METHOD OF MAKING A MANGANESE CONTAINING SUPPORTED SILVER CATALYST INTERMEDIATE

FIELD OF INVENTION

[0001] The invention relates to methods of making a manganese-containing supported silver catalyst.

BACKGROUND

[0002] Ethylene oxide can be commercially produced by the direct epoxidation of ethylene over a supported silver-containing catalyst at elevated temperature. As the catalyst is an important element in the direct oxidation of ethylene to ethylene oxide, much effort has been expended to improve catalyst stability, efficiency, selectivity, and/or other aspects of the performance of the catalyst in producing ethylene oxide.

[0003] Using suitable promoters is an effective and proven way to enhance the performance of the catalyst in the production of ethylene oxide, and is well known to those skilled in the art. There are at least two types of promoters--solid promoters and gaseous promoters. A solid promoter can be incorporated into the catalyst prior to its use, either as a part of the carrier (i.e., support) or as a part of the silver component applied thereto. Typically, the silver-containing supported catalyst is prepared by impregnating the support in an impregnation solution containing silver and optionally one or more promoters.

[0004] U.S. Pat. No. 5,504,053 describes a silver-containing, supported catalyst containing a stability, efficiency and/or activity enhancing amount of a manganese-containing component. The manganese is present in the silver-containing supported catalyst in an amount of at least 20 parts per million weight (ppmw), or at least 60 ppmw, preferably 70 to 1000 ppmw, more preferably 80 to 500 ppmw, ppmw calculated as the weight of manganese based on the total weight of the catalyst.

[0005] WO2005/023417A1, WO2008/054564A1 and US2007/0111886 describe adding diammonium ethylenediaminetetraacetic acid with the manganese-containing component in order to stabilize the manganese-containing component in an impregnation solution.

[0006] In US2007/0032670, promoters and solubilizers are added to an impregnating solution which includes neat potassium nitrate, manganese EDTA ($K_2MnEDTA$) solution and diammonium EDTA solution. One equivalent of diammonium EDTA is added with the manganese promoter in order to increase the stability of the manganese-containing ion in the impregnation solution.

[0007] EP 480,537A1 discloses preparing a solid manganese complex of tetrahydrate of ethylene diamine tetraacetatomanganic II-acid ($H_2MnEDTA$), which can be then introduced into the impregnation solution. EP 480,537A1 discloses that the metal-containing promoter(s), including manganese may be present as complexes in the impregnating solution containing silver, prior to being associated with the carrier. Such complexes may conveniently be derived by including one or more complexing agents effective to form a complex with at least one metal species (a) in the silver-containing impregnating solution or (b) in a solution containing a metal-containing promoter precursor in an amount effective to enhance the solubility and/or solubility stability of the metal-containing promoter in the impregnating solution or solution precursor. The term "solubility stability" is defined as the measure of the ability of a metal-containing promoter to remain in solution over time: the longer the time in solution, the more solubility stable the metal-containing promoter is. The enhancement in solubility and/or solubility stability of the metal-containing promoter solutions, as described in EP 480,537A1, refers to solutions *not* containing metal-containing promoters in the complexed form.

[0008] Typically a stoichiometric amount of manganese-containing component corresponding to the desired target level is provided in an impregnation solution for impregnating a support. However, many times the impregnated support or the catalyst may not have the desired target level of manganese or they exhibit variability in the amount of manganese. If the resultant catalyst exhibits variability of the order of 10% or more from the desired target level, the performance of the catalyst is adversely affected. Therefore a much simplified, commercially viable, and yet reliable way of providing manganese component in supported silver catalyst is desirable.

SUMMARY

[0008a] In one aspect, there is provided a method of making manganese-containing supported sliver catalyst intermediate comprising the steps of:

(i) preparing a first solution comprising a manganese component and a complexing agent, wherein a pH of the first solution at any time during or after step (i) is less than or equal to 7;

(ii) combining the first solution with a second solution comprising silver to form an impregnation solution; and

(iii) impregnating a support with at least a portion of the impregnation solution to form the catalyst intermediate, wherein the impregnation solution has a pH of greater than 7.

[0008b] In another aspect, there is provided a vapor phase process for the continuous production of ethylene oxide comprising contacting in a vapor phase ethylene with oxygen or an oxygen-containing gas in the presence of a manganese-containing supported silver catalyst prepared from manganese-containing supported silver catalyst intermediate as defined above.

BRIEF DESCRIPTION

[0009] According to embodiments of the present invention, variability in the amount of manganese on the manganese-containing supported silver catalyst can be lowered by following the inventive method of making a manganese-containing supported silver catalyst intermediate. The method includes the step (i) of preparing a first solution comprising a manganese component and a complexing agent. The pH of the first solution at any time during or after step (i) is less than or equal to 7. At step (ii), the first solution is combined with a second solution comprising silver to form an impregnation solution. At step (iii), a support is subsequently impregnated with at least a portion of the impregnation solution to form the catalyst intermediate. The impregnation solution has a pH of greater than 7. By decreasing the variability in the amount of manganese on the catalyst, the catalyst performance such as efficiency, activity, aging and/or other aspects of catalyst performance is improved.

DRAWINGS

[0010] FIG. 1 is a plot of variability in the amount of manganese in an impregnation solution against impregnation solution batches prepared using a prior art method and is expressed as the percentage variation in manganese content from the desired target levels;

[0011] FIG. 2 is a plot of variability in the amount of manganese in an impregnation solution against impregnation solution batches prepared using embodiments of the present invention and is expressed as the percentage variation in manganese content from the desired target levels;

[0012] FIG. 3 is a comparison of performance of catalyst batches prepared using a prior art method example 4* and an inventive method example 3; and

[0013] FIG. 4 is a comparison of variation in the amount of manganese in manganese-containing silver-amine-oxalate solution batches prepared using a prior art method example 5* and an inventive method example 4.

DETAILED DESCRIPTION

[0014] Supported silver catalysts containing manganese promoters show enhanced stability, activity and/or selectivity upon ethylene epoxidation to produce ethylene oxide,

when compared to silver catalysts not having manganese promoters in them. We have surprisingly found that when a first solution comprising a manganese component and a complexing agent is combined with a second solution comprising silver to form an impregnation solution, a catalyst obtained by impregnation of this impregnation solution shows better performance characteristics than compared to a catalyst obtained using an impregnation solution prepared using a method which does not include preparing the first solution comprising the manganese component and the complexing agent. In one embodiment, the inventive method provides lower variability in the amount of manganese on the manganese-containing supported silver catalyst compared to a prior art method which does not include preparing the first solution.

[0015] In a typical epoxidation reaction, an alkylene, such as ethylene, reacts with oxygen or an oxygen-containing gas in presence of a supported silver catalyst in a reactor to form an alkylene oxide such as ethylene oxide. The epoxidation reaction can be characterized in terms of "activity", "productivity" and/or "selectivity" of the epoxidation reaction.

[0016] The activity of the epoxidation reaction can be quantified in a number of ways, one being the mole percent of alkylene oxide contained in an outlet stream of the reactor relative to that in the inlet stream (the mole percent of alkylene oxide in the inlet stream typically, but not necessarily, approaches zero percent) while the reactor temperature is maintained substantially constant; and another being the temperature required to maintain a given rate of alkylene oxide production. In many instances, activity is measured over a period of time in terms of the mole percent of alkylene oxide produced at a specified constant temperature. The activity can be defined as the reaction rate towards the alkylene oxide formation per unit of catalyst volume in the reactor. Alternatively, activity can be measured as a function of the temperature required to sustain production of a specified constant mole percent of alkylene oxide, such as ethylene oxide, given other conditions such as pressure and total moles in the feed.

[0017] The productivity of the reaction is a measure of the reaction rate normalized by the amount of catalyst. In many instances, productivity can be expressed as moles or kilograms of alkylene oxide produced per hour per volume of the catalyst measured as the

packed volume of the reactor. In certain instances, the productivity can be expressed as mole percent of alkylene oxide in the outlet stream of the reactor at specified process conditions such as a space velocity.

[0018] The "selectivity" of the epoxidation reaction, which is synonymous with "efficiency," refers to the relative amount (as a fraction or in percent) of converted or reacted olefin that forms a particular product. For example, the "efficiency to alkylene oxide" refers to the percentage on a molar basis of converted or reacted alkylene that forms alkylene oxide.

[0019] "Deactivation" or "aging", as used herein, refers to a permanent loss of activity and/or efficiency that is a decrease in activity and/or efficiency that cannot be recovered. Lower rates of deactivation are generally desirable.

[0020] As used herein, the term "compound" refers to the combination of a particular element with one or more different elements by surface and/or chemical bonding, such as ionic and/or covalent and/or coordinate bonding. The term "ionic" or "ion" refers to an electrically charged chemical moiety; "cationic" or "cation" being positive and "anionic" or "anion" being negative. The term "oxyanionic" or "oxyanion" refers to a negatively charged moiety containing at least one oxygen atom in combination with another element. An oxyanion is thus an oxygen-containing anion. It is understood that ions do not exist in vacuo, but are found in combination with charge-balancing counter ions when added as a compound to the catalyst.

[0021] As used herein, the term "solution" refers to clear solutions and also includes suspensions and colloidal solutions.

[0022] The term "support", as used herein, refers to a support or a carrier that is commonly used for preparing epoxidation catalysts. An "impregnated support" refers to a support that has been impregnated with silver or upon which silver has been deposited. The term "catalyst intermediate", as used herein, refers to a support which has been impregnated or deposited with at least manganese and silver, according to embodiments of the present invention by following steps (i) to (iii) of the method of making a manganese-containing

supported silver catalyst intermediate. The "catalyst intermediate" is otherwise also referred to as "manganese-containing supported silver catalyst intermediate".

[0023] As used herein, the term "catalyst" refers to the finished catalyst obtained after further processing of the "catalyst intermediate". The "catalyst" is also otherwise termed as the "manganese-containing supported silver catalyst" prepared according to embodiments of the present invention and that which can be directly charged in the reactor for use in commercial ethylene oxide production.

[0024] As used herein, the term "variability" is defined as the variation or the deviation in the amount of manganese deposited or present on a catalyst intermediate, or a finished catalyst or in an impregnation solution from the desired target level. In one embodiment, variability is expressed as the percentage variation in the amount of manganese from the desired target level.

[0025] As used herein, the term the "pH of the first solution at any time during or after step (i)" means the pH of the first solution at least one point in time after the combination of the manganese component and the complexing agent. It does not mean "at any and all times" subsequent to the combination of the manganese component and the complexing agent.

[0026] The manganese component (manganese promoter) can be provided in various forms, e.g., as a covalent compound such as manganese dioxide, as a cation or as an anion such as a manganate anion. Manganese components present in the first solution, can include, but are not limited to, manganese acetate, manganese ammonium sulfate, manganese citrate, manganese dithionate, manganese oxalate, manganous nitrate, manganous sulfate, and manganate anion, e.g., permanganate anion, manganate anion, and the like. Mixtures of manganese components may also be used. The manganese species that provides enhanced activity and/or stability is not certain and may be the component added or that generated either during catalyst preparation or during use as a catalyst. Although the manganese species that provide the beneficial properties to the catalysts are not known with specificity, generally acceptable results are obtained when the manganese

component is added to the first solution in the form of permanganate ion $(MnO_4)^{1-}$ and/or as manganous cation, e.g., as in $Mn(NO_3)_2$. Moreover, different added manganese components may also have different optimum concentrations to achieve the results. Often, the manganese in the manganese component has an oxidation state of +2, +3, +4 and/or +7, preferably +2, +3, and/or +7.

[0027] The desired amount of the manganese promoter on the catalyst intermediate or the catalyst may be decided based upon the silver content of the catalyst intermediate or the catalyst, the amounts and types of other promoters present and the chemical and physical properties of the support. In one embodiment, the manganese is present on the catalyst intermediate or the catalyst in an amount of at least 20 ppmw, more preferably at least 60 ppmw calculated as the weight of manganese. In some embodiments, the amount of manganese on the catalyst intermediate or the catalyst falls within the range of 70 ppmw to 1000 ppmw, preferably 80 ppmw to 500 ppmw calculated as the weight of manganese. If too much manganese is present, the catalyst performance, e.g., stability, efficiency and/or activity, may suffer. If too little manganese is present, it is also possible that the performance of the catalyst will suffer. In determining desired amounts of manganese, a traverse of manganese concentrations in the catalyst composition can be effected with the catalysts being evaluated for performance. In some instances, it may be desirable to vary the amounts of other components, e. g., silver and other promoters, to achieve beneficial combinations of effects and optimal catalyst performance.

[0028] Examples of complexing agents in the first solution include ethylenediaminetetraacetic acid (EDTA); N, N'-ethylenediaminediacetic acid; N-hydroxyethylethylenediaminetriacetic acid; diethylenetriaminepentaacetic acid (DTPA); nitrilotriacetic acid; 1,2-cyclohexylenedinitrilotetraacetic acid (CDTA); N-hydroxyethyliminodiacetic acid; N-dihydroxyethylglycine and any derivatives thereof. In one embodiment, the complexing agent is EDTA.

[0029] The amount of complexing agent employed varies widely, for example, depending on the specific complexing agent and specific manganese component to be complexed, as well as on the amount of manganese component to be complexed. Preferably, the amount of complexing agent is at least 50%, more preferably at least 100%,

of that needed to form complexes with the manganese component in the first solution. Excesses of complexing agent over that needed to form the desired complexes may be employed, for example, so that the complexes can be maintained over a relatively long period of time. For example, the complexing agent may be included in an amount of at least 150% or at least 200% or at least 400% or more of that needed to form the desired complexes.

[0030] At step (i), the manganese component solution and the complexing agent solution can be combined simultaneously, or sequentially, to form the first solution. In one embodiment, a complexing agent solution is combined with an aqueous solution containing manganese component. In another embodiment, the manganese component is in solid form and can be added to the complexing agent solution. Additionally, heating may be required for dissolving the complexing agent, the manganese component or both. The pH of the first solution at any time during or after the preparation of the first solution is less than or equal to 7. The pH of the first solution can be measured using conventional pH meters or using pH papers. In one embodiment, the pH of the first solution is less than or equal to 7 after combining the manganese component and the complexing agent or during the preparation of the first solution. In another embodiment, following the preparation of the first solution it is stored at a pH of less than or equal to 7. It is believed, without being bound to any theory, that the manganese component may exhibit enhanced solubility in the first solution comprising the complexing agent at pH of less than or equal to 7. As is known to those of skill in the art, the pH of the first solution can be adjusted if necessary to a pH of less than or equal to 7 through the use of an acid. Examples of suitable acids include acetic acid and formic acid and other acids that do not leave a residue upon subsequent roasting of the impregnated support. In yet other embodiments, the pH of the first solution prepared according to the invention may subsequently be increased above 7 prior to step (ii), through addition of a basic compound, such as an amine, for example, monoethanolamine.

[0031] The first solution may additionally include one or more other promoters other than manganese. In one embodiment, the one or more other promoters does not comprise potassium.

[0032] At step (ii), a second solution comprising silver is combined with the first solution to form an impregnation solution. In one embodiment, the pH of the first solution at the time of combining with the second solution is less than or equal to 7. In another embodiment, the pH of the first solution at the time of combining with the second solution is greater than 7. The second solution comprising silver includes a silver compound in a solvent or a solubilizing agent such as the silver solutions disclosed in the art. The particular silver compound employed may be chosen, for example, from among silver complexes, silver nitrate, silver oxide or silver carboxylates, such as silver acetate, oxalate, citrate, phthalate, lactate, propionate, butyrate and higher fatty acid salts. In one embodiment, the silver oxide compound complexed with amines is the preferred form of silver in the second solution.

[0033] A wide variety of solvents or solubilizing agents may be employed to solubilize silver compound to the desired concentration in the second solution. Among those disclosed as being suitable for this purpose are lactic acid (U.S. Pat. Nos. 2,477,436 and 3,501,417); ammonia (U.S. Pat. No. 2,463,228); alcohols, such as ethylene glycol (U.S. Pat. Nos. 2,825,701 and 3,563,914); and amines and aqueous mixtures of amines (U.S. Pat. Nos. 2,459,896; 3,563,914; 3,215,750; 3,702,259; 4,097,414; 4,374,260 and 4,321,206). In a preferred embodiment of the invention, the solubilizing agent is an amine/oxalate combination or aqueous mixtures of amines and oxalate and the resulting impregnation solution has a pH that is greater than 7.

[0034] Silver oxide (Ag_2O) can be dissolved in a solution of oxalic acid and ethylenediamine to an extent of approximately 30% by weight of silver. Vacuum impregnation of such a solution onto an alpha alumina support of approximately 0.7 cc/g porosity results in a catalyst containing approximately 25% by weight of silver based on the entire weight of the catalyst.

[0035] In some embodiments, the catalyst intermediate or catalyst contain a high concentration of silver, generally at least 25 or 30 percent by weight, based on the total weight of the catalyst, more generally in the range of from 25 or 30 percent to 60 percent by weight. Accordingly, in order to obtain catalysts having a silver loading of greater than 25 or 30 weight %, and more, it may be necessary to subject the support or the catalyst

intermediate to at least one or more sequential impregnations of silver, with or without promoters, until the desired amount of silver is deposited on the support, as will be described in detail.

[0036] In one embodiment, the silver particle size on manganese-containing silver catalyst is in the range of 10 angstroms to 10,000 angstroms in diameter. A preferred silver particle size ranges from greater than 100 angstroms to less than 5,000 angstroms in diameter. It is desirable that the silver be relatively uniformly dispersed within, throughout, and/or on the manganese-containing silver catalyst.

[0037] The second solution may additionally include one or more promoters other than manganese, and these may also be added subsequent to the combining of the first and second solutions, before impregnation of the support. These promoters are provided in a promoting amount. As used herein, the term "promoting amount" refers to an amount of a component of the catalysts that works effectively to provide an improvement in one or more of the catalytic properties of that catalyst when compared to a catalyst not containing said component. Examples of catalytic properties include, inter alia, operability (resistance to run-away), efficiency, activity, conversion, stability and yield. It is understood by one skilled in the art that one or more of the individual catalytic properties may be enhanced by the "promoting amount" while other catalytic properties may or may not be enhanced or may even be diminished. It is further understood that different catalytic properties may be enhanced at different operating conditions. For example, a catalyst having enhanced efficiency at one set of operating conditions may be operated at a different set of conditions wherein the improvement shows up in the activity rather than the efficiency.

[0038] The promoting effect provided by the promoters can be affected by a number of variables such as for example, operating conditions, catalyst preparative techniques, surface area and pore structure and surface chemical properties of the support, the silver and other promoter content of the catalyst, the presence of other cations and anions present on the catalyst. The presence of other activators, stabilizers, promoters, enhancers or other catalyst improvers can also affect the promoting effects. During the reaction to make ethylene oxide, the specific form of the promoter on the catalyst may be unknown, and the promoter may be present without the counterion added during the preparation of the catalyst. For

example, a catalyst made with cesium hydroxide may be analyzed to contain cesium but not hydroxide in the finished catalyst. Likewise, compounds such as alkali metal oxide, for example cesium oxide, or transition metal oxides, for example MoO_3, while not being ionic, may convert to ionic compounds during catalyst preparation or in use. For the sake of ease of understanding, the promoters will be referred to in terms of cations and anions regardless of their form in the catalyst under operating conditions.

[0039] Examples of solid promoter compositions and their characteristics as well as methods for incorporating the promoters as part of the catalyst are described in U.S. Patent No. 5,187,140, particularly at columns 11 through 15; U.S. Patent Nos. 6,511,938, 5,102,848, 4,916,243, 4,908,343, 5,059,481 4,761,394, 4,766,105, 4,808,738, 4,820,675 and 4,833,261.

[0040] Examples of well-known promoters other than manganese for catalysts used to produce ethylene oxide include halides and/or oxyanions of elements other than oxygen having an atomic number of 5 to 83 and being from the groups 3b to 7b, and 3a to 7a, of the Periodic Table. One or more of the oxyanions of nitrogen, sulfur, tantalum, molybdenum, tungsten and rhenium may be preferred for some applications. In some embodiments, the promoters include compounds of rhenium, rubidium, cesium, sulfur, molybdenum, and tungsten. In one embodiment, the one or more promoters is selected from a group consisting of Group IA metals, Group IIA metals, phosphorus, boron, sulfur, molybdenum, tungsten, chromium, titanium, hafnium, zirconium, vanadium, thallium, thorium, tantalum, niobium, gallium, germanium and any mixtures thereof, and in another embodiment, excluding potassium. In yet another embodiment, the one or more promoters comprises Group IA metals selected from cesium, lithium, sodium and any mixtures thereof.

[0041] The types of anion promoters other than manganates suitable for use in the catalysts of this invention comprise, by way of example only, oxyanions such as sulfate, SO_4^{-2}, phosphates, for example, PO_4^{-3}, titanates, e g., TiO_3^{-2}, tantalates, for example, $Ta_2O_6^{-2}$, molybdates, for example, MoO_4^{-2}, vanadates, for example, $V_2O_4^{-2}$, chromates, for example, CrO_4^{-2}, zirconates, for example, ZrO_3^{-2}, polyphosphates, nitrates, chlorates, bromates, borates, silicates, carbonates, tungstates, thiosulfates, cerates and the like. The halides may also be present, including fluoride, chloride, bromide and iodide.

[0042] It is well recognized that many anions have complex chemistries and may exist in one or more forms, for example, orthovanadate and metavanadate; and the various molybdate oxyanions such as MoO_4^{-2}, and $Mo_7O_{24}^{-6}$ and $Mo_2O_7^{-2}$. The oxyanions may also include mixed metal-containing oxyanions including polyoxyanion structures. For instance, manganese and molybdenum can form a mixed metal oxyanion. Similarly, other metals, whether provided in anionic, cationic, elemental or covalent form may enter into anionic structures.

[0043] While an oxyanion, or a precursor to an oxyanion, may be used in solutions for impregnating the support, it is possible that during the conditions of preparation of the catalyst and/or during use, the particular oxyanion or precursor initially present may be converted to another form. Indeed, the element may be converted to a cationic or covalent form. In many instances, analytical techniques may not be sufficient to precisely identify the species present. The invention is not intended to be limited by the exact species that may ultimately exist on the catalyst during use.

[0044] The amount of anion promoter other than manganates may vary widely, for example, from 0.0005 weight percent to 2 weight percent, preferably from 0.001 weight percent to 0.5 weight percent based on the total weight of the catalyst.

[0045] The catalyst prepared using embodiments of the present invention may comprise a rhenium promoter. The rhenium promoter can be provided in various forms, for example, as the metal, as a covalent compound, as a cation or as an anion. Rhenium promoted supported silver containing catalysts are known from U.S. Pat. No. 4,761,394 and U.S. Pat. No. 4,766,105. The catalysts comprise silver, rhenium or compound thereof, and in some embodiments, a second promoter such as a further metal or compound thereof and optionally a third promoter such as one or more of sulfur, phosphorus, boron, and compounds thereof, on the support material.

[0046] The rhenium species that provides the enhanced efficiency and/or activity is not certain and may be the component added or that generated either during preparation of the catalyst or during use as a catalyst. Examples of rhenium compounds include the rhenium salts such as rhenium halides, the rhenium oxyhalides, the rhenates, the perrhenates, the oxides and the acids of rhenium. However, the alkali metal perrhenates, ammonium

perrhenate, alkaline earth metal perrhenates, silver perrhenates, other perrhenates and rhenium heptoxide can also be suitably utilized. Rhenium heptoxide, Re_2O_7, when dissolved in water, hydrolyzes to perrhenic acid, $HReO_4$, or hydrogen perrhenate. Thus, for purposes of this specification, rhenium heptoxide can be considered to be a perrhenate, that is, ReO_4. Similar chemistries can be exhibited by other metals such as molybdenum and tungsten.

[0047] When used, the rhenium component is often provided in an amount of at least 1 ppmw, say, at least 5 ppmw, for example, 10 ppmw to 2000 ppmw, often between 20 ppmw and 1000 ppmw, calculated as the weight of rhenium based on the total weight of the catalyst.

[0048] In some instances, the one or more promoters other than manganese comprise a mixture of cations, for example cesium and at least one other alkali metal to obtain a synergistic efficiency enhancement, as disclosed in U.S. No. 4,916,243. In some embodiments of the present invention, potassium is not one of these alkali metal promoters.

[0049] The concentration of the alkali metal promoters in the finished catalyst is not narrow and may vary over a wide range. The optimum alkali metal promoter concentration for a particular catalyst will be dependent upon performance characteristics, such as catalyst efficiency, rate of catalyst aging and reaction temperature.

[0050] The concentration of alkali metal (based on the weight of cation, for example cesium) in the finished catalyst may vary from 0.0005 to 1.0 wt. %, preferably from 0.005 to 0.5 wt. %. The preferred amount of cation promoter deposited on or present on the surface of the support or catalyst generally lies between 10 ppm and 4000 ppm, preferably 15 ppm and 3000 ppm, and more preferably between 20 ppm and 2500 ppm by weight of cation calculated on the total support material. Amounts between 50 ppm and 2000 ppm are frequently most preferable. When the alkali metal cesium is used in mixture with other cations, the ratio of cesium to any other alkali metal and alkaline earth metal salt(s), if used, to achieve desired performance is not narrow and may vary over a wide range. The ratio of cesium to the other cation promoters may vary from 0.0001:1 to 10,000:1, preferably from 0.001:1 to 1,000:1.

[0051] At step (iii), a support or impregnated support is impregnated with at least a portion of the impregnation solution to form the catalyst intermediate. According to preferred embodiments of the present invention, the impregnation solution used for impregnating the support has a pH of greater than 7. Suitable support materials of the catalyst intermediate can include porous refractory carrier or materials that are relatively inert in the presence of the reaction mixture introduced for epoxidation and the product epoxide, and are able to withstand preparation conditions when converted into catalyst. For example, the support can comprise alpha-alumina, silicon carbide, silicon dioxide, zirconia, magnesia, pumice, zeolites, charcoal, various clays, alkaline earth metal carbonates, such as calcium carbonate and mixtures thereof. In one embodiment, the support comprises alpha-alumina.

[0052] There are many well-known methods of preparing supports suitable for use in alkylene oxide catalysts. Some of such methods are described in, for example, U.S. Patent Nos. 4,379,134, 4,806,518, 5,063,195, 5,384,302, 6,831,037 and the like. For example, an alpha-alumina support of at least 95% purity can be prepared by compounding (mixing) the raw materials, extrusion, drying and a high temperature calcination. In this case, the starting raw materials usually include one or more alpha-alumina powder(s) with different properties, a clay-type material which may be added as binder to provide physical strength, and a burnout material (usually an organic compound) used in the mix to provide desired porosity and/or pore size distribution after its removal during the calcination step. The levels of impurities in the finished support are determined by the purity of the raw materials used, and their degree of volatilization during the calcination step. Common impurities may include silica, alkali and alkaline earth metal oxides and trace amounts of metal and/or non-metal-containing additives. Another method for preparing a support having particularly suitable properties for alkylene oxide catalyst usage comprises optionally mixing zirconium silicate with boehmite alumina (AlOOH) and/or gamma-alumina, peptizing the aluminas with a mixture containing an acidic component and halide anions (preferably fluoride anions) to provide peptized halogenated alumina, forming (for example, by extruding or pressing) the peptized halogenated alumina to provide formed peptized halogenated alumina, drying the formed peptized halogenated alumina to provide dried formed alumina, and calcining the dried formed alumina to provide pills of modified alpha-alumina support.

[0053] There have been employed alumina which has a very high purity, that is, at least 98 wt. % alpha-alumina, any remaining components being silica, alkali metal oxides (for example, sodium oxide) and trace amounts of other metal-containing and/or non-metal-containing additives or impurities. Likewise, there have been employed alumina of lower purity, that is, 80 wt. % alpha-alumina, the balance being one or more of amorphous and/or crystalline alumina and other alumina oxides, silica, silica alumina, mullite, various alkali metal oxides (for example, potassium oxide and cesium oxide), alkaline earth metal oxides, transition metal oxides (for example, iron oxide and titanium oxide), and other metal and non-metal oxides. In addition, the material used to make the support may comprise compounds which have been known for improving catalyst performance, for example, rhenium, (such as rhenates) and molybdenum.

[0054] In one embodiment, the support material comprises at least 80 weight percent alpha-alumina and comprises less than 30 parts per million acid-leachable alkali metals by weight, the weight percent of the alpha-alumina and the concentration of the acid-leachable alkali metals being calculated on the weight of the support, where the acid-leachable alkali metals are selected from lithium, sodium, potassium, and mixtures thereof.

[0055] The alpha-alumina support preferably has a pore volume of at least 0.3 cubic centimeters per gram (cm^3/g), and more preferably, from 0.4 cm^3/g to 2.0 cm^3/g; and a median pore diameter from 1 to 50 microns.

[0056] The alpha-alumina support preferably has a specific surface area of at least 0.5 square meters per gram (m^2/g), and more preferably, at least 0.7 m^2/g. The surface area is typically less than 10 m^2/g, and preferably, less than 5 m^2/g.

[0057] In one embodiment, the alpha-alumina support includes particles each of which has at least one substantially flat major surface having a lamellate or platelet morphology which approximates the shape of a hexagonal plate (some particles having two or more flat surfaces), at least 50 percent of which (by number) have a major dimension of less than 50 microns.

[0058] The alpha-alumina support can be of any suitable shape. Exemplary shapes of the support includes pills, chunks, tablets, pieces, pellets, rings, spheres, wagon wheels,

toroids having star shaped inner and/or outer surfaces, and the like. The support can be of any size suitable for employment in reactors. For example, in a fixed bed ethylene oxide reactor having a plurality of parallel elongated tubes (in a suitable shell) 1 to 3 inches (2.5 to 7.5 cm) outer diameter and 15 to 45 feet (4.5 to 13.5 m) long filled with catalyst, it is desirable to employ alpha alumina support having a rounded shape, such as, for example, spheres, pellets, rings, cross-partitioned rings, penta-rings, tablets, and the like, having diameters from 0.1 inch (0.25 cm) to 0.8 inch (2 cm).

[0059] The support or impregnated support is impregnated with at least a portion of the impregnation solution to form the catalyst intermediate. Impregnation of similar supports is given in U.S. Patent Nos. 6,511,938 and 5,187,140. Following impregnation, the catalyst intermediate is separated from any remaining non-absorbed impregnation solution. This is conveniently accomplished by draining the excess impregnation solution or, alternatively, by using another separation technique, such as filtration or centrifugation.

[0060] The impregnation step (iii) may be followed by roasting or other procedures to render the silver insoluble, after separating the non-absorbed impregnation solution. Generally in roasting process, the catalyst intermediate is heat treated to effect decomposition and reduction of the catalytic material, for example, silver metal compound (complexes in most cases), to metallic form and the deposition of manganese and any other promoters. 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, for example, convert substantially all of any salt, for example, silver salt, to metal, for example, silver metal.

[0061] Although a wide range of heating periods have been suggested in the art to thermally treat impregnated support (for example, U.S. Pat. No. 3,563, 914 suggests heating for less than 300 seconds to dry, but not roast to reduce, the catalytic material; U.S. Pat. No. 3,702,259 discloses heating from 2 to 8 hours at a temperature of from 100°C to 375°C to reduce silver salt in the catalyst), it is only important that the reduction time be correlated with temperature such that substantially complete reduction of, for example, the silver salt to metal is accomplished. A continuous or step-wise heating program is desirably used for this purpose. Continuous roasting of the catalyst intermediate for a short period of time, such as for not longer than 1 hour is preferred and can be effectively done in making the

catalysts of this invention. When more than one roasting is carried out, it is not necessary that the roasting conditions be the same in each roasting.

[0062] Heat treatment is preferably carried out in air, but nitrogen, hydrogen, carbon dioxide or other atmospheres may also be employed. The equipment used for such heat treatment may use a static or flowing atmosphere of such gases to effect reduction, but a flowing atmosphere is much preferred. In some embodiments, the catalyst intermediate can be chemically treated to reduce any silver compounds to metallic silver.

[0063] In one embodiment, the method of making the manganese-containing supported silver catalyst includes following steps (i) to (iii) to form the catalyst intermediate which is then roasted or chemically treated to form the manganese-containing silver catalyst. In some embodiments, two or more impregnation steps are used to make the manganese-containing supported silver catalysts. For example in a sequential impregnation, a support is impregnated with at least a portion of a first impregnation solution containing silver, manganese and optionally one or more promoters other than manganese to form a first catalyst intermediate, by following steps (i) to (iii). The first catalyst intermediate is then roasted or chemically treated to form a second catalyst intermediate. For subsequent impregnation, the second catalyst intermediate is impregnated with at least a portion of a second impregnation solution by following steps (i) to (iii), or by any known impregnation process. In another embodiment, a support is impregnated with at least a portion of a first impregnation solution containing silver to form a first impregnated support. The first impregnated support is roasted to form a silver-impregnated support. The silver-impregnated support is subjected to a second impregnation step following steps (i) to (iii) to form a first catalyst intermediate.

[0064] In embodiments where sequential impregnation is followed, a concentration of the silver may be higher in the second impregnation solution than in the first impregnation solution. For example, if a total silver concentration of 30% were desired in the catalyst, a low amount of silver of 10% by weight would be deposited on the support as a result of the first impregnation followed by a second silver impregnation on the support depositing the remaining 20% by weight, all percentages being calculated on the basis of the finished catalyst. In other embodiments, approximately equal amounts of silver are deposited during

each impregnation step. Often, to effect the equal deposition in each impregnation step, the silver concentration in the subsequent impregnation solutions may need to be greater than that in the initial impregnation solutions. In further embodiments, a greater amount of silver is deposited on the support in the initial impregnation than that deposited in subsequent impregnations. Impregnation of the catalyst support may be effected using one or more solutions containing silver and promoters in accordance with well-known procedures for coincidental or sequential depositions. For coincidental deposition, following impregnation the impregnated support is heat or chemically treated to reduce the silver compound to silver metal and deposit the salts onto the catalyst surfaces.

[0065] The manganese-containing supported silver catalysts of the invention are particularly suitable in the vapor phase process for the continuous production of ethylene oxide by contacting in vapor phase ethylene with oxygen or an oxygen containing gas. The epoxidation reaction can be air-based or oxygen-based, see Kirk-Othmer's Encyclopedia of Chemical Technology, 3rd ed., Vol. 9, 1980, p. 445-447. The commercially-practiced processes are carried out by continuously introducing a feed stream containing ethylene and oxygen to a manganese-containing supported silver catalyst containing reactor at a temperature of from 200 °C to 300 °C, and a pressure which may vary from five atmospheres to 30 atmospheres depending upon the mass velocity and productivity desired. Residence times in large-scale reactors are generally on the order of 0.1 to 5 seconds. The feed stream may also include gas-phase modifiers such as organic chlorides; ethane; carbon dioxide; and water.

[0066] The oxygen can be provided to the process as pure molecular oxygen, or alternatively, as an oxygen-containing gas, wherein the gas may further contain one or more gaseous components, for example, gaseous diluents, such as nitrogen, helium, methane, and argon, which are essentially inert with respect to the oxidation process. The raw ethylene feed stream may also contain other hydrocarbons, such as ethane, present as an impurity. Ethane can also be added to a commercial reactor to provide better control of the organic chloride's inhibitor action. The relative volumetric ratio of ethylene to oxygen in the reaction mixture can range in accordance with any of such known conventional values.

[0067] The gas-phase modifiers are also otherwise termed as inhibitors and/or enhancers. Suitable gas-phase modifiers can be selected from a group containing C1-C8 chlorohydrocarbons. It is believed that the ability of the gas-phase modifiers to enhance the efficiency and/or activity of the epoxidation process depends on the extent to which the gas-phase modifiers chlorinates the surface of the catalyst, for example, by depositing particular chlorine species such as atomic chlorine or chloride ions on the catalyst. However, hydrocarbons lacking chlorine atoms are believed to strip chlorides from the catalyst, and therefore, detract from the overall efficiency enhancement provided by the gaseous chlorine-containing promoter species. Discussions of this phenomenon may be found in Berty, "Inhibitor Action of Chlorinated Hydrocarbons in the Oxidation of Ethylene to Ethylene Oxide," Chemical Engineering Communications, Vol. 82 (1989) at 229-232 and Berty, "Ethylene Oxide Synthesis," Applied Industrial Catalysis, Vol. I (1983) at 207-238. Paraffinic compounds, such as ethane or propane, are believed to be especially effective at stripping chlorides from the catalyst. However, olefins such as ethylene and propylene, are also believed to act to strip chlorides from the catalyst. Some of these hydrocarbons may also be introduced as impurities in the ethylene feed or may be present for other reasons (such as the use of recycle stream) in the feed stream.

[0068] Carbon dioxide is generally considered an inhibitor, and the inhibitor effect of carbon dioxide on process efficiency may be variable with its concentration. With different types of promoters used in preparation of the catalysts of this invention, different concentrations of carbon dioxide may be more desirable in certain commercial processes. Typically, the amount of carbon dioxide used in commercial processes can vary from less than 2 to 15 mole percent for achieving optimization under both air process conditions and oxygen process conditions. The amount of carbon dioxide may also be dependent on the size and type of carbon dioxide scrubbing system employed.

[0069] Typically, the volumetric ratio of alkylene to oxygen in the reaction mixture can vary from 1/1 to 10/1. Likewise, the quantity of inert gases, diluents, or other gaseous components, such as water, carbon dioxide, gas-phase modifiers and gaseous by-product inhibitors, can vary in accordance with known conventional ranges as found in the art.

[0070] Suitable reactors for the epoxidation reaction include fixed bed reactors, fixed bed tubular reactors, continuously stirred tank reactors (CSTR), fluid bed reactors and a wide variety of reactors that are well known to those skilled in the art. The reaction conditions for carrying out the epoxidation reaction are well-known and extensively described in the prior art. This applies to reaction conditions, such as temperature, pressure, residence time, concentration of reactants, gas phase diluents (e.g., nitrogen, methane and carbon dioxide), gas phase inhibitors (e.g., organic chlorides), and the like. 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. The ethylene oxide produced according to embodiments of the present invention is separated and recovered from the reaction products using conventional methods.

[0071] The ethylene oxide produced by the present epoxidation process may typically be processed to provide further downstream products, such as, for example, ethylene glycol, ethylene glycol ether, ethylene carbonate, and ethanol amine. The conversion of ethylene oxide into ethylene glycol or ethylene glycol ether may comprise, for example, reacting the desired ethylene oxide with water, suitably in the presence of an acidic or basic catalyst. For example, for preferential production of the ethylene glycol over the ethylene glycol ether, the ethylene oxide may be reacted with a tenfold molar excess of water, in a liquid phase reaction in the presence of an acid catalyst, e.g., 0.5-1.0 wt% sulfuric acid, based on the total reaction mixture, at 50-70 °C at 1 bar absolute, or in a gas phase reaction, at 130-240°C and 20-40 bar absolute, preferably in the absence of a catalyst. If the proportion of water is lowered, the proportion of the ethylene glycol ether in the reaction mixture will be increased. Alternatively ethylene glycol ether may be prepared by converting the ethylene oxide with an alcohol, such as methanol or ethanol, or by replacing at least a portion of the water with the alcohol. The resulting ethylene glycol and ethylene glycol ether may be utilized in a wide variety of end-use applications in the food, beverage, tobacco, cosmetic, thermoplastic polymer, curable resin system, detergent, heat transfer system, etc., industries.

[0072] The conversion of ethylene oxide produced via the method of the present invention into ethanolamine may comprise, for example, reacting the ethylene oxide with

ammonia. Anhydrous or aqueous ammonia may be used. The resulting ethanolamine may be used, for example, in the treatment of natural gas. The ethylene oxide may be converted into the corresponding ethylene carbonate by reacting ethylene oxide with carbon dioxide. If desired, ethylene glycol may be prepared by subsequently reacting ethylene carbonate with water or an alcohol to form the ethylene glycol. For applicable methods, reference is made to U. S. Patent No. 6,080,897.

[0073] Ethylene glycol is used in two significant applications: as a raw material for poly(ethylene terephthalate) for use in polyester fiber, film, and containers, and as an automotive antifreeze. Di-, tri-, and tetraethylene glycols are coproducts of ethylene glycol.

EXAMPLES

[0074] Preparation of silver-amine-oxalate solution: An amine solution is prepared by mixing 11.47 weight parts of ethylenediamine (high purity grade) with 20.00 weight parts of distilled water. Then 11.60 weight parts of oxalic acid dihydrate (reagent grade) is slowly added to the amine solution at ambient conditions. The addition of the oxalic acid dihydrate is at a rate that the exotherm does not cause the temperature of the amine-oxalate solution to rise above 40°C. Then 19.82 weight parts of silver oxide are added followed by 4.01 weight parts of monoethanolamine (Fe and Cl free). Distilled water is then added to adjust the solution weight to 70.00 weight parts to form the silver-amine-oxalate solution. The silver-amine-oxalate solution has a pH in the range between 11 and 12.

Stability studies of manganese in solutions

COMPARATIVE EXAMPLE 1

[0075] Preparation of Solution A for stability study of manganese in solution: About 0.293 grams of aqueous manganese(II) nitrate solution (0.157 grams Mn/gram solution) are added to 588.3 grams of the above silver-amine-oxalate solution. Other (non-Mn-containing) promoter-containing compounds are then added as aqueous solutions (about 16.14 grams in total), followed by stirring for 30 minutes at 20 °C to obtain solution A. A sample of Solution A is withdrawn and filtered through a 0.1μ filter paper and the concentration of manganese in the filtrate is analyzed by X-Ray Fluorescence (XRF). The

XRF analysis error is typically about ±3 ppm and the result is given in Table 1. In the Table, the calculated Mn (manganese) refers to the stoichiometric amount of manganese in the solution. XRF Mn is the amount of manganese remaining in the solution after filtration measured by XRF. XRF Mn value is about 60.9 ± 3 ppm indicating precipitation of manganese from the solution A.

Solution	Calculated Mn (ppm)	XRF Mn (ppm)
A	76	60.9 ± 3
B	76	54.6 ± 3
C	76	80 ± 3

Table 1: XRF analyses of Solution A, Solution B and Solution C

COMPARATIVE EXAMPLE 2

[0076] Preparation of Solution B for stability study of manganese in solution: About 1.0724 grams of aqueous diammonium EDTA solution (46 wt% EDTA) is added to solution A and stirred for 30 minutes at 20 °C to obtain Solution B. A sample of Solution B is withdrawn for XRF analysis and is analyzed according to the method described previously. Solution B has an XRF value of about 54.6 ± 3 ppm, as shown in Table 1, indicating higher precipitation of manganese compared to Solution A.

EXAMPLE 1

[0077] Preparation of Solution C for stability study of manganese in solution: The experiment of Comparative Example 2 is repeated except that prior to addition to the silver-amine-oxalate solution, about 0.293 grams of aqueous manganese (II) nitrate solution (0.157 grams Mn/gram solution) is combined with about 1.072 grams of aqueous diammonium EDTA solution (46 wt% EDTA) and mixed thoroughly to form a first solution. The first solution thusly prepared has a pH of less than or equal to 7. The first solution is then added to the silver-amine-oxalate solution, followed by the addition of the

other (non-Mn-containing) promoter solutions and stirring for 30 minutes at 20 °C to obtain Solution C. Solution C has a pH which is greater than 7. Solution C shows a XRF Mn value of about 80.0±3 ppm which matches the calculated Mn value indicating minimal precipitation of manganese from the solution.

Variability studies on the amount of manganese in impregnation solution batches

COMPARATIVE EXAMPLE 3

Preparation of catalyst batches according to prior art method

[0078] Preparation of first impregnated support: An alpha-alumina support is vacuum impregnated with a first silver impregnation solution typically containing 31 weight percent silver oxide, 18 weight percent oxalic acid, 18 weight percent ethylenediamine, 6 weight percent monoethanolamine and 27 weight percent distilled water. The first silver impregnation solution is prepared by mixing 1.14 parts of ethylenediamine (high purity grade) with 1.75 parts of distilled water to form aqueous ethylenediamine solution. This is followed by slow addition of 1.16 parts of oxalic acid dihydrate (reagent grade) to the ethylenediamine solution such that the temperature of the solution does not exceed 40° C, followed by addition of 1.98 parts of silver oxide and 0.40 parts of monoethanolamine (Fe and Cl free) to form the first silver impregnation solution. The first silver impregnation solution has a pH which is in the range between 11 and 12.

[0079] The alpha-alumina support is impregnated with the first silver impregnation solution. The support remains immersed in the first silver impregnation solution at ambient conditions for 5 to 30 minutes. The impregnated support is then taken out and thereafter drained of excess solution for 10 to 30 minutes.

[0080] The impregnated support is then roasted to effect reduction of silver on the support surface to form a first impregnated support. For roasting, the impregnated support is spread out in a single layer on stainless steel wire mesh trays which is placed on a belt and transported to a heating zone for 2.5 minutes. The heating zone is maintained at 500° C by passing hot air upward through the belt and the impregnated support. After roasting in the heating zone, the first impregnated support is kept in the open and brought to room

temperature and weighed. Preparation of first catalyst intermediate: The first impregnated support is vacuum impregnated with a second silver impregnation solution to form a first catalyst intermediate. The second silver impregnation solution comprises drained solutions from previous silver impregnation solution(s) and fresh aliquots of each of the manganese nitrate and diammonium EDTA in separate additions directly into the silver-amine-oxalate solution. The second impregnation solution includes one or more promoters selected from cesium, lithium, sodium and any mixtures thereof. Following impregnation, the first catalyst intermediate is drained of excess solution and roasted as described previously with reference to the first impregnated support to form a first catalyst. The weight percent of silver is calculated based on the weight of first catalyst and the support. The concentration of the promoters is calculated, assuming a similar rate of deposition for the promoters as is for the silver. The manganese content of the first catalyst can be correlated to the manganese content of the impregnation solution and is determined using XRF, as described in previous examples on stability studies of manganese in solutions. Various first catalyst batches are prepared following this method having a wide range of desired target levels and also at various scale-up levels. The wide range of desired target levels can be achieved by varying the stoichiometry of the impregnating solutions. FIG. 1 is a plot of variability in the amount of manganese as determined by XRF analyses in the silver impregnation solution batches prepared for use in preparing first catalyst batches and is expressed as the percentage variation in manganese content from the desired target levels. This Example shows large variability in the amount of manganese in the impregnation solution ranging from about +20% to about -90% relative to the target values. The catalysts prepared using such impregnation solutions are expected to reflect this variability in manganese as well.

EXAMPLE 2

Preparation of catalyst batches according to inventive method

[0081] Preparation of second catalyst intermediate according to the inventive method: The first impregnated support is prepared according to the method of Comparative Example 3 and then is vacuum impregnated with a third silver impregnation solution to form a second catalyst intermediate. The third silver impregnation solution comprises drained solution from previous silver impregnation solution(s) and fresh aliquots of each of the first

solution and the second solution. The first solution comprises manganese(II) nitrate and diammonium EDTA and at any time, i.e. at least one point in time during or after the preparation of the first solution it has a pH which is less than or equal to 7. The second solution comprises silver-amine-oxalate solution. The third silver impregnation solution includes one or more promoters selected from cesium, lithium, sodium and any mixtures thereof. The third silver impregnation solution has a pH of greater than 7. Following impregnation, the second catalyst intermediate is drained of excess solution and roasted as described previously with reference to the first impregnated support to form a second catalyst. The weight percent of silver and the concentrations of the promoters are calculated. The manganese content in the second catalyst can be correlated to the manganese content of third silver impregnation solution and is measured using XRF. Various second catalyst batches are prepared having a wide range of desired target levels and also at various scale-up levels. FIG. 2 is a plot of variability in the amount of manganese as determined by XRF in the impregnation solution batches prepared according to the invention for use in preparing second catalyst batches and is expressed as the percentage variation in manganese content from the desired target levels. The variability in the manganese concentration is within ±10% relative to the targets. This Example indicates that the inventive method of forming a first solution by combining manganese nitrate and diammonium EDTA, prior to addition to second solution comprising silver, lowers the variability in the amount of manganese in the resulting impregnation solution. The catalysts prepared using such impregnation solutions are expected to reflect this lower variability as well.

COMPARATIVE EXAMPLE 4

[0082] Manganese-containing first catalyst batches 4-1 to 4-5 are prepared in large-scale generally according to the procedure as described in Comparative Example 3. The concentrations of manganese on the first catalyst batches 4-1 to 4-5 are determined using XRF and are provided in Table 2.

[0083] Catalyst performance studies: Multiple 80-cc samples are withdrawn from each of the first catalyst batches and evaluated in backmixed (CSTR) Berty-type autoclave reactors under the following conditions: inlet concentrations of 8.0 vol% oxygen, 6.5 vol%

carbon dioxide, 30.0 vol% ethylene, 0.50 vol% ethane, 3.5 ppmv ethyl chloride, balance nitrogen; with a pressure of 1900 kPa gauge; a total flow of 640 standard liters per hour (measured as nitrogen); and a startup temperature of 230°C. Following startup, the temperature is adjusted to produce an outlet concentration of 2.0 vol% ethylene oxide. For each batch, the average autoclave temperature required to attain an outlet concentration of 2.0 vol% ethylene oxide after seven days of testing is shown in Table 2.

Catalyst batch	Manganese in ppm	T in °C
4-1	91	240.2
4-2	82	238.8
4-3	84	238.3
4-4	92	236.7
4-5	87	238.7

Table 2 Manganese content and average activity of the first catalyst batches 4-1 to 4-5

EXAMPLE 3

[0084] This Example illustrates the performance improvement in a manganese-containing silver catalyst prepared using the inventive method.

[0085] Manganese-containing second catalyst batches 3-1 to 3-6 are prepared in large-scale generally according to the procedure outlined in Example 2. The concentrations of manganese on the second catalyst batches 3-1 to 3-6 are determined using XRF and are provided in Table 3. The second catalyst batches 3-1 to 3-6 are evaluated following the procedure for catalyst performance studies provided in Comparative Example 4. The manganese concentrations of the second catalyst batches and the temperature, which is the average autoclave temperature required to attain an outlet concentration of 2.0 vol% ethylene oxide after seven days of testing, are shown in Table 3.

Catalyst batch	Manganese in ppm	T in °C
3-1	91	234.9
3-2	87	235.4
3-3	83	236.7
3-4	88	236.5
3-5	95	235.6
3-6	91	233.2

Table 3 Manganese content and average activity of the second catalyst batches 3-1 to 3-6

[0086] Figure 3 is a comparison of the activity of second catalyst batches of Example 3 and first catalyst batches of Comparative Example 4. The significantly lower temperatures required to produce 2.0 vol% ethylene oxide for the second catalyst batches of Example 3 indicates an improvement in catalyst activity over the first catalyst batches of Comparative Example 4. Advantageously, the improvement in catalyst activity may also benefit a lifetime of the second catalyst batches of Example 3.

COMPARATIVE EXAMPLE 5

[0087] This example highlights the variability in the manganese content during the course of preparing the large scale first catalyst batches (4-1 to 4-5), as described in Comparative Example 4. Figure 4 is a plot of normalized manganese content of manganese-containing silver-amine-oxalate solution batches prepared for use in the preparation of first catalyst batches 4-1 to 4-5 (marked as 5*), where normalized manganese content is the ratio of the measured manganese content in the solution batches (as analyzed by XRF) to the target manganese content, divided by the average of the ratio across all the solution batches. Multiple points on the plot of Figure 4 thus correspond to each of the

large-scale first catalyst batches of Comparative Example 4 and is indicative of the variation in manganese content from solution-batch to solution-batch even within each first catalyst batch when preparing manganese-containing silver catalysts according to the prior art method.

EXAMPLE 4

[0088] This example illustrates the benefit of the inventive method observed during preparation of the large scale second catalyst batches (3-1 to 3-6) as described in Example 3. Figure 4 is a plot of normalized manganese content of Mn-containing silver-amine-oxalate solution batches prepared in accordance with inventive method for use during preparation of second catalyst batches 3-1 to 3-6 (marked as 4), where normalized manganese content is the ratio of the measured manganese content in the solution batches (as analyzed by XRF) to the target manganese content, divided by the average of the ratio across all the solution batches. Multiple points on the plot of Figure 4 therefore correspond to each of the large-scale second catalyst batches of Example 3. When compared to Mn-containing silver-amine-oxalate solution batches prepared using a prior art method (marked as 5*), the solution batches prepared using inventive method show lower variability in the amount of manganese from batch to batch.

CLAIMS:

1. A method of making a manganese-containing supported silver catalyst intermediate comprising the steps of:

(i) preparing a first solution comprising a manganese component and a complexing agent, wherein a pH of the first solution at any time during or after step (i) is less than or equal to 7;

(ii) combining the first solution with a second solution comprising silver to form an impregnation solution; and

(iii) impregnating a support with at least a portion of the impregnation solution to form the catalyst intermediate, wherein the impregnation solution has a pH of greater than 7.

2. The method of claim 1, wherein the manganese component comprises one or more of manganese acetate, manganese ammonium sulfate, manganese citrate, manganese dithionate, manganese oxalate, manganous nitrate, manganous sulfate, permanganate anion, manganate anion and any combinations thereof.

3. The method of claim 1 or 2 wherein the complexing agent is selected from the group consisting of ethylenediaminetetraacetic acid, N, N'-ethylenediaminediacetic acid, N-hydroxyethylethylenediaminetriacetic acid, diethylenetriaminepentaacetic acid, nitrilotriacetic acid, 1,2-cyclohexylenedinitrilotetraacetic acid, N-hydroxyethyliminodiacetic acid, N-dihydroxyethylglycine and any derivatives thereof.

4. The method of any of claims 1-3 wherein the complexing agent is ethylenediaminetetraacetic acid.

5. The method of any of claims 1-4, wherein the first solution, or the second solution, or both further comprises one or more promoters other than a manganese component.

6. The method of claim 5, wherein the one or more promoters other than a manganese component is selected from a group consisting of Group IA metals, Group IIA metals, phosphorus, boron, sulfur, rhenium, molybdenum, tungsten, chromium, titanium,

hafnium, zirconium, vanadium, thallium, thorium, tantalum, niobium, gallium, germanium and any mixtures thereof.

7. The method of any of claims 1-6, wherein manganese is present in the manganese-containing supported silver catalyst intermediate in an amount of at least 20 ppmw calculated as the weight of manganese based on the total weight of the catalyst.

8. The method of any of claims 1-7, wherein manganese is present in the manganese-containing supported silver catalyst intermediate in an amount from 20 ppmw to 1000 ppmw calculated as the weight of manganese based on the total weight of the catalyst.

9. A vapor phase process for the production of ethylene oxide comprising contacting in a vapor phase ethylene with oxygen or an oxygen-containing gas in the presence of a manganese-containing supported silver catalyst prepared from manganese-containing supported silver catalyst intermediate according to any of claims 1-8.

10. The process of claim 9 further comprising converting the ethylene oxide to one or more of an ethylene carbonate, an ethylene glycol, an ethanol amine or an ethylene glycol ether.

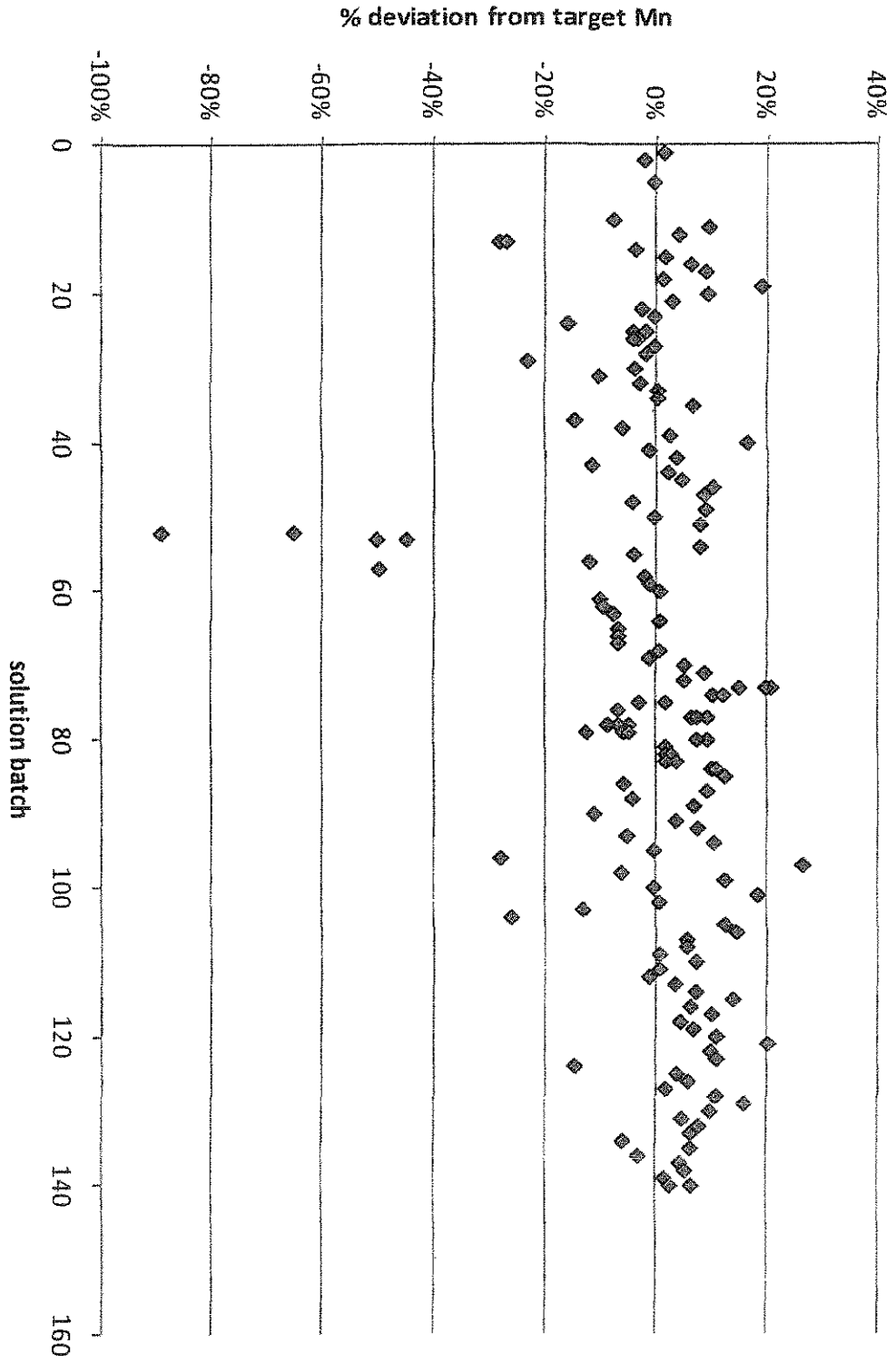
% deviation from target Mn
40%
20%
0%
-20%
-40%
-60%
-80%
-100%
0
20
40
60
80
100
120
140
160
solution batch

FIGURE 1

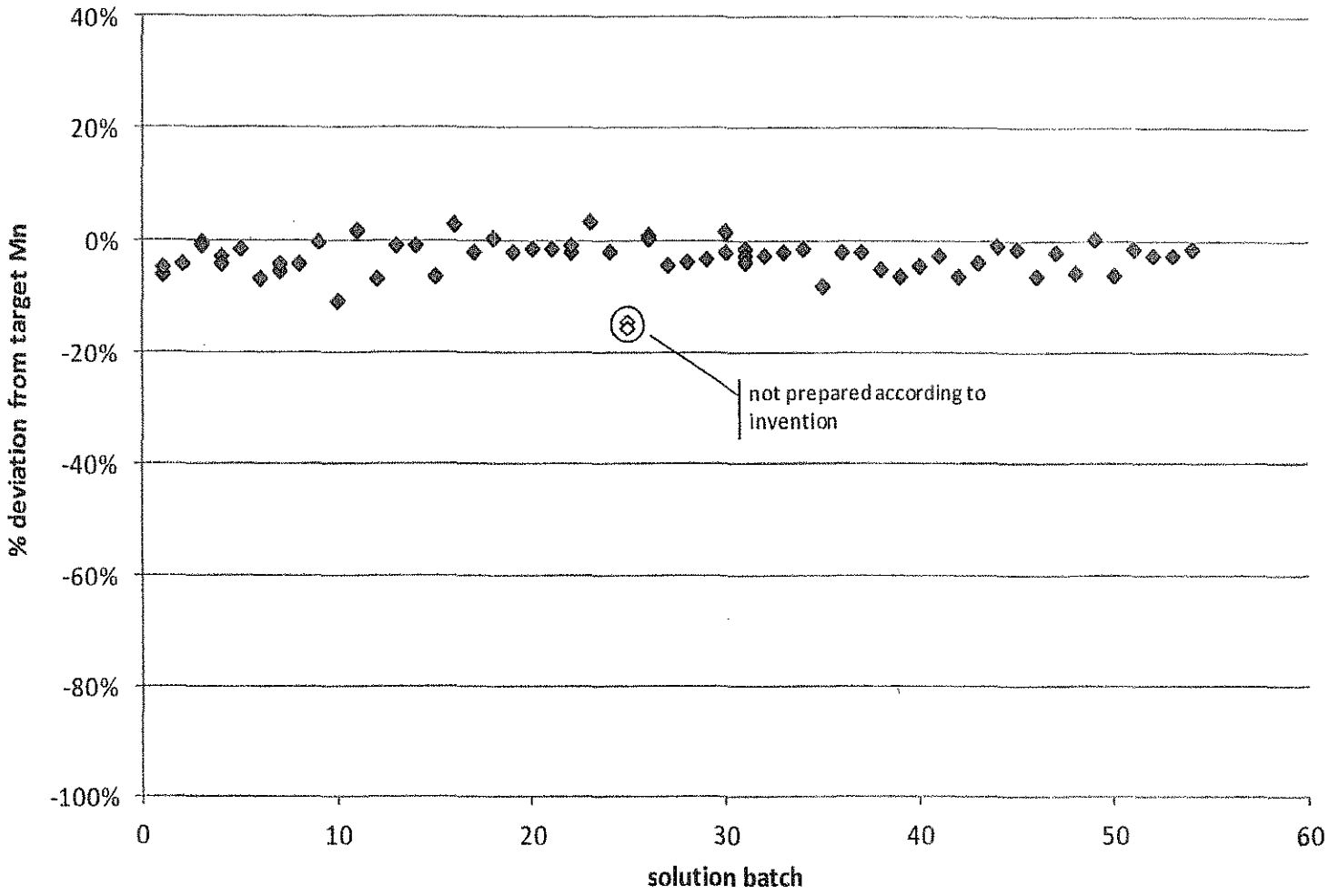
40%
20%
0%
-20%
-40%
-60%
-80%
-100%
% deviation from target Mn
0
10
20
30
40
50
60
solution batch
not prepared according to invention

FIGURE 2

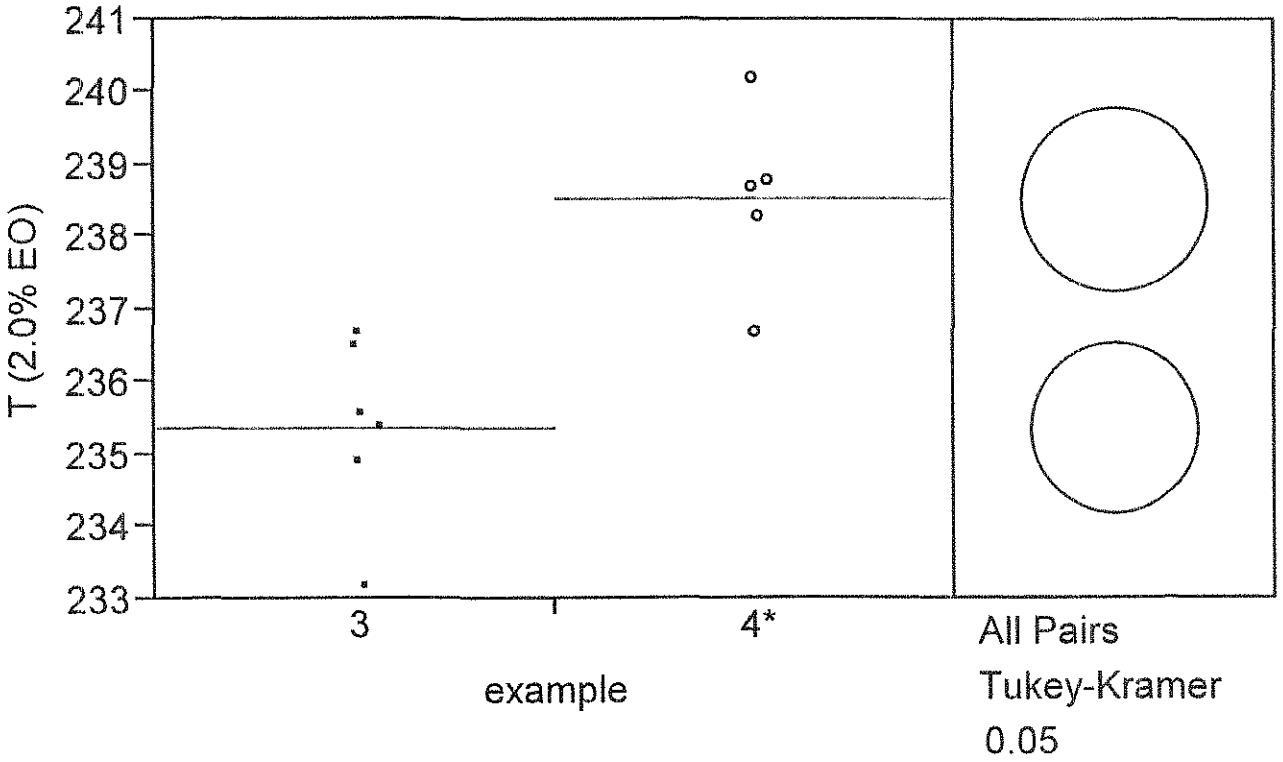
241
240
239
238
237
236
235
234
233
T (2.0% EO)
3
4*
example
All Pairs
Tukey-Kramer
0.05

FIGURE 3

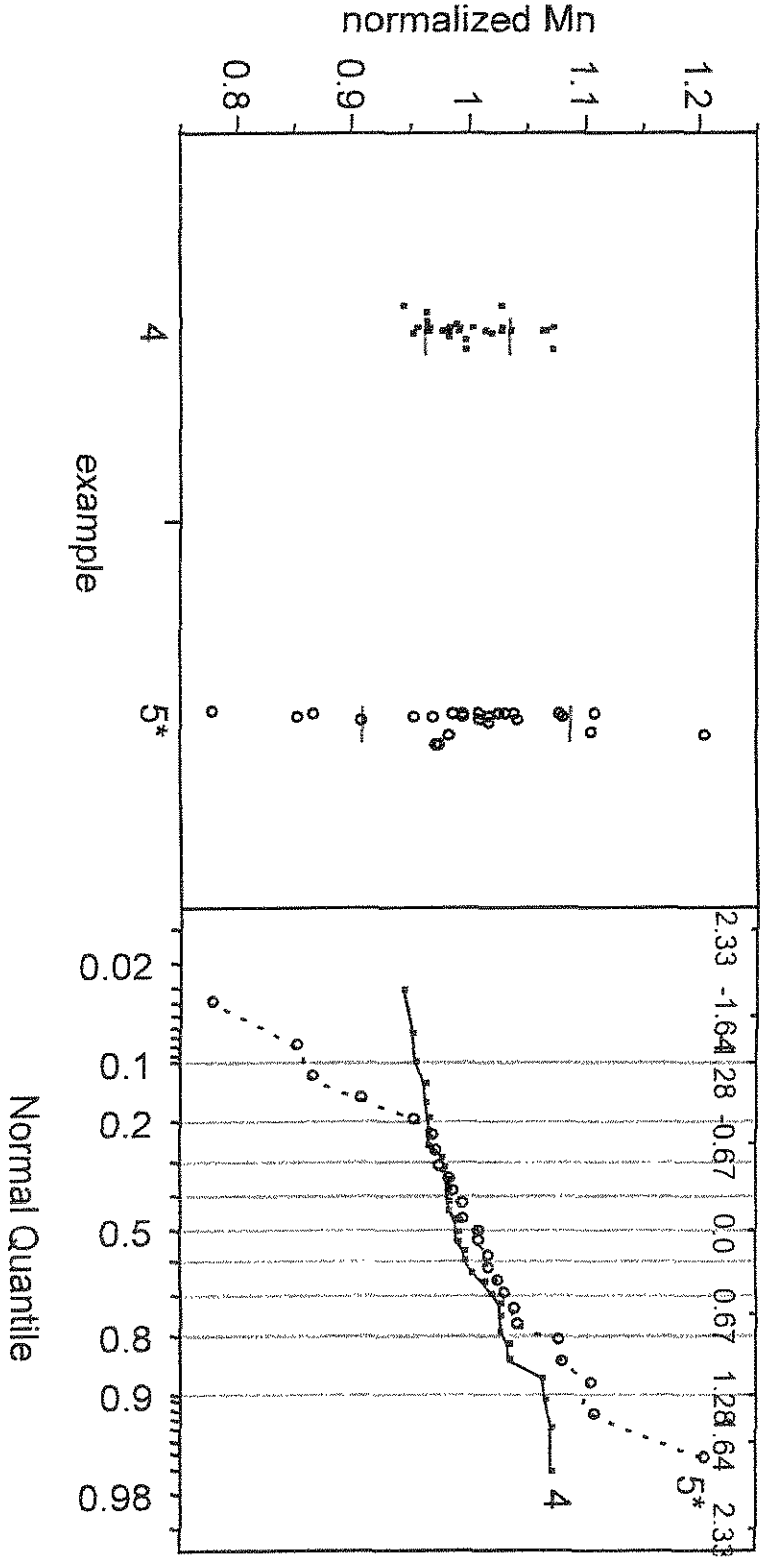
normalized Mn
1.2
1.1
1
0.9
0.8
4
5*
example
2.33
-1.64
28
-0.67
0.0
0.67
1.28
1.64
2.33
5*
4
0.02
0.1
0.2
0.5
0.8
0.9
0.98
Normal Quantile

FIGURE 4