catalyst was prepared from Carrier E in the same manner as outlined in Example 1. The cesium target was 360 ppm/gram finished catalyst. In addition, LiOH was dissolved in water and added to the stock impregnation solution to lower the hydrogen ion activity to a "measured pH" of 13.2.

Example 11

Carrier E was used to prepare a catalyst in the same manner as described in Example 10; however, the carrier was subjected to the carrier washing procedure before impregnation. The cesium target was 510 ppm/gram finished catalyst. In addition, LiOH was dissolved in water and added to the stock impregnation solution to lower the hydrogen ion activity to a "measured pH" of 13.2.

Example 12

100 g of Carrier A were immersed in 300 ml of a boiling 0.1 M solution of barium acetate at 25 °C for 15 min, then immersed in 300 ml of de-ionized water at 25 °C for 15 minutes, followed by immersion three times in 300 ml of boiling de-ionized water for 15 minutes each. The carrier was then removed and dried in a well ventilated oven at 150 °C for 18 hours. The carrier was then

impregnated as described in Example 1. The cesium target was 400 ppm/gram finished catalyst. In addition, LiOH was dissolved in water and added to the stock impregnation solution to lower the hydrogen ion activity to a "measured pH" of 13.2.

Example 13

Carrier A was subjected to carrier washing and impregnation as described in Example 1. The cesium target was 650 ppm/gram finished catalyst. In addition, LiOH was dissolved in water and added to the stock impregnation solution to lower the hydrogen ion activity to a "measured pH" of 13.2 and NH_4ReO_4 was dissolved in water and added to the stock impregnation solution to provide 1.5 micromoles Re/gram finished catalyst.

The catalysts of Examples 1-13 were used to produce ethylene oxide from ethylene and oxygen. 3 to 5 grams of crushed catalyst were loaded into a 6.35 mm inside diameter stainless steel U-shaped tube. The U tube was immersed in a molten metal bath (heat medium) and the ends were connected to a gas flow system. The weight of the catalyst used and the inlet gas flow rate were adjusted to achieve a gas hourly space velocity of 6800 ml of gas per ml of catalyst per hour. The inlet gas pressure was 1450 kPa.

The gas mixture passed through the catalyst bed (in a once-through operation) during the entire test run (including start-up) consisted of 25% ethylene, 7.0% oxygen, 5% carbon dioxide, 63% nitrogen, and 2.0 to 6.0 ppmv ethyl chloride.

The initial reactor (heat medium) temperature was 180 °C. The temperature was ramped at a rate of 10 °C per hour from 180 °C to 225 °C, and then adjusted so as to achieve a constant ethylene oxide level of 1.5 %v in the outlet gas stream. Performance data at this conversion level are usually obtained when the catalyst has been on stream for a total of at least 1-2 days. Due to slight differences in feed gas composition, gas flow rates, and the calibration of analytical instruments used to determine the feed and product gas compositions, the measured selectivity and activity of a given catalyst may vary slightly from one test run to the next.

The initial performance values for selectivity at 1.5% ethylene oxide were measured and are reported in Table III.

TABLE III. Performance Characteristics of Catalysts Prepared From Unwashed and Washed α-Alumina

Example	Carrier	Pre-Impregnation Condition	Base Addition	Impregnating Solution "measured pH"	Selectivity (%)	Temperature (°C)
1	A	water wash	none	11.2	82.7	229
1a	A	no wash	none	11.2	81.3	237
2	B	water wash	none	11.2	82.5	226
2a	B	no wash	none	11.2	82.0	232
3	C	water wash	none	11.2	82.0	229
3a	C	no wash	none	11.2	82.0	235
4	D	water wash	none	11.2	82.5	227
4a	D	no wash	none	11.2	82.2	245
5	A	water wash	TEAH	13.2	82.7	226
6	A	TEAH wash + water wash	TEAH	13.6	82.7	222
7	A	water wash	TEAH	13.2	89.4	245
8	A	water wash	LiOH	13.2	82.7	226
8a	A	no wash	LiOH	13.2	82.0	227
9	A	ammonium acetate wash	LiOH	13.2	83.1	222
10	E	raw material wash	LiOH	13.2	83.0	225
11	E	raw material wash + water wash	LiOH	13.2	82.7	222
12	A	barium acetate wash	LiOH	13.2	82.7	226
13	A	water wash	LiOH	13.2	86.2	232

It can be seen that significant improvement in catalyst properties are seen when the carrier is washed before the catalytic metal is deposited on the carrier. Even further improvement is seen when the material used to make the carrier is washed before the carrier is formed.

The hydrogen ion activity of the deposition solution for catalysts in Examples 5-13 was lowered by the addition of a base. It can be seen that lowering the hydrogen ion activity of the deposition solution further improves the catalytic properties. It is also evident that the phenomenon of the pH effect is not restricted to a particular catalyst formulation, as best illustrated in Examples 7 and 13, where a selectivity enhancing dopant, such as rhenium, is added to the impregnating solution.

The reference to any prior art in this specification is not, and should not be taken as, an acknowledgment or any form of suggestion that that prior art forms part of the common general knowledge in Australia.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A process for improving the properties of a carrier for a catalyst by a treatment which is performed on one or more of the materials from which the carrier is formed and/or on the complete carrier and which is effective in lowering the concentration of one or more ionizable silicates present on the surface of the complete carrier, the lowering being expressed as the lowering of the relative concentration of Si atoms, as measured by X-ray Photoelectron Spectroscopy (XPS) performed on the untreated and treated carrier.

2. A process according to claim 1 characterized in that the treatment is performed by means effective in rendering the ionizable silicates ionic, rendering the ionizable silicates insoluble, or rendering the ionizable silicates immobile.

3. A process according to claim 2 characterized in that said means is selected from washing, ion exchange, volatilization, precipitation, sequestration, and combinations thereof

4. A process according to claim 3, characterized in that said washing is performed with an aqueous and/or organic solvent-based solution, selected from water, tetraethylammonium hydroxide, ammonium acetate, lithium carbonate, barium acetate, strontium acetate, crown ether, methanol, ethanol, dimethylformamide, and mixtures thereof.

5. A process according to any one of claims 1 to 4, characterized in that the concentration, as measured by XPS, of Si on the surface of the carrier is lowered by at least 5 percent.

6. A process according to any one of claims 1 to 5, characterized in that the concentration lowering treatment is followed by a drying

step.

7. A process according to claim 1 substantially as hereinbefore described.

8. A process for preparing a catalyst, by depositing a catalytically effective amount of one or more catalytically reactive metals and optionally one or more promoter materials on a carrier prepared by a process according to any one of claims 1 to 7.

9. A process according to claim 8, characterized in that said catalytically reactive metal and optional promoter material deposition is effected by submerging said carrier in an impregnation solution wherein a hydrogen ion activity of said solution is lowered.

10. A process according to claim 8 or claim 9, characterized in that the catalyst is suitable for the vapor phase epoxidation of an alkene.

11. A process according to claim 10, characterized in that the catalyst is suitable for the epoxidation of ethylene to ethylene oxide, containing silver as the main catalytically reactive metal on an alumina-based carrier.

12. A process for the catalytic epoxidation of any alkene with an oxygen containing gas, wherein a catalyst as prepared by a process according to claim 8 or claim 9 is used.

13. A process according to claim 12, characterized in that at least one of the nitrogen oxides is added to the oxygen containing gas.

14. A process according to claim 8 substantially as hereinbefore described.

Dated this 28th day of May 2002

Shell Internationale Research Maatschappij B.V.

by DAVIES COLLISON CAVE
Patent Attorneys for the Applicant(s)