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(54) **SILVER-CONTAINING CATALYSTS, THE  
MANUFACTURE OF SUCH  
SILVER-CONTAINING CATALYSTS, AND  
THE USE THEREOF**

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(57) **ABSTRACT**

A high activity and high selectivity silver catalyst comprising silver and, optionally, one or more promoters supported on a suitable support material having the form of a shaped agglomerate. The structure of the shaped agglomerate is that of a hollow cylinder having a small inside diameter compared to the outside diameter. The catalyst is made by providing the shaped material of a particular geometry and incorporating the catalytic components therein. The catalyst is useful in the epoxidation of ethylene.

**SILVER-CONTAINING CATALYSTS, THE  
MANUFACTURE OF SUCH SILVER-CONTAINING  
CATALYSTS, AND THE USE THEREOF**

[0001] This invention relates to silver-containing catalyst compositions that are particularly suitable for use in the manufacture of such silver-containing catalysts.

[0002] Ethylene oxide is an important industrial chemical used as a feedstock for making such chemicals as ethylene glycol and detergents. One method of manufacturing ethylene oxide is by the catalyzed partial oxidation of ethylene with oxygen. There are continuing efforts to develop catalysts that can improve the operating efficiency of such ethylene oxide manufacturing processes. Some of the desirable properties of an ethylene oxide catalyst include good selectivity and good activity.

[0003] It is, thus, an object of this invention to provide a catalyst that has certain desirable catalytic properties that make it particularly suitable for use in the manufacture of ethylene oxide.

[0004] It is another object of this invention to provide a method of making a catalyst that exhibits at least some of the aforementioned desirable catalytic properties.

[0005] Yet another object of this invention is to provide an economically efficient process for manufacturing ethylene oxide by utilizing a catalyst having certain desirable catalytic properties.

[0006] Other aspects, objects and the several advantages of the invention will become more apparent in light of the following disclosure.

[0007] According to one invention, a catalyst is provided which has a high silver concentration and at least one promoter compound. The silver and promoter compound are supported on a support material having a high water pore volume.

[0008] According to another invention, a method is provided for making a catalyst by providing a shaped support material and impregnating the shaped support material with a silver-containing solution such that the amount of silver metal in the shaped support material exceeds 15 weight percent of the total weight of the shaped support material. The silver impregnated shaped support material is then heat treated to provide the catalyst.

[0009] According to yet another invention, the above described catalyst or catalyst made by the above-described method is used in a process for manufacturing ethylene oxide by contacting the catalyst, under suitable epoxidation process conditions, with a feed stream that comprises ethylene and oxygen.

[0010] The catalyst composition of the present invention is a novel combination of catalytic components and support material. The support material has specific physical properties and is preferably formed into a shaped agglomerate of the support material having a hollow cylinder geometric configuration or structure with a small internal diameter relative to the outer diameter of the cylinder.

[0011] The support material of the catalyst composition can be any porous refractory material that is relatively inert in the presence of ethylene oxidation feeds, products and reaction conditions; provided, such support material has the

physical properties required for the inventive catalyst composition especially when used to support the catalytic components of the inventive composition. Generally, the support material is an inorganic oxide which can include, for example, alumina, silicon carbide, silica, zirconia, magnesia, silica-alumina, silica-magnesia, silica-titania, alumina-titania, alumina-magnesia, alumina-zirconia, thoria, silica-titania-zirconia and various clays.

[0012] The preferred support material comprises alumina preferably of a high purity of at least 90 weight percent alumina and, more preferably, at least 98 weight percent alumina. Among the various available forms of alumina alpha-alumina is the most preferred.

[0013] An important aspect of the inventive catalyst composition is for the support material to have a high water absorption value generally exceeding about 40%. This high water absorption value allows for the loading of a greater amount of silver onto the support material than can be loaded onto other inorganic oxide materials that have a lower value for water absorption. It has, thus, been found that for the inventive catalyst composition it is important for the water absorption of the support material to be greater than 42.5%, preferably, greater than 45% and, most preferably, greater than 46%.

[0014] As used herein, the term "water absorption" means the value as determined by test procedure ASTM C393, which is incorporated herein by reference. Water absorption can be expressed as the weight of the water that can be absorbed into the pores of the carrier, relative to the weight of the carrier.

[0015] The surface area of the support material as measured by the B.E.T. method can be in the range of from 0.03 m<sup>2</sup>/g to 10 m<sup>2</sup>/g, preferably from 0.05 m<sup>2</sup>/g to 5 m<sup>2</sup>/g and most preferably from 0.1 m<sup>2</sup>/g to 3 m<sup>2</sup>/g. The B.E.T. method of measuring surface area has been described in detail by Brunauer, Emmet and Teller in *J. Am. Chem. Soc.* 60 (1938) 309-316, which is incorporated herein by reference.

[0016] Another important aspect of the inventive catalyst composition is for the support material to be in the form of a shaped agglomerate, and it is particularly important for the shaped agglomerate of support material to have a hollow cylinder geometric configuration with an inner diameter, or bore size, that is small relative to the outer diameter of the hollow cylinder. The smaller bore diameter helps provide for an improvement in the average crush strength of the agglomerate by offsetting the loss in crush strength that results from using a support material having a greater porosity (i.e. water absorption). Another benefit from the smaller bore diameter is that it provides for packing a greater amount of support material into the same volume, i.e., packing density, thus, allowing for more silver to be loaded into the same volume.

[0017] While it is an important aspect of the invention for the bore size of the shaped agglomerate to be small relative to the outer diameter of the shaped agglomerate, it is also important for the inside bore of the shaped agglomerate to have at least some dimension. It has been found that the void space defined by the inside bore diameter provides for certain benefits in the manufacturing of the inventive catalyst and its catalytic properties. While not wanting to be bound to any particular theory, it is believed, however, that the void space provided by the inside bore diameter of the

hollow cylinder allows for improved carrier impregnation and catalyst drying. The catalytic benefits associated with the inventive catalyst is demonstrated and discussed in more detail elsewhere herein.

**[0018]** The hollow cylinder geometric configuration can be defined by an outer diameter, an inner diameter, or bore diameter, and a length. It is understood that these dimensions are nominal and approximate, since, methods of manufacturing the shaped agglomerates are not necessarily precise. The hollow cylinder should have a length-to-outside diameter ratio in the range of from about 0.3 to about 2.0, preferably from about 0.5 to about 1.6 and, most preferably, from 0.9 to 1.1. An important, if not critical feature of the invention is for the bore diameter to be small relative to the outside diameter of the hollow cylinder. For instance, the ratio of bore diameter-to-outside diameter can range upwardly to 0.3, preferably, from 0.01 to 0.25 and, most preferably, from 0.02 to 0.2.

**[0019]** In addition to the support material that is formed into an agglomerate having a specific geometric configuration, incorporated into the support material is at least a catalytically effective amount of silver and, optionally, one or more promoters and, optionally, one or more copromoters. Thus, the inventive catalyst comprises a shaped support material, a catalytically effective amount of silver and, optionally, one or more promoters and, optionally, one or more copromoters.

**[0020]** Another particularly important feature of the inventive catalyst is for the support to be highly loaded with silver. Indeed, it is the combination of using a high porosity support material having a shaped configuration that, in combination, helps provide for the high silver loading. The silver loading is generally such that the amount of silver in the catalyst composition exceeds about 15 weight percent based on the total weight of the catalyst or even exceeding 16 weight percent. Preferably, however, the silver content of the catalysts should exceed 17 weight percent and, most preferably, 18 weight percent.

**[0021]** In general, the catalyst of the present invention is prepared by impregnating the shaped agglomerate of support material with silver and, optionally, one or more promoters, such as, for example, rare earths, magnesium, rhenium and alkali metals (lithium, sodium, potassium, rubidium and cesium) and, optionally, one or more copromoters, such as, for example, sulfur, molybdenum, tungsten and chromium. Among the promoter components that can be incorporated into the shaped agglomerate of support material, rhenium and the alkali metals, in particular, the higher alkali metals, such as potassium, rubidium and cesium, are preferred. Most preferred among the higher alkali metals is cesium. Either the rhenium promoter may be used without an alkali metal promoter being present or an alkali metal promoter may be used without a rhenium promoter being present or a rhenium promoter and an alkali metal promoter can both be present in the catalyst system. The copromoters can include sulfur, molybdenum, tungsten, and chromium.

**[0022]** Silver is incorporated into the shaped agglomerate of support material by contacting it with a silver solution formed by dissolving a silver salt, or silver compound, or silver complex in a suitable solvent. The contacting or impregnation is preferably done in a single impregnation step whereby the silver is deposited onto the shaped agglom-

erate so as to provide, for instance, at least about 15 weight percent silver, based on the total weight of the catalyst.

**[0023]** The one or more promoters can also be deposited on the shaped agglomerate either prior to, coincidentally with, or subsequent to the deposition of the silver, but, preferably, the one or more promoters are deposited on the shaped agglomerate coincidentally or simultaneously with the silver.

**[0024]** Promoting amounts of alkali metal or mixtures of alkali metal can be deposited on a shaped agglomerate support using a suitable solution. Although alkali metals exist in a pure metallic state, they are not suitable for use in that form. They are used as ions or compounds of alkali metals dissolved in a suitable solvent for impregnation purposes. The shaped agglomerate is impregnated with a solution of alkali metal promoter ions, salt(s) and/or compound(s) before, during or after impregnation of the silver ions or salt(s), complex(es), and/or compound(s) has taken place. An alkali metal promoter may even be deposited on the shaped agglomerate after the silver component has been reduced to metallic silver.

**[0025]** The promoting amount of alkali metal utilized will depend on several variables, such as, for example, the surface area and pore structure and surface chemical properties of the carrier used, the silver content of the catalyst and the particular ions and their amounts used in conjunction with the alkali metal cation.

**[0026]** The amount of alkali metal promoter deposited upon the shaped agglomerate or present on the catalyst is generally in the range of from about 10 parts per million to about 3000 parts per million, preferably between about 15 parts per million and about 2000 parts per million and more preferably, between about 20 parts per million and about 1500 parts per million by weight of total catalyst.

**[0027]** The alkali metal promoters are present on the catalysts in the form of cations (ions) or compounds or complexes or surface compounds or surface complexes rather than as the extremely active free alkali metals, although for convenience purposes in this specification and claims they are referred to as "alkali metal" or "alkali metal promoters" even though they are not present on the catalyst as metallic elements. For purposes of convenience, the amount of alkali metal deposited on the support or present on the catalyst is expressed as the metal. Without intending to limit the scope of the invention, it is believed that the alkali metal compounds are oxidic compounds. More particularly, it is believed that the alkali metal compounds are probably in the form of mixed surface oxides or double surface oxides or complex surface oxides with the aluminum of the support and/or the silver of the catalyst, possibly in combination with species contained in or formed from the reaction mixture, such as, for example, chlorides or carbonates or residual species from the impregnating solution(s).

**[0028]** The shaped agglomerate can also be impregnated with rhenium ions, salt(s), compound(s), and/or complex(es). This may be done at the same time that the alkali metal promoter is added, or before or later; or at the same time that the silver is added, or before or later. Preferably, rhenium, alkali metal, and silver are in the same impregnating solution, although it is believed that their presence in different solutions will still provide suitable catalysts.

[0029] The preferred amount of rhenium, calculated as the metal, deposited on or present on the shaped agglomerate or catalyst ranges from about 0.1 micromoles ( $\mu\text{mole}$ ) per gram to about 10 micromoles per gram, more preferably from about 0.2 micromoles per gram to about 5 micromoles per gram of total catalyst, or, alternatively stated, from about 19 parts per million to about 1860 parts per million, preferably from about 37 parts per million to about 930 parts per million by weight of total catalyst. The references to the amount of rhenium present on the catalyst are expressed as the metal, irrespective of the form in which the rhenium is actually present.

[0030] The rhenium compound used in the preparation of the instant catalyst includes rhenium compounds that can be solubilized in an appropriate solvent. Preferably, the solvent is a water-containing solvent. More preferably, the solvent is the same solvent used to deposit the silver and the alkali metal promoter.

[0031] Examples of suitable rhenium compounds used in making the inventive catalyst include the rhenium salts such as rhenium halides, the rhenium oxyhalides, the rhenates, the perrhenates, the oxides and the acids of rhenium. A preferred compound for use in the impregnation solution is the perrhenate, preferably ammonium perrhenate. However, the alkali metal perrhenates, alkaline earth metal perrhenates, silver perrhenates, other perrhenates and rhenium heptoxide can also be suitably utilized. Rhenium heptoxide,  $\text{Re}_2\text{O}_7$ , when dissolved in water, hydrolyzes to perrhenic acid,  $\text{HReO}_4$ , or hydrogen perrhenate. Thus, for purposes of this specification, rhenium heptoxide can be considered to be a perrhenate, i.e.,  $\text{ReO}_4^-$ .

[0032] It is also understood that there are many rhenium compounds that are not soluble in water but can be solubilized in water by utilizing various acids, bases, peroxides, alcohols, and the like. After solubilization, these compounds can be used, for example, with an appropriate amount of water or other suitable solvent to impregnate the shaped agglomerate. Of course, it is also understood that upon solubilization of many of these compounds, the original compound no longer exists in the same form after solubilization. For example, rhenium metal is not soluble in water. However, it is soluble in concentrated nitric acid as well as in hydrogen peroxide solution. Thus, by using an appropriate reactive solvent, one could use rhenium metal to prepare a solubilized rhenium-containing impregnating solution. In a preferred embodiment of the instant invention, the rhenium present on the catalyst is present in a form that is extractable in a dilute aqueous base solution.

[0033] The one or more copromoters can be deposited on the shaped agglomerate by any suitable manner known to those skilled in the art. The copromoter is deposited on the shaped agglomerate either prior to, coincidentally with, or subsequent to the deposition of the silver, but preferably, the one or more copromoters are deposited on the shaped agglomerate coincidentally or simultaneously with the silver. A copromoting amount of copromoter is deposited on the shaped agglomerate and can generally be in the range of from about 0.01 to about 25, or more,  $\mu\text{moles}$  per gram of total catalyst.

[0034] The catalysts according to the present invention have a particularly high activity and high selectivity for ethylene oxide production in the direct oxidation of ethylene

with molecular oxygen to ethylene oxide. For instance, the inventive catalyst can have an initial selectivity of at least about 86.5 mole percent, preferably, at least 87 mole percent and, most preferably, at least 88.5 mole percent.

[0035] As it is used herein with reference to the selectivity of a catalyst, the term "selectivity",  $S_w$ , means the mole percent (%) of the desired ethylene oxide formed relative to the total of ethylene converted at a given work rate,  $w$ , for a catalyst with the work rate being defined as the amount of ethylene oxide produced per unit volume of catalyst (e.g.,  $\text{kg per m}^3$ ) per hour. As it is used herein with reference to the activity of a catalyst, the term "activity",  $T_w$ , means the temperature needed to reach a given work rate.

[0036] The term "initial selectivity" referred to herein means the selectivity of the given catalyst when it has been used for less than two weeks in accordance with the following described standard testing procedure. The initial selectivity of a given catalyst is determined by measuring the selectivity of the catalyst using a standard testing procedure. In this standard testing procedure, a crushed catalyst (14-20 mesh) is placed within the  $\frac{1}{4}$  inch diameter stainless steel U-tube of a micro-reactor operated under certain specified process conditions. A standard feed of 30 mole percent ethylene, 5 mole percent carbon dioxide, and 8 mole percent oxygen, and 57 mole percent nitrogen is introduced into the micro-reactor at a pressure of 210 psig and at such a rate as to provide a gaseous hourly space velocity of  $3300 \text{ hr}^{-1}$ . The selectivity,  $S_w$ , and activity,  $T_w$ , are determined for a work rate of 200 kg ethylene oxide yield per hour per cubic meter of catalyst. The selectivity is presented in terms of mole percent, and the activity is presented in terms of temperature in degrees centigrade.

[0037] The conditions for carrying out the epoxidation oxidation reaction in the presence of the inventive catalysts according to the present invention broadly comprise those already described in the prior art. This applies, for example, to suitable temperatures, pressures, residence times, diluent materials such as nitrogen, carbon dioxide, steam, argon, methane or other saturated hydrocarbons, to the presence of moderating agents to control the catalytic action, for example, 1-2, dichloroethane, vinyl chloride, ethyl chloride or chlorinated polyphenyl compounds, to the desirability of employing recycle operations or applying successive conversions in different reactors to increase the yields of ethylene oxide, and to any other special conditions which may be selected in processes for preparing ethylene oxide. Pressures in the range of from atmospheric to about 500 psig are generally employed. Higher pressures, however, are not excluded. The molecular oxygen employed as reactant can be obtained from any suitable source including conventional sources. A suitable oxygen charge can include relatively pure oxygen, or a concentrated oxygen stream comprising oxygen in major amount with lesser amounts of one or more diluents, such as nitrogen and argon, or any other oxygen-containing stream, such as air. The use of the present catalysts in ethylene oxide reactions is in no way limited to the use of specific conditions among those that are known to be effective.

[0038] For purposes of illustration only, the following table shows the range of conditions that are often used in current commercial ethylene oxide reactor units.

TABLE I

*GHSV	1500–10,000
Inlet Pressure	150–400 psig
Inlet Feed	
Ethylene	1–40%
Oxygen	3–12%
Carbon dioxide	0–15%
Ethane	0–3%
Argon and/or methane and/or nitrogen	balance
Diluent chlorohydrocarbon moderator	0.3–20 ppmv total
Coolant temperature	180–315° C.
Catalyst temperature	180–325° C.
O <sub>2</sub> conversion level	10–60%
Ethylene Oxide (EO) Production (Work Rate)	2–20 lbs. EO/cu. ft. catalyst/hr.

\*Cubic feet of gas at standard temperature and pressure passing over one cubic foot of packed catalyst per hour.

[0039] In a preferred application, ethylene oxide is produced when an oxygen-containing gas is contacted with ethylene in the presence of the inventive catalysts under suitable epoxidation reaction conditions such as at a temperature in the range of from about 180° C. to about 330° C., and, preferably, 200° C. to 325° C., and a pressure in the range of from atmospheric to about 500 psig and, preferably, from 150 psig to 400 psig.

[0040] The following examples are intended to illustrate the advantages of the present invention and are not intended to unduly limit the scope of the invention.

## EXAMPLE I

[0041] This Example I describes the preparation of a stock silver impregnation solution used for impregnating various support materials as described in the following examples.

[0042] In a 5-liter stainless steel beaker 415 grams of reagent grade sodium hydroxide was dissolved in 2340 ml of deionized water. The temperature of the solution was adjusted to about 50° C. In a 4-liter stainless steel beaker 1699 grams of silver nitrate was dissolved in 2100 ml of deionized water. The temperature of the solution was adjusted to about 50° C. The sodium hydroxide solution was slowly added to the silver nitrate solution with stirring while the temperature was maintained at about 50° C. The resulting slurry was stirred for about 15 minutes. The pH of the solution was maintained at above 10 by the addition of NaOH solution as required. A washing procedure was used which included removing liquid by the use of a filter wand followed by the replacement of the removed liquid with an equivalent volume of deionized water. This washing procedure was repeated until the conductivity of the filtrate dropped below 90 micro-mho/cm. After the completion of the last wash cycle, 1500 ml of deionized water was added and followed by the addition of 630 grams of oxalic acid dihydrate (4.997 moles) in increments of 100 grams while stirring and maintaining the solution at about 40° C. ( $\pm 5^\circ$  C.). The pH of the solution was monitored during the addition of the last 130 grams of oxalic acid dihydrate to ensure that it did not drop below 7.8 for an extended period of time. Water was removed from the solution with a filter wand and the slurry was cooled to less than 30° C. Slowly added to the solution was 732 grams of 92% ethylenediamine. The temperature was maintained below 30° C. during this addition. A spatula was used to manually stir the mixture

until enough liquid was present to mechanically stir. The final solution was used as a stock silver impregnation solution for preparing the catalysts of Example III.

## EXAMPLE II

[0043] This Example II presents information concerning the properties and geometric configuration of the three types of carrier supports (i.e., Carrier A, Carrier B, and Carrier C) used in the preparation of the catalysts as described in Example III. Presented in the following Table II are certain properties of each of the carrier supports.

TABLE II

Properties of Carrier Supports			
	Carrier A	Carrier B	Carrier C
<u>Properties</u>			
Water Absorption (%)	39.2	45.6	46.5
Packing Density	50.3	45.5	52.7
ASTM Attrition Loss, %	10.8	14.6	14.7
Average Crush Strength	28.6	21.4	29.3
Surface Area	0.80	0.78	0.77
<u>Geometric Configuration</u>			
Nominal Size (mm)	8	8	8
Average Length	8.1	8.1	7.7
Length, Range		7.6–8.8	6.6–8.6
Diameter	8.5	8.5	8.6
Bore Size, mm	3.8	3.8	1.02
Length/Outside Diameter	approx. 1	0.95	0.90
Internal Diameter, mm	3.8	3.8	1.0

[0044] Each carrier support presented in the above Table II had a nominal size of 8 mm and a hollow cylinder geometric configuration. The inner diameter of both Carrier A and Carrier B was 3.8 mm, while the inner diameter of Carrier C was only 1 mm. The water pore volumes of Carrier B and Carrier C were significantly greater than the water pore volume of Carrier A. This explains the reduction in crush strength and packing density of Carrier B relative to Carrier A; however, with the reduction of the inner diameter of Carrier C relative to both Carrier A and Carrier B, the crush strength and packing density are improved such that these properties have values that exceed such values for Carrier A.

## EXAMPLE III

[0045] This Example III describes the preparation of the comparison catalyst and the inventive catalysts and certain of their physical properties.

## Catalyst A

[0046] The impregnation solution for preparing Catalyst A was made by mixing 153 grams of silver stock solution of specific gravity 1.5673 g/cc with a solution of 0.1235 g of  $\text{NH}_4\text{ReO}_4$  in 2 g of 1:1 EDA/ $\text{H}_2\text{O}$ , 0.0574 g of ammonium metatungstate dissolved in 2 g of 1:1 ammonia/water and 0.3174 g  $\text{LiNO}_3$  dissolved in water. Additional water was added to adjust the specific gravity of the solution to 1.465 g/cc. 50 grams of such doped solution was mixed with 0.1016 g of 50% CsOH solution. This final impregnating solution was used to prepare Catalyst A. 30 grams of Carrier A was evacuated to 20 mm Hg for 1 minute and the final

impregnating solution was added to Carrier A while under vacuum, then the vacuum was released and the carrier allowed to contact the liquid for 3 minutes. The impregnated Carrier A was then centrifuged at 500 rpm for 2 minutes to remove excess liquid. Impregnated Carrier A pellets were placed in a vibrating shaker and dried in flowing air at 250° C. for 5½ minutes. The final Catalyst A composition was 13.2% Ag, 460 ppm Cs/g catalyst, 1.5 µmole Re/g catalyst, 0.75 µmole W/g catalyst, and 15 µmole Li/g catalyst.

#### Catalyst B

[0047] The impregnation solution for preparing Catalyst B was made by mixing 153 grams of silver stock solution of specific gravity 1.589 g/cc with a solution of 0.1051 g of  $\text{NH}_4\text{ReO}_4$  in 2 g of 1:1 EDA/ $\text{H}_2\text{O}$ , 0.0488 g of ammonium metatungstate dissolved in 2 g of 1:1 ammonia/water and 0.270 g  $\text{LiNO}_3$  dissolved in water. Additional water was added to adjust the specific gravity of the solution to 1.588 g/cc. 50 grams of such doped solution was mixed with 0.0940 g of 50% CsOH solution. This final impregnating solution was used to prepare Catalyst B. 30 grams of Carrier B was evacuated to 20 mm Hg for 1 minute and the final impregnating solution was added to Carrier B while under vacuum, then the vacuum was released and the carrier allowed to contact the liquid for 3 minutes. The impregnated Carrier B was then centrifuged at 500 rpm for 2 minutes to remove excess liquid. Impregnated Carrier B pellets were placed in a vibrating shaker and dried in flowing air at 250° C. for 5½ minutes. The final Catalyst B composition was 17.5% Ag, 500 ppm Cs/g catalyst, 1.5 µmole Re/g catalyst, 0.75 µmole W/g catalyst, and 15 µmole Li/g catalyst.

#### Catalyst C

[0048] The impregnation solution for preparing Catalyst C was made by mixing 204 grams of silver stock solution of specific gravity 1.573 g/cc with a solution of 0.1378 g of  $\text{NH}_4\text{ReO}_4$  in 2 g of 1:1 EDA/ $\text{H}_2\text{O}$ , 0.0064 g of ammonium metatungstate dissolved in 2 g of 1:1 ammonia/water and 0.3542 g  $\text{LiNO}_3$  dissolved in water. Additional water was added to adjust the specific gravity of the solution to 1.558 g/cc. 50 grams of such doped solution was mixed with 0.0850 g of 50% CsOH solution. This final impregnating solution was used to prepare Catalyst C. 30 grams of Carrier C was evacuated to 20 mm Hg for 1 minute and the final impregnating solution was added to Carrier C while under vacuum, then the vacuum was released and the carrier allowed to contact the liquid for 3 minutes. The impregnated Carrier C was then centrifuged at 500 rpm for 2 minutes to remove excess liquid. Impregnated Carrier C pellets were placed in a vibrating shaker and dried in flowing air at 250° C. for 7 minutes. The final Catalyst C composition was 17.8% Ag, 460 ppm Cs/g catalyst, 1.5 µmole Re/g catalyst, 0.75 µmole W/g catalyst, and 15 µmole Li/g catalyst.

[0049] Presented in Table III are the silver loadings of each of the catalysts. It is significant to note that the silver component of the inventive catalyst systems was incorporated into the support material by use of a single impregnation instead of by use of multiple impregnations. Catalyst B includes a significantly higher amount of silver than does Catalyst A. This is thought to be due to the higher water absorption of Carrier B as compared to Carrier A. As for Catalyst C, while it contains close to the same weight percent silver as does Catalyst B, a greater total amount of

silver is able to be loaded into a given reactor volume with Catalyst C as opposed to Catalyst A or Catalyst B due to the modified geometry.

TABLE III

<u>Silver Content of Catalyst Systems</u>	
Weight % Silver in Catalyst	
Catalyst A	13.2
Catalyst B	17.5
Catalyst C	17.8

#### EXAMPLE IV

[0050] This Example IV describes the procedure for testing certain of the catalytic properties, such as, selectivity and activity, of the catalysts described in Example III.

[0051] Catalysts A, B and C were tested for their ability to produce ethylene oxide from a feed containing ethylene and oxygen. To do this, 4 to 5 g of crushed catalyst was loaded into a ¼ inch stainless steel U-shaped tube. The tube was immersed in a molten metal bath (heat medium) and the ends were connected to a gas flow system. The weight of catalyst used and the inlet gas flow rate were adjusted to give a gas hourly space velocity of 3300  $\text{NI}/(\text{l.h.})$ , as calculated for uncrushed catalyst. As the catalyst packing density and silver loading changes, the amount of catalyst loaded in the test reactor was changed to reflect larger amounts of silver packed into a reactor. The catalyst loadings were as follows: Catalyst A (comparative) 4.2 grams, Catalyst B (invention) 4.01 g and Catalyst C (invention) 4.66 g. The gas flow was 16.9  $\text{NI}/\text{h}$ . The inlet gas pressure was 1550 kPa. The catalysts were treated with nitrogen at 225° C. for 2 hours prior to testing. The testing gas mixture passed through the catalyst bed, in a "once-through" operation, consisted of 30% v ethylene, 8% v oxygen, 5% v carbon dioxide, 57% v nitrogen and 2.0 to 6.0 parts by million by volume (ppmv) ethyl chloride. Ethyl chloride concentration was adjusted to obtain maximum selectivity.

TABLE IV

<u>Catalytic Performance of Catalysts</u>		
	Selectivity Percent (%)	Activity Temp (° C.)
Catalyst A	88.0	262
Catalyst B	89.1	263
Catalyst C	89.4	254

[0052] As can be seen from the catalyst performance data presented in Table IV, Catalyst B demonstrates an improved selectivity compared to that of Catalyst A having a selectivity of 89.1% at 263° C. versus a selectivity of 88.0% at 262° C. for Catalyst A. As the term is used herein, "selectivity" means the mole percent of the ethylene oxide formed relative to the total ethylene converted. It is believed that this improvement in selectivity is attributable to the high water absorption of Catalyst B relative to Catalyst A that permits the packing of more silver into the reactor to thereby provide for greater selectivity.

[0053] Catalyst C demonstrates an even greater improvement in selectivity relative to Catalyst A than does Catalyst

B, with Catalyst C having a selectivity of 89.4% at 254° C. versus 88.0% at 262. Catalyst C also demonstrates a greater activity than both Catalyst A and Catalyst B by requiring a significantly lower reaction temperature that gives a significantly greater selectivity. It is believed that the improved selectivity of Catalyst C over that of both Catalyst A and Catalyst B is attributable to the greater amount of silver that can be packed into a reactor due to the high silver loading achievable with the catalyst having a higher water absorption. The improved activity is believed to result from the use of a carrier support material having a hollow cylinder geometric configuration with a small bore diameter in the manufacture of the catalyst.

[0054] While this invention has been described in terms of the presently preferred embodiment, reasonable variations and modifications are possible by those skilled in the art. Such variations and modifications are within the scope of the described invention and the appended claims.

That which is claimed is:

1. A catalyst, comprising:

Silver at a high concentration level and at least one promoter compound, wherein said silver and said at least one promoter compound are supported on a support material having a high water absorption.

2. A catalyst as recited in claim 1, wherein said support material is in the form of a shaped agglomerate having a hollow cylinder geometric configuration such that the L/D ratio of said shaped agglomerate is in the range of from about 0.3 to about 1.6 and the internal diameter is in the range upwardly to about 30 percent of the outer diameter of said shaped agglomerate.

3. A catalyst as recited in claim 2, wherein said high concentration level of silver is in the range exceeding 15 weight percent of the total weight of the said catalyst.

4. A catalyst as recited in claim 3, wherein said high water absorption is in the range of exceeding 42.5%.

5. A catalyst as recited in claim 4, wherein said support material further has a surface area in the range of from 0.03 m<sup>2</sup>/g to 10 m<sup>2</sup>/g.

6. A catalyst as recited in claim 1, wherein said high concentration level of silver is in the range exceeding 15 weight percent of the total weight of the said catalyst.

7. A catalyst as recited in claims 1 or 2, wherein said high water absorption is in the range exceeding 42.5%.

8. A catalyst as recited in claims 1, 2 or 3, wherein said support material further has a surface area in the range of from 0.03 m<sup>2</sup>/g to 10 m<sup>2</sup>/g.

9. A catalyst as recited in claim 1, wherein said support material is in the form of a shaped agglomerate having a hollow cylinder geometric configuration such that the L/D ratio of said shaped agglomerate is in the range of from about 0.3 to about 1.6 and the ratio of internal diameter to outside diameter is in the range of from 0.01 to 0.25.

10. A catalyst as recited in claim 9, wherein said high concentration level of silver is in the range exceeding 16 weight percent of the total weight of the said catalyst.

11. A catalyst as recited in claim 10, wherein said high water absorption is in the range of exceeding 45%.

12. A catalyst as recited in claim 11, wherein said support material further has a surface area in the range of from 0.05 m<sup>2</sup>/g to 5 m<sup>2</sup>/g.

13. A catalyst as recited in claim 1, wherein said high concentration level of silver is in the range exceeding 16 weight percent of the total weight of the said catalyst.

14. A catalyst as recited in claims 1 or 9, wherein said high water absorption is in the range of exceeding 45%.

15. A catalyst as recited in claims 1, 9 or 10, wherein said support material further has a surface area in the range of from 0.05 m<sup>2</sup>/g to 5 m<sup>2</sup>/g.

16. A catalyst as recited in claim 1, wherein said support material is in the form of a shaped agglomerate having a hollow cylinder geometric configuration such that the L/D ratio of said shaped agglomerate is in the range of from about 0.3 to about 1.6 and the ratio of inside diameter to outside diameter is in the range of from 0.02 to 0.25.

17. A catalyst as recited in claim 16, wherein said high concentration level of silver is in the range exceeding 17 weight percent of the total weight of the said catalyst.

18. A catalyst as recited in claim 17, wherein said high water absorption is in the range of exceeding 46%.

19. A catalyst as recited in claim 18, wherein said support material further has a surface area in the range of from 0.1 m<sup>2</sup>/g to 3 m<sup>2</sup>/g.

20. A catalyst as recited in claim 1, wherein said high concentration level of silver is in the range exceeding 17 weight percent of the total weight of the said catalyst.

21. A catalyst as recited in claims 1 or 16, wherein said high water absorption is in the range of exceeding 46%.

22. A catalyst as recited in claims 1, 16 or 17, wherein said support material further has a surface area in the range of from 0.03 m<sup>2</sup>/g to 10 m<sup>2</sup>/g.

23. A catalyst, comprising:

a shaped support material having a hollow cylinder geometric configuration such that the L/D ratio of said shaped support material is in the range of from about 0.3 to about 1.6 and the internal diameter is in the range upwardly to about 30 percent of the outer diameter of said shaped support material; and

a silver component, wherein the concentration of silver in said catalyst is in the range exceeding 15 weight percent of the total weight of said catalyst.

24. A catalyst as recited in claim 23, wherein said shaped support material has a water absorption greater than 42.5%.

25. A catalyst as recited in claim 24, wherein said shaped support material comprises an inorganic oxide having a surface area in the range of from 0.03 m<sup>2</sup>/g to 10 m<sup>2</sup>/g.

26. A catalyst as recited in claim 25, wherein the ratio of internal diameter to outside diameter of said shaped support material is in the range of from 0.01 to 0.25.

27. A catalyst as recited in claim 26, wherein the concentration of silver in said catalyst exceeds 16 weight percent.

28. A catalyst as recited in claim 27, wherein said catalyst further comprises a promoter component.

29. A catalyst as recited in claim 23, wherein said shaped support material comprises an inorganic oxide having a surface area in the range of from 0.03 m<sup>2</sup>/g to 10 m<sup>2</sup>/g.

30. A catalyst as recited in claims 23 or 24, wherein the ratio of internal diameter to outside of said shaped support material is in the range of from 0.01 to 0.25.

31. A catalyst as recited in claims 23, 24 or 25,

wherein the concentration of silver in said catalyst exceeds 16 weight percent of the total weight of said catalyst.

**32.** A catalyst as recited in claims **23**, **24**, **25**, or **26** wherein said catalyst further comprises a promoter component.

**33.** A method, comprising:

providing a shaped support material; and

impregnating said shaped support material with a silver-containing solution such that an amount of silver metal incorporated into said shaped support material exceeds 15 weight percent of the total weight of said shaped support material to thereby provide a silver impregnated shaped support material.

**34.** A method as recited in claim **33**, wherein said impregnating step is a single impregnation step by which said amount of silver metal is incorporated into said shaped support material.

**35.** A method as recited in claim **34**, wherein said shaped support material has a geometric configuration such that the L/D ratio is in the range of from about 0.3 to about 1.6 and the internal diameter is in the range upwardly to about 30 percent of the outer diameter of said shaped catalyst support.

**36.** A method as recited in claim **35**, wherein said shaped material has a water absorption in the range exceeding 42.5% and wherein said shaped material comprises an inorganic oxide having a surface area in the range of from 0.03 m<sup>2</sup>/g to 10 m<sup>2</sup>/g.

**37.** A method as recited in claim **33**, wherein said shaped support material has a geometric configuration such that the L/D ratio is in the range of from about 0.3 to about 1.6 and the internal diameter is in the range upwardly to about 30 percent of the outer diameter of said shaped catalyst support.

**38.** A method as recited in claims **33** or **34**, wherein said shaped material has a water absorption in the range exceeding 42.5% and wherein said shaped material comprises an inorganic oxide having a surface area in the range of from 0.03 m<sup>2</sup>/g to 10 m<sup>2</sup>/g.

**39.** A method as recited in claim **33**, wherein said impregnating step is a single impregnation step by which said amount of silver metal that is incorporated into said shaped support material exceeds 16 weight percent.

**40.** A method as recited in claim **39**, wherein said shaped support material has a geometric configuration such that the L/D ratio is in the range of from about 0.3 to about 1.6 and the ratio of internal diameter to outside diameter is in the range of from 0.01 to 0.25.

**41.** A method as recited in claim **40**, wherein said shaped material has a water absorption in the range exceeding 42.5% and wherein said shaped material comprises an inorganic oxide having a surface area in the range of from 0.03 m<sup>2</sup>/g to 10 m<sup>2</sup>/g.

**42.** A process for manufacturing ethylene oxide, said process comprises:

Contacting, under suitable epoxidation process conditions, a feed stream, comprising ethylene and oxygen, with the catalyst of claim **1**.

**43.** A catalyst composition made by the method of claim **33**.

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