Description

This invention relates to the production of supported silver catalysts for the manufacture of ethylene oxide, more specifically, the invention is concerned with preparing an alkali metal cation promoted silver catalyst capable of oxidizing ethylene with an oxygen-containing gas in the vapor phase to product ethylene oxide at high efficiencies.

Background art

In characterizing catalysts useful for the manufacture of ethylene oxide, the term "selectivity" is employed herein as defined in U.S. Patent No. 3,420,784, at column 3. The terms "efficiency" and "selectivity" as used throughout the specification with regard to the aforesaid catalysts are intended to be synonymous.

Processes for preparing metal cation-promoted silver catalysts for the production of ethylene oxide are extensively described in the patent literature. The vast majority of these processes employ impregnation techniques wherein solutions containing solubilized compounds of silver and metal cation promoters are used to impregnate a porous carrier or support followed by heat treatment of the impregnated support to effect deposition of the silver and metal cation on the support. Processes for making coated catalysts employ techniques wherein silver and metal cations are coated onto a catalyst support from an emulsion or slurry followed by a heating step to remove the liquid present from the carrier and effect deposition of the silver and metal promoter. Coated catalysts are generally considered today to be less satisfactory than impregnated catalysts in commercial practice because it is generally believed that coating methods are unable to accomplish substantial deposition of silver into the interior surfaces of the carrier and consequently, the coated catalysts are more susceptible to silver loss by mechanical abrasion.

The impregnation methods described in the art for preparing ethylene oxide catalysts include a wide variety of methods of depositing silver and metal cations onto a carrier. These methods are generally distinguished by the process conditions they employ such as low-temperature impregnation, high temperature impregnation, activation in an inert gas atmosphere and/or choice of solvent for the silver impregnating solution.

Criticality is often taught to reside in the order of addition of the metal cation and silver to the carrier. Such processes are characterized by their employing either a coincidental (or simultaneous) method of depositing silver and metal cation onto the carrier or a sequential method of addition wherein silver is added either before or after the metal cation. The addition of silver to a carrier subsequent to the addition of metal cation is referred to herein as a "metal-first" sequential process of preparation, while the addition of silver to the carrier prior to the addition of the metal cation is referred to herein as a "silver-first" method of preparation. The coincidental (or simultaneous) addition of silver and metal cation to a carrier is referred to herein as a "coincidental method" of preparation. The use of the term "addition" of a metal cation and/or silver to a carrier is meant to include the steps of impregnating the porous carrier with a solution containing silver and/or metal cation, as the case may be, followed by deposition of same upon the carrier, usually by heat treatment.

The comparative performance of catalysts produced by coincidental and sequential methods of impregnation has been reported in the art. For example, U.S. Patent No. 3,563,914 in Table III, compares the effect of the order of addition of alkali metal promoter and silver to a catalyst support on catalyst efficiency. The data in Table III is said to illustrate the advantage of adding an alkali metal promoter to the support before the silver compound. Specifically, the catalysts prepared by an alkali metal-first preparation procedure are shown to have an efficiency of 4—5 percent higher than catalysts prepared by a coincidental deposition of alkali metal and silver. Further, a catalyst prepared by the addition of silver to the carrier prior to alkali metal addition was by far the least efficient in that the selectivity was about 12 percent below that of a similar catalyst prepared by a coincidental method of deposition. In contrast with Wattimena's conclusion regarding the superiority of an alkali metal-first sequential order of addition, Belgian patent 793,658 and U.S. Patent Nos. 3,962,136, 4,101,115 and 4,012,425 indicate that the coincidental deposition of silver and alkali metal is the preferred method of catalyst preparation insofar as it results in the highest catalyst efficiencies. The aforementioned Belgian patent also provides a direct comparison of catalysts prepared by a method of coincidental deposition of silver and potassium with catalysts of similar composition prepared by a sequential process wherein silver is deposited prior to potassium. Specifically, Example III of the Belgian patent indicates that the maximum efficiency achieved with catalyst containing 7.8 weight percent silver and varying amounts of co-deposited potassium was 76.3% under the stated test conditions whereas in Example VII of the patent the maximum selectivity achieved under the same conditions with catalysts containing the same amount of silver and similar amounts of potassium but prepared by a silver-first process was 73—74%, thus confirming the data in US—P—3563914 concerning the inherent inefficiency of catalysts prepared by a silver-first sequential order of addition.

U.S. Patent 4,207,210, based upon British specification 1,489,335, describes an alkali metal-first process for preparing ethylene oxide catalysts which is said to provide catalysts equivalent or even superior to those produced by coincidental methods of deposition such as set forth in the aforementioned U.S. Patents

39 62 136 and 40 12 425. According to the procedure described in US—P—42 07 210, an aqueous solution containing alkali metal is used to impregnate the porous carrier which is then dried to fix the alkali metal and thereafter the silver is supplied to the support. Tables A through E of the U.S. Patent 42 07 210 provide comparisons of catalysts prepared in accordance with the disclosed alkali metal-first method of addition with catalysts of similar composition prepared by the simultaneous addition of alkali metal and silver. The criticality of the alkali metal-first method of addition is, however, called into question by the reported data which fails to indicate any discernible difference between either method of preparation based on the measured catalyst efficiencies. Indeed, the alkali metal-first method of addition appears to be inherently identical to the coincidental deposition method used in the US Patents 39 62 136 and 40 12 425 as evidenced by the fact that thest three disclose that the alkali metal which is added to the carrier can be subsequently removed, if desired, using an alkanol solvent. This suggests that in the preparation procedure US—P—42 07 210, the alkali metal which is initially deposited on the carrier is resolubilized in the silver-containing impregnating solution thereby inherently effecting a coincidental deposition of silver and alkali metal. (Compare this to U.S. 3,563,914, discussed above).

As noted in the prior art, processes for preparing catalysts by the silver-first method have obvious drawbacks with regard to the resulting catalyst efficiencies. The prior art has documented the markedly lower efficiencies of catalysts produced by the silver-first method relative to similar catalysts prepared by a coincidental method, the latter appearing to be essentially equivalent to an alkali metal-first order of addition. Thus, as discussed above, U.S. Patent No. 3,563,914 and Belgian Patent No. 793,658 contain comparative data clearly illustrating the relative inefficiency of catalysts produced by a silver-first sequential method of addition relative to a coincidental method of addition. While other patents in the art directed to silver-first methods of preparation do not provide sufficient data to allow such side-by-side comparisons to be made, nevertheless, the data which is provided appears to indicate that silver-first methods are the less preferred methods. U.S. Patent No. 4,033,903, for example, discloses a silver-first method of addition wherein used ethylene oxide catalysts are reactivated by the addition of an alkali metal promoter to the aged catalyst. The process of the patent is said to be equally effective for enhancing the efficiency of freshly prepared catalysts by employing a heat treatment step intermediate to the steps of silver addition and alkali metal addition to the carrier. The effectiveness of this method of preparation seems somewhat doubtful, however, in view of the data shown in Table III of the patent wherein catalysts R and T, catalysts prepared by a silver-first method are shown to be inferior to catalyst Q, a silver catalyst containing no alkali metal promoter. Accordingly, based upon the data in the aforementioned patents there appears to be an obvious need in the art for a silver-first sequential method of catalyst preparation capable of providing catalysts which are no less efficient than those produced by the coincidental or metal-first methods.

A common characteristic of the various silver-first methods of preparation described in the literature is their use of the same solvents for metal cation addition. That is, the methods disclosed in this literature suggest using water or a lower alcohol, such as, methanol or ethanol, as the solvent for effecting metal cation impregnation. Thus, for example, the aforementioned U.S. Patent 35 63 914 describes in Example III a silver-first addition wherein water is employed as the solvent for the alkali metal impregnation step. Belgian Patent 793,658 which discloses a silver-first method of addition in Example VII thereof states that aqueous solutions of potassium were used as the impregnating medium for the promoter. U.S. Patent No. 4,066,575 describes a process of catalyst preparation characterized by an activation step wherein the carrier is heated in an inert gas atmosphere following its impregnation with a silver solution. An alkali metal promoter is thereafter deposited on the carrier employing as a solvent for the alkali metal, water or a lower alkanol such as, methanol, ethanol or propanol. Great Britain Patent Application 2,045,636A attempts to distinguish itself from the prior art processes by its low-temperature deposition technique whereby the carrier impregnated with a silver-containing solution is maintained at temperatures below 200°C prior to the so-called post deposition of alkali metal. The suggested solvents for such post-deposition of alkali metal are water and ethanol. German Offenlegungsschrift 2,914,640 discloses a sequential order of impregnation wherein silver is initially applied to the carrier from a suspension and the carrier thereafter immediately dried. Alkali metal is then added to the carrier from a solution using water as the solvent. U.S. Patent 4,248,740 describes a catalyst preparation procedure employing a silver-first order of addition. The patentees recommend impregnating the carrier with an alkali metal solution containing water or a lower alcohol, such as methanol, ethanol or propanol. The solvent is then evaporated, care being taken to prevent heating of the catalyst to above 200°C, a critical feature of the described process. In U.S. Patent No. 4,168,247, there is described a preparation procedure for catalysts identified by the numbers 34—37 which consists of a silver-first order of addition. The alkali metal promoters were dissolved in water with further addition of methanol, and the resulting solution used to impregnate the carrier. EP—A—2045 discloses a "post-treatment" of a used or stabilized silver catalyst by impregnating such catalyst with a

(10)

solution containing an alkali metal promoter, an organic compound capable of forming a complex salt with silver ion and an alcohol of 1 to 4 carbon atoms. No alcohol other than methanol was used in the impregnating solution described in the examples. A further distinction between the process of the reference and the present invention resides in the fact that the improved efficiencies achieved in the examples of the reference can be attributable to the presence of an oxide of nitrogen in the catalyst (see, for example, GB 2,014,133A which discloses the beneficial effects of nitrates or nitrite forming substances in the manufacture of ethylene oxide), rather than, the promoting effect of alkali metal in accordance with the present invention.

The invention in GB—A—2043481 relates to the production of supported silver catalyst for the manufacture of ethylene oxide which contains a combination of (a) cesium and (b) at least one other alkali metal selected from lithium, sodium, potassium and rubidium, which combination comprises (a) and (b) in amounts in relation to the amount of silver therein sufficient to increase the efficiency of ethylene oxide manufacture to a value greater than the efficiencies obtainable under common conditions from respective catalyst which are the same as said catalyst except that instead of containing both (a) and (b), one contains the respective amount of (a), and the other contains the respective amount of (b). The silver content of the supported catalysts being about 2 to 20 wt.%, cesium and potassium are present in a weight ratio of from about 100:1 to 1:100; the catalyst support comprises α-alumina, the surface area thereof is less than about 1 m^2/g. According to example 9 a catalyst containing 13.09 wt.% Ag, 0.0089 wt.% Cs and 0.0026 wt.% K was prepared on a catalyst carrier comprising 98.5 wt.% α-alumina, 0.74 wt.% silicon dioxide, 0.22 wt.% calcium oxide, 0.16 wt.% sodium oxide, 0.14 wt.% ferric oxide, 0.04 wt.% potassium oxide and 0.03 wt.% magnesium oxide—surface area about 0,3 m^2/g, pore volume about 0.50 cm^3/g, packing density 0.70 g/cm^3 and medium pore diameter 21 µm—by a sequential impregnation methode, whereby silver was depointed upon the carrier prior to the deposition of potassium and cesium. Said supported silver catalysts are used for the production of ethylene oxide wherein ethylene and oxygen are reacted in the vapor phase at a temperature of from about 200 to 300°C.

Disclosure of invention

The invention describes a process for preparing a supported silver catalyst for the production of ethylene oxide by the vapor phase oxidation of ethylene with an oxygen-containing gas, the catalyst produced by such process and the use of such silver catalyst for ethylene oxide manufacture. The process comprises impregnating a porous catalyst support with a solution comprising a solvent or a solubilizing agent, and silver salt in an amount sufficient to deposit the desired amount of silver on said support. The impregnated support is then heat treated to convert at least a fraction of the silver salt to silver metal and effect deposition of silver on the surface of said support. Following silver deposition, the support is impregnated with a liquid containing a compound of at least one alkali metal cation promoter in an amount sufficient to deposit the desired amount of metal cation on said support dissolved in an organic solvent in which water is soluble at ambient temperature in an amount no greater than 50 weight %, based on the weight of the water-solvent solution. The impregnated support is thereafter heat treated to effect deposition of the promoter on the surface of said support.

The catalyst preparation process of the invention, in its broadest aspect, concerns a process wherein silver and a alkali metal promoter are sequentially deposited on the surfaces of a porous carrier by a silver-first method. The particular metal promoter employed is not critical to the invention and may be, for example, lithium, sodium, potassium, rubidium and/or cesium.

Details of invention

The process of the invention is predicated on the discovery that a catalyst preparation procedure employing a silver-first addition of silver and alkali metal cation to a porous carrier can provide catalysts as efficient as those produced by the coincidental deposition of the same onto the same or similar carrier provided that the solvent for the metal cation impregnating solution is selected in accordance with the invention. That is, contrary to prior art experiences with silver-first methods of preparation wherein the resulting catalysts invariably are less efficient, even at their optimum, than corresponding catalysts prepared by a method of coincidental deposition, the catalysts of the invention provide improved selectivities to ethylene oxide and are equally as efficient as catalysts produced by coincidental methods of preparation.

As used herein with reference to the silver catalyst and process of the invention, the term "optimum" efficiency is defined as the highest efficiency obtainable at any concentration of promoter for a given silver content, catalyst carrier, and method of preparation when tested at fixed operating conditions.

The solvent employed in the metal cation impregnating solution is an essential feature of the present invention. The organic solvents useful for the invention are characterized by the limited solubility of water in such solvent. Suitable solvents are those in which water has a solubility of no greater than 50 weight %, preferably no greater than 30 weight %, and most preferably, no greater than 25 weight %, based on the weight of the water-solvent solution. Suitable solvents for alkali metal promoters which result in the production of selective catalysts for the production of ethylene oxide in accordance with

the process of the invention include alcohols containing at least 4 carbon atoms, such as, n-butanol, iso-butanol, and primary amyl alcohols (isomeric mixtures); aldehydes such as propionaldehyde; glycols, such as 2-ethyl-1,3-hexanediol; ketones, such as methyl ethyl ketone; and glycol ethers, such as hexyl Cellosolve (Trademark), and Propasol Solvent B (Trademark). n-Butanol and iso-butanol are the preferred solvents for the purposes of this invention. The term solvent in this specification and the claims may comprise a single liquid or a mixture of liquids.

In addition to the aforementioned improved catalyst efficiencies, another important characteristic of the process of the invention and one which provides an unexpected advantage over conventional methods of catalyst preparation relates to the fact that the amount of alkali metal promoter deposited upon the carrier need not be as narrowly controlled as in the prior art to achieve an optimum catalyst efficiency. It is known in the art that the coincidental method of producing ethylene oxide catalysts requires strict control of the amount of promoter added to the carrier in order to maximize the catalyst efficiency for the given carrier and silver content. By way of comparison, in the present process the promoter concentration required to produce catalysts having optimum selectivities to ethylene oxide is not as narrowly critical. For example, the range of alkali metal concentrations capable of providing the optmum efficiency is far broader than the corresponding range for catalysts produced by coincidental methods of preparation in which alkali metals are the promoters. Thus, an important advantage of the present process resides in the fact that commercial-scale batches of ethylene oxide catalysts can be manufactured within a relatively broad specification of the metal content and still achieve optimum efficiency.

The amount of alkali metal needed on the catalyst support according to the process of this invention to achieve an optimum efficiency is at least 10 wt.% greater than that amount of like alkali metal which provides the maximum enhancement of efficiency when used in a coincidental method of preparation with the same amount of silver and the same catalyst support. Even though this is the case, the amount of alkali metal to achieve optimum efficiency is still not as narrowly critical as in the said coincidental method and will vary depending upon silver content, the catalyst support employed, the solvent for the alkali metal impregnating solution, and other catalyst preparation variables.

Catalyst preparation

The catalyst preparation method of the invention concerns a silver-first sequential addition of silver and alkali metal cation promoter to a porous carrier. Stated simply, the process involves a sequence of steps carried out in the following order:

1). impregnating a porous catalyst support by immersing same in a silver-containing impregnating solution;
2). heat treating the impregnated support to effect deposition of silver on the surface of said support;
3). impregnating the product of step 2 by immersing same in a alkali metal cation-containing impregnating solution as defined herein; and
4). heat treating the impregnated support to effect deposition of the alkali metal promoter on the surface of said support.

Silver deposition is generally accomplished by heating the impregnated carrier at elevated temperatures to evaporate the liquid within the support and effect deposition of the silver onto the interior and exterior carrier surfaces. Alternatively, a coating of silver may by formed on the carrier from an emulsion or slurry containing the same followed by heating the carrier as described above. Impregnation of the carrier is generally the preferred technique for silver deposition because it utilizes silver more efficiently than coating procedures, the latter being generally unable to effect substantial silver deposition onto the interior surface of the carrier.

The silver solution used to impregnate the carrier is comprised of a silver salt or compound in a solvent or complexing/solubilizing agent such as the silver solutions disclosed in the art. The particular silver salt employed is not critical and may be chosen, for example, from among silver nitrate, silver oxide or silver carboxylates, such as, silver acetate, oxalate, citrate, phthalate, lactate, propionate, butyrate and higher fatty acid salts.

A wide variety of solvents or complexing/solubilizing agents may be employed to solubilize silver to the desired concentration in the impregnating medium. Generally, the silver concentration in the impregnating medium should be sufficient to deposit on the support from 2 to 20 wt.% of silver based on the total weight of the catalyst. Among solvents disclosed in the art as being suitable for this purpose are lactic acid (U.S. Patent Nos. 2,477,435; and 3,501,417); ammonia (U.S. Patent 2,463,228); alcohols, such as ethylene glycol (U.S. Patent Nos. 2,825,701; and 3,563,914); and amines and aqueous mixtures of amines (U.S. Patent Nos. 2,459,896; 3,563,914; 3,702,259; and 4,097,414).

Following impregnation of the catalyst carried with silver, the impregnated carrier particles are separated from any remaining non-absorbed solution or slurry. This is conveniently accomplished by draining the excess impregnating medium or alternatively by using separation techniques, such as, filtration or centrifugation. The impregnated carrier is then generally heat treated (e.g., roasted) to effect decomposition and reduction of the silver metal salt to metallic silver. Such roasting may be carried out at a temperature of from 100°C to

900°C, preferably from 200°C to 700°C, for a period of time sufficient to convert substantially all of the silver salt to silver metal. In general, the higher the temperature, the shorter the required reduction period. For example, at a temperature of from 400°C to 900°C, reduction may be accomplished in 1 to 5 minutes. Although a wide range of heating periods have been suggested in the art to thermally treat the impregnated support, (e.g., U.S. Patent 3,563,914 suggests heating for less than 300 seconds to dry but not roast reduce the catalyst; U.S. Patent 3,702,259 discloses heating from 2 to 8 hours at a temperature of from 100°C to 375°C to reduce the silver salt in the catalyst; and U.S. Patent 3,962,136 suggests 1/2 to 8 hours for the same temperature range) it is only important that the reduction time be correlated with temperature such that substantially complete reduction of the silver salt to metal is accomplished. A continuous or step-wise heating program may be used for this purpose.

Impregnation of the carrier with a solution containing a promoter salt or compound is carried out after silver deposition has been effected. The impregnating solution is prepared using one or more solvents as herein defined and contains an amount of promoter sufficient to achieve the desired concentration of promoter in the finished catalyst. The impregnated carrier particles are conveniently separated from any remaining non-absorbed solution by draining the excess impregnating solution or alternatively by using separation techniques, such as, filtration and centrifugation. The impregnated carrier is then generally heat treated at ambient or sub-atmospheric pressure to remove the solvent (or solvents) present and deposit (with or without decomposition) the alkali metal ions on to the silver and carrier surfaces. Such heating may be carried out at a temperature of from 50°C to 900°C, preferably from 100°C to 700°C and most preferably from 200°C to 600°C.

Suitable alkali metal promoter compounds include all those soluble in the particular solvent or solubilizing agent employed. Accordingly, inorganic and organic compounds of alkali metals, such as, nitrates, halides, hydroxides, sufates and carboxylates may be used. An inherent advantage of the process of the invention is that it allows the use of certain promoter compounds which could not ordinarily be used in conjunction with known coincidental methods of preparation because of the incompatibility of such salts with the impregnating solution used in the latter processes. As an illustration, alkaline earth salts such as salts of barium, calcium and magnesium can readily be solubilized in an impregnating solution and deposited upon the carrier in accordance with the process of the invention, but can not be added to an impregnating solution containing, for example, oxalic acid or carboxylic acid, solutions commonly employed in conventional coincidental methods of preparation for purposes of silver solubilization.

The types of solvents useful for preparing the promoter impregnating solution are set forth above. Such solvents may be employed individually or in various combinations with each other provided that the salt of desired promoter is sufficiently soluble therein. In the event that the promoter salt is not sufficiently soluble in the organic solvent to provide the desired concentration in the resulting impregnating solution, water may be added as a co-solvent for the promoter salt. Thus, the impregnating solution may be an aqueous solution containing as little as 50 wt.% of organic solvent and still produce the improved silver catalysts of the invention. In general, it is preferred that the concentration of organic solvent in the impregnating solution be as high as possible.

Heat treatment of the impregnated carriers is preferably carried out in air, but a nitrogen, carbon dioxide or hydrogen atmosphere may also be employed. The equipment used for such heat treatment may use a static or flowing atmosphere of such gases to effect reduction.

The particle size of silver metal deposited upon the carrier is a function of the catalyst preparation procedure employed. Thus, the particular choice of solvent and/or complexing agent, silver salt, heat treatment conditions and catalyst carrier may affect, to varying degrees, the size of the resulting silver particles. For carriers of general interest for the production of ethylene oxide, a distribution of silver particle sizes in the range of 0.05 to 2.0 µm is typically obtained.

Carrier selection

The catalyst carrier employed in practicing the invention may be selected from conventional, porous, refractory materials which are essentially inert to ethylene, ethylene oxide and other reactants and products at reaction conditions. These materials are generally labelled as "macroporous" and consist of porous materials having surface areas less than 10 m^2/g and preferably less than 1 m^2/g. The surface area is measured by the conventional B.E.T. method described by Brunauer, S., Emmet, P., and Teller, E., in J. Am. Chem. Soc. Vol. 60, pp 309—16, (1928). They typically possess pore volumes in the range of 0.15—0.8 cm/g. A more preferred range is 0.2—0.6 cm^3/g. Pore volumes may be measured by conventional mercury porosimetry or water absorption techniques. Median pore diameters for the above-described carriers range from 0.01 to 100 µm, a more preferred range being from 0.5 to 50 µm.

Preferably, the carrier should not contain undesirable ions which are exchangeable with the metal cations supplied to the catalyst, either in the preparation or use of the catalyst. If the carrier contains such ion, the ion should be removed by standard chemical techniques such as leaching.

The chemical composition of the carrier is not narrowly critical. Carriers may contain fused or bonded particles, of, for example, of alpha-alumina, silicon carbide, silicon dioxide, zirconias,

magnesia and various clays. In general, alpha-alumina based materials are preferred. These alpha-alumina based materials may be of very high purity, i.e., 98 + weight % alpha-alumina, the remaining components being silica, alkali metal oxides (e.g., sodium oxide) and trace amounts of other metal and non-metal impurities; or they may be of lower purity, i.e., about 80 weight % alpha-alumina, the balance being a mixture of silicon dioxide, various alkali oxides, alkaline earth oxides, iron oxide, and other metal and non-metal oxides. The lower purity carriers are formulated so as to be inert under catalyst preparation and reaction conditions. A wide variety of such carriers are commercially available. The carriers are preferably shaped, in the form of pellet, extruded particles, spheres or rings, for use in commercial reactors. The size of the carriers may vary from 1.6—12.7 mm. The carrier size and shape is chosen to be consistent with the type of reactor employed. In general, for fixed bed reactor applications, sizes in the range of 3.2—9.5 mm have been found to be most suitable in the typical tubular reactor used in commercial operations.

Ethylene oxide production

The silver catalysts of the invention are particularly suitable for use in the production of ethylene oxide by the vapor phase oxidation of ethylene with molecular oxygen. The products of the reactions are ethylene oxide and CO_2 as a consequence of the following two competing reactions:

(1) $C_2H4+1/2\ O_2 \rightarrow C_2H_4O$

(2) $C_2H_4+3\ O_2 \rightarrow 2CO_2+2H_2O$

Thee success in making reaction (1) more favored results in higher process efficiencies to ethylene oxide. The reaction conditions for carrying out the oxidation reaction are well-known and extensively described in the literature. This applies to reaction conditions, such as, temperature, pressure, residence time, concentration of reactants, diluents (e.g., nitrogen, methane and recycled CO_2), and inhibitors (e.g., ethylene dichloride). In addition, the desirability of recycling unreacted feed, or employing a single-pass system, or using successive reactions to increase ethylene conversion by employing reactors in series arrangement can be readily determined by those skilled in the art. The particular mode of operation selected will usually be dictated by process economics.

Generally, the process is carried out by continuously introducing a feed stream containing ethylene and oxygen to a catalyst-containing reactor at a temperature of from 200° to 300°C, and a pressure which may vary from 1 to 30 bar depending upon the mass velocity and productivity desired. Residence times in large-scale reactors are generally on the order of 1—5 seconds. Oxygen may be supplied to the reaction in an oxygen-containing stream, such as, air or as commercial oxygen. The resulting ethylene oxide is separated and recovered from the reaction products using conventional methods. Byproduct CO_2 is usually recycled in part with the unreacted ethylene to the reaction in commercial operations.

Catalyst testing

The catalysts cited in the Tables of the Examples below were all evaluated under standard test conditions using backmixed, bottom-agitated "Magnedrive" autoclaves as described in Figure 2 of the paper by J. M. Berty entitled "Reactor for Vapor Phase-Catalytic Studies", in Chemical Engineering Progress, Vol. 70, No. 5, pages 78—84, 1974. The reactor was operated at 1.0 mole % ethylene oxide in the outlet gas under the following standard inlet conditions:

Component	Mole %
Oxygen	6.0
Ethylene	8.0
Ethane	0.50
Carbon dioxide	6.5
Nitrogen	Balance of gas
Ethyl chloride	7.5 ppm

The pressure was maintained constant at 19 bar and the total outlet flow maintained at 634 l/h[1]. The outlet ethylene oxide concentration was maintained at 1.0 % by adjusting the reaction temperature. Thus, temperature and catalyst efficiency are obtained as the responses describing the catalyst performance.

A typical catalyst test procedure is comprised of the following steps:

1. 80 cm^3 of catalyst is charged to a backmixed autoclave. The volume of catalyst is measured in a 25.4 mm I.D. graduated cylinder after tapping the cylinder several times to thoroughly pack the catalyst. The weight of the catalyst is noted.

2. The backmixed autoclave is heated to about reaction temperature in a nitrogen flow of 566 l/h with the fan operating at 1500 rpm. The nitrogen flow is then discontinued and the above-described feed stream is introduced into the reactor. The total gas outlet flow is adjusted to 634 l/h. The temperature is adjusted over the next few hours so that the ethylene oxide concentration in the outlet gas is approximately 1.0 %.

3. The outlet oxide concentration is monitored over the next 4—6 days to make certain that the catalyst has reached its peak steady state performance. The temperature is periodically

[1] 0°C, 1 bar abs.

adjusted to achieve 1 % outlet oxide. The selectivity of the catalyst to ethylene oxide and the temperature are thus obtained.

The standard deviation of a single test result reporting catalyst efficiency in accordance with the procedure described above is 0.7 % efficiency units.

It should be noted that the above-described back mixed autoclave generates lower efficiencies than tubular reactors, hence, the efficiencies described herein are not directly comparable with those obtained in a tubular reactor. In addition, the catalyst particles tested in the following examples are shaped for use in commercial sized tubular reactors. Such particles are known to yield lower efficiencies than crushed catalyst or catalyst made on a crushed support, but they have a significant advantage for operation in a commercial reactor in that they do not create an undesirable pressure drop across the catalyst bed as would crushed catalyst or catalyst made on a crushed support.

Example 1

A catalyst containing 13 weight % Ag was prepared as hereinafter described on an alpha-alumina carrier "A" shaped as a ring having a diameter of 8 mm, a length of 8 mm and a 1.6 mm diameter hole. The carrier had the following chemical composition and physical properties.

Chemical composition of carrier "A"

Alpha-Alumina	98.6 wt. %
Silicon Dioxide	0.74 wt. %
Calcium Oxide	0.22 wt. %
Sodium Oxide	0.16 wt. %
Ferric Oxide	0.14 wt. %
Potassium Oxide	0.04 wt. %
Magnesium Oxide	0.03 wt. %

Physical properties of carrier "A"

Surface Area[1]	−0.3 m^2/g
Pore Volume[2] (or water absorption)	−0.50 cm^3/g
Packing Density[3]	0.70 g/ml
Median Pore Diameter	21 µm

Pore size distribution, % Total pore volume (% TPV)[4]

Pore size, µm	% TPV
0.1—1.0	1.5
1.0—10.0	38.5
10.0—30.0	20.0
30—100	32.0
>100	8.0

(1) Method of measurement described in "Adsorption, Surface Area and Porosity", S. J. Gregg and K. S. W. Sing, Academic Press (1967), pages 316—321.

(2) Method of Measurement as described in ASTM C20—46

(3) Calculated value based on conventional measurement of the weight of the carrier in a known volume container.

(4) Method of measurement described in "Application of Mercury Penetration to Materials Analysis", C. Orr Jr., Powder Technology, Vol. 3, pp. 177—123 (1970).

The carrier "A" was impregnated under vacuum as hereinafter described with a solution of silver salts which was prepared at a concentration such that the finished catalyst contained the desired amount of silver. The required concentration of silver in solution for the given carrier is calculated from the packing density (g/cm^3) and the pore volume of the carrier which are either known or readily determined. Assuming that all of the silver in the impregnating solution contained in the pores of carrier "A" is deposited upon the carrier, approximately 23.6 weight % silver in solution is needed to prepare a catalyst containing about 13 weight % silver.

Preparation of silver impregnating solution

774.9 g of ethylenediamine (high purity grade) was mixed with 1600 g of distilled water with continuous stirring in a 7 liter stainless steel beaker containing a three inch stirring bar, the vessel being mounted on a 152×152 mm magnetic stirrer-hot plate. The ingredients were added to the vessel in the order described with constant stirring. The resulting solution was cooled to 25°C and 812 g of oxalic acid dihydrate (reagent grade) was added in small portions, with continuous stirring, at a rate which maintained the temperature below 50°C. Silver oxide powder, 1423.5 g, (Handy and Harmon, 850 Third Avenue,

New York, New York 10022) was then added intermittently to the aqueous ethylenediamine oxalic acid solution while maintaining the temperature of the solution below 50°C. Finally, 283 g of monoethanolamine and 703 g of distilled water were added to bring the total volume of the impregnating solution to 4000 cm^3. The specific gravity of the resulting solution was about 1.385.

Catalyst preparation

A 2636 grams charge of carrier "A" was placed in a 5 liter, round bottomed vessel equipped with a side arm fitted with a stopcock connected to a 0,9 m long, 6,35 mm O.D. tubing for the introduction of the impregnating solution which was contained in the above-described 7 liter stainless steel beaker located adjacent to the vessel. The vessel containing the carrier was evacuated to approximately 2,66 mbar pressure for about 20 minutes after which the impregnating solution was slowly added to the carrier by opening the stopcock between the vessel and the beaker containing the impregnating solution until the carrier was completely immersed in solution. The vessel was then opened to the atmosphere to achieve atmospheric pressure, the carrier remaining immersed in the impregnating solution at ambient conditions for about one hour and thereafter drained of excess solution for about 30 minutes.

The impregnating carrier was removed from the vessel and heat treated as follows to effect reduction of the silver salt. The impregnated carrier was spread out in a single layer of pellets on a 66.7 mm wide endless stainless steel belt (spiral weave) and transported through a 50×50 mm heating zone for 2.5 minutes, the heating zone being maintained at 500°C by passing hot air upward through the belt and about the catalyst particles at the rate of 7,528 l/h. The hot air was generated by passing it through a 1,8 m long 50 mm I.D. stainless steel pipe which was externally heated by an electric furnace (Lindberg™ tubular furnace: 63.5 mm I.D., 0.9 m long heating zone) capable of delivering 5400 watts. The heated air in the pipe was discharged from a square 50×50 mm discharge port located immediately beneath the moving belt carrying the catalyst carrier. After being roasted in the heating zone, the silver impregnated catalyst was weighed, and based upon the weight gain of the carrier, was calculated to contain 13.1 weight % silver. The silver-containing catalyst is referred to as catalyst 1.

Addition of promoters

To demonstrate the effect which the solvent in the alkali metal impregnating solution has on the efficiency of the finished catalyst, two (2) catalysts of similar composition were prepared (1A—1B) using a different impregnating solution for each one, each solution containing a different solvent as described below. Catalysts containing 13.1 wt. % silver, 0.00906 wt. % cesium and 0.00268 wt. % potassium were prepared from the above described catalyst 1 by the sequential addition of cesium and potassium promoters in accordance with the following general procedure.

Each of the impregnating solutions used to prepare catalyst 1A and 1B, respectively, was prepared by adding (a) 5.825 ml of an aqueous cesium hydroxide solution containing 0.0566 g of cesium and (b) 4.456 ml of an aqueous potassium carbonate solution containing 0.0167 g of potassium, to a 250 ml graduated cylinder. To each of the graduated cylinders there was added one of solvents A or B, identified below, in an amount sufficient to provide 250 ml of total solution.

Solvents

A. Water

B. n-Butanol.

For the preparation of each catalyst a 100 g sample of catalyst 1 was placed in a 305 mm×38 mm I.D. glass cylindrical vessel equipped with a side arm fitted with a stopcock so as to allow the evacuation of the vessel using a vacuum pump. A 500 ml separatory funnel containing one of the impregnating solutions described above was inserted through a rubber stopper in the top of the vessel. The impregnating vessel containing catalyst 1 was evacuated to approximately 2,66 mbar pressure for about 20 minutes after which the impregnating solution was slowly added to the carrier by slowly opening the stopcock between the separatory funnel and the impregnating vessel until catalyst 1 was completely immersed. Following the addition of solution, the system was opened to the atmosphere, catalyst 1 remaining immersed in the impregnating solution at ambient conditions for about 30 minutes. The impregnated carrier was drained of excess solution and heat treated to effect deposition of alkali metal on the carrier in the same manner as described above with regard to the preparation of catalyst 1. The finished catalysts prepared from the impregnating solutions containing one of the solvents A and B are designated 1A and 1B, respectively.

Table I below summarizes the test results for catalysts 1A and 1B when used for the oxidation of ethylene in accordance with the procedure detailed earlier.

TABLE I

Catalyst	Selectivity, %	Temperature °C
1A	70.6	261.4
1B	76.3	260.5

Catalyst 1B, prepared with an impregnating solution containing n-butanol, provided a selectivity of 76.3 %, nearly a (6 %) improvement in efficiency relative to catalyst 1A which was prepared in accordance with the method of the prior art.

Example 2

A series of catalysts containing about 13.2 wt. % silver, 0.013 wt. % cesium and 0.0038 wt. % potassium was prepared on a different batch of the previously described alpha-alumina carrier A using a silver-first method of catalyst preparation similar to that described in Example 1.

Preparation of silver impregnating solution

The solution was prepared following the procedure described in Example 1, by mixing the following: 120 g distilled water, 100 g ethylene diamine (high purity grade) 100.4 g oxalic acid dihydrate (reagent grade), 176 g of silver oxide powder (Handy and Harmon), 37.2 g of monoethanolamine and 162 g distilled water. The final volume of solution was 500 ml.

Catalyst preparation

Using the apparatus and method described in Example 1, 505 grams of carrier "A" were impregnated with the above-described silver impregnating solution. Heat treatment to effect reduction of the silver salt was carried out as described in Example 1. Based on the weight gain of the carrier, the catalyst was calculated to contain 13.17 wt.% silver. This silver-containing catalyst is referred to as catalyst 2.

Addition of promoters

To demonstrate the effect which the solvent in the alkali metal impregnating solution has on the efficiency of the finished catalyst, (6) catalysts containing 13.17 wt.% silver, and nominally 0.0130 wt.% cesium and 0.0038 wt.% potassium were prepared by the deposition of cesium and potassium promoters on catalyst 2 as described in Example 1 using a different alkali metal impregnating solution containing one of the solvents described below for each catalyst:

A. 119 g Water

B. 6.8 g H_2O, 93 g Methanol

C. 6.8 g H_2O, 94 g Ethanol

D. 6.8 g H_2O, 103 g n-Butanol.

E. 6.8 g H_2O, 103 g n-Butoxypropanol

F. 6.8 g H_2O, 104 g Ethylene glycol monohexyl ether.

The various impregnating solutions were prepared by adding each of the above-described solvents to respective solutions containing (a) 4.14 ml cesium hydroxide solution containing 0.00974 g Cs per gram solution and (b) 2.65 ml K_2CO_3 solution containing 0.0045 g K per gram solution.

The resulting catalysts 2A—2F, corresponding to the impregnating solutions containing solvents A—F above, were prepared as described in Example 1.

Table II below summarizes the test results for catalysts 2A—2F.

TABLE II

Catalyst	Selectivity	Temperature °C
2A	70.9	270.5
2B	72.2	273.6
2C	72.8	261.0
2D	75.0	261.8
2E	74.4	258.7
2F	74.1	258.8

As noted from Table II, catalysts 2A, 2B and 2C, which were prepared with the use of impregnating solutions of the prior art, provided markedly lower selectivities in comparison with catalysts 2D, 2E and 2F, all of which were prepared by the process of the invention.

Example 3

For purposes of comparison, a series of catalysts containing 13 weight % silver, 0.0088 weight % cesium and 0.0026 weight % potassium was prepared on carrier "A" by a method of coincidental deposition of silver and promoters and by the method of the present invention.

Method of coincidental deposition

The impregnating solution containing silver and alkali metal promoters was prepared as follows:

50.75 g of ethylenediamine (high purity grade) was mixed with 100 ml of distilled water with continuous stirring in a 400 ml glass beaker containing a 38 mm stirring bar, the beaker being mounted on as magnetic stirrer-hot plate. 50.89 g of oxalic acid dihydrate was then added slowly to the resulting solution with continuous stirring. During the addition of the oxalic acid the solution temperature was between 40—50°C due to the reaction exotherm. Silver oxide powder 88.97 g (Handy and Harmon) was then added intermittently to the diamine-oxalic acid-water solution while maintaining the solution temperature below 50°C. Finally, 17.69 g of monoethanolamine, 5.825 g of an aqueous cesium hydroxide solution (0.0097 g Cs/g of solution or 0.0566 g Cs), and 4.456 g of an aqueous potassium carbonate solution (0.00375 g K/g of solution or 0.0167 g K) were added to the aqueous diamine-oxalic acid solution. Distilled water was then added to bring the total volume to 250 ml.

Catalyst preparation

125 g of carrier "A" was impregnated with the above-described solution following the procedure described in Example 1 and then heat treated as described in Example 1 to produce catalyst 3A

containing 13.1 weight % silver, 0.0088 % cesium and 0.0026 wt.% potassium. Catalysts 3B and 3C were prepared by an identical method except that they employed 1.5 and 2 times the amount of the above-described aqueous cesium and potassium solutions used in the preparation of catalyst 3A.

Silver-first method

Catalysts 3A', 3B' and 3C' were prepared by depositing cesium and potassium promoters upon catalyst 1 (described in Example 1) from butanol solution by the method of alkali metal addition set forth in Example 1. The promoter concentration for catalysts 3A', 3B' and 3C' was the same as used in the preparation of 3A, 3B and 3C, respectively.

Table III below provides a comparison of the test results achieved with the above-described catalysts.

TABLE III

Alkali level gew[1]×10⁵/kg catalyst	Catalyst	Deposition method	Selectivity %	Temp. °C
132	3A'	Silver-first	76.3	260.5
	3A	Coincidental	76.6	257.5
200	3B'	Silver-first	76.0	257.0
	3B	Coincidental	76.1	271.0
260	3C'	Silver-first	76.0	262.5
	3C	Coincidental	73.0	292.0

[1] "gew" refers to gram equivalent weights.

The data in Table III demonstrates the fact that optimum selectivities were provided over a broad range of alkali metal concentration with catalysts 3A', 3B' and 3C', prepared by the silver-first method. In contrast thereto, catalyst 3C, prepared by a method of the prior art, provided a selectivity of 73% which is at least 3% below the optimum achieved with catalysts 3A and 3B, thus demonstrating the narrow criticality of promoter concentration to achieve optimum efficiency when using catalysts prepared by a coincidental method of silver and promoter addition.

Claim

A process for preparing a supported silver catalyst for the production of ethylene oxide by the vapor phase oxidation of ethylene with an oxygen-containing gas comprising:

(a) impregnating a porous catalyst support with a solution comprising a solvent or a solubilizing agent, and silver salt;

(b) heat treating the impregnated support to convert at least a fraction of the silver salt to silver metal and effect deposition of silver on the surface of said support;

(c) impregnating the support treated in step (b) with a compound of at least one alkali metal promoter dissolved in an organic solvent in which water is soluble at ambient temperature in an amount no greater than about 50 wt.% based on the weight of water-solvent solution; and

(d) heat treating the impregnated support produced in step (c) to effect deposition of said promoter on the surface of said support, characterized in that the amount of alkali metal deposited on the catalyst support is at least 10 wt.% greater than that amount of like alkali metal which provides the maximum enhancement of efficiency when used in a coincidental method of preparation with the same amount of silver and the same catalyst support.

Patentanspruch

Verfahren zur Herstellung eines Silber-Trägerkatalysators für die Ethylenoxid-Herstellung durch Dampfphasenoxidation von Ethylen mit einem sauerstoffhaltigen Gas, indem

(a) ein poröser Katalysatorträger mit einer Lösung aus einem Lösungsmittel oder solubilisierenden Mittel und Silbersalz imprägniert wird;

(b) der imprägnierte Katalysatorträger erhitzt wird, um zumindest einen Teil des Silbersalzes in Silbermetall zu überführen und die Abscheidung des Silbers auf der Oberfläche des Katalysatorträgers zu bewirken;

(c) des aus der Stufe (b) erhaltene Katalysatorträger mit einer Verbindung zumindest eines Alkalimetall-Promotors, gelöst in einem organischen Lösungsmittel, in welchem Wasser bei Raumptemperatur in einer Menge von nicht mehr als etwa 50 Gew.-% bezogen auf das Gewicht der Wasser/Lösungsmittel-Lösung löslich ist, imprägniert wird und

(d) das Produkt aus der Stufe (c) erhitzt wird zur

containing 13.1 weight % silver, 0.0088 % cesium and 0.0026 wt.% potassium. Catalysts 3B and 3C were prepared by an identical method except that they employed 1.5 and 2 times the amount of the above-described aqueous cesium and potassium solutions used in the preparation of catalyst 3A.

Silver-first method

Catalysts 3A', 3B' and 3C' were prepared by depositing cesium and potassium promoters upon catalyst 1 (described in Example 1) from butanol solution by the method of alkali metal addition set forth in Example 1. The promoter concentration for catalysts 3A', 3B' and 3C' was the same as used in the preparation of 3A, 3B and 3C, respectively.

Table III below provides a comparison of the test results achieved with the above-described catalysts.

TABLE III

Alkali level gew[(1)]×10^5/kg catalyst	Catalyst	Deposition method	Selectivity %	Temp. °C
132	3A'	Silver-first	76.3	260.5
	3A	Coincidental	76.6	257.5
200	3B'	Silver-first	76.0	257.0
	3B	Coincidental	76.1	271.0
260	3C'	Silver-first	76.0	262.5
	3C	Coincidental	73.0	292.0

[(1)] "gew" refers to gram equivalent weights.

The data in Table III demonstrates the fact that optimum selectivities were provided over a broad range of alkali metal concentration with catalysts 3A', 3B' and 3C', prepared by the silver-first method. In contrast thereto, catalyst 3C, prepared by a method of the prior art, provided a selectivity of 73% which is at least 3% below the optimum achieved with catalysts 3A and 3B, thus demonstrating the narrow criticality of promoter concentration to achieve optimum efficiency when using catalysts prepared by a coincidental method of silver and promoter addition.

Claim

A process for preparing a supported silver catalyst for the production of ethylene oxide by the vapor phase oxidation of ethylene with an oxygen-containing gas comprising:

(a) impregnating a porous catalyst support with a solution comprising a solvent or a solubilizing agent, and silver salt;

(b) heat treating the impregnated support to convert at least a fraction of the silver salt to silver metal and effect deposition of silver on the surface of said support;

(c) impregnating the support treated in step (b) with a compound of at least one alkali metal promoter dissolved in an organic solvent in which water is soluble at ambient temperature in an amount no greater than about 50 wt.% based on the weight of water-solvent solution; and

(d) heat treating the impregnated support produced in step (c) to effect deposition of said promoter on the surface of said support, characterized in that the amount of alkali metal deposited on the catalyst support is at least 10 wt.% greater than that amount of like alkali metal which provides the maximum enhancement of efficiency when used in a coincidental method of preparation with the same amount of silver and the same catalyst support.

Patentanspruch

Verfahren zur Herstellung eines Silber-Trägerkatalysators für die Ethylenoxid-Herstellung durch Dampfphasenoxidation von Ethylen mit einem sauerstoffhaltigen Gas, indem

(a) ein poröser Katalysatorträger mit einer Lösung aus einem Lösungsmittel oder solubilisierenden Mittel und Silbersalz imprägniert wird;

(b) der imprägnierte Katalysatorträger erhitzt wird, um zumindest einen Teil des Silbersalzes in Silbermetall zu überführen und die Abscheidung des Silbers auf der Oberfläche des Katalysatorträgers zu bewirken;

(c) des aus der Stufe (b) erhaltene Katalysatorträger mit einer Verbindung zumindest eines Alkalimetall-Promotors, gelöst in einem organischen Lösungsmittel, in welchem Wasser bei Raumptemperatur in einer Menge von nicht mehr als etwa 50 Gew.-% bezogen auf das Gewicht der Wasser/Lösungsmittel-Lösung löslich ist, imprägniert wird und

(d) das Produkt aus der Stufe (c) erhitzt wird zur

* C L M S *

Abscheidung des Promotors auf der Oberfläche des Katalysatorträgers, dadurch gekennzeichnet, daß die Menge an auf dem Katalysatorträger abzuscheidenden Alkalimetals um zumindest 10 Gew.-% größer ist als die Menge des gleichen Alkalimetalls, welches maximale Verbesserung der Wirksamkeit bewirkt, wenn der Trägerkatalysator mit der gleichen Menge an Silber unter Verwendung des gleichen Katalysatorträgers nach der Methode der gleichzeitigen Abscheidung (von Silber und Promotor) hergestellt wird.

Revendication

Procédé de préparation d'un catalyseur à l'argent fixé sur un support pour la production d'oxyde d'éthylène par l'oxydation en phase vapeur de l'éthylène avec un gaz contenant de l'oxygène, qui consiste:

(a) à imprégner un support poreux de catalyseur avec une solution comprenant un solvant ou un agent solubilisant, et un sel d'argent;

(b) à traiter à la chaleur le support imprégné pour convertir au moins une fraction du sel d'argent en argent métallique et pour effectuer le dépôt d'argent sur la surface dudit support;

(c) à imprégner le support traité dans l'étape (b) d'un composé d'au moins un métal alcalon promoteur dissous dans un solvent organique dans lequel l'eau est soluble à la température ambiante, en une quantité n'excédant pas environ 50 % en poids sur la base du poids de la solution dans le mélange eau-solvant; et

(d) à traiter par la chaleur le support imprégné produit dans l'étape (c) pour effectuer le dépôt dudit promoteur à la surface dudit support, caractérisé en ce que la quantité de métal alcalin déposée sur le support du catalyseur est supérieure d'au moins 10 % en poids à la quantité du même métal alcalin qui favorise au maximum le rendement lorsqu'on l'utilise dans un procédé de préparation coïncidant avec la même quantité d'argent et le même support de catalyseur.

* C L M S *