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**(54) Title:** PROPYLENE OXIDE PROCESS USING CALCIUM CARBONATE–SUPPORTED SILVER CATALYSTS CONTAINING POTASSIUM AND MAGNESIUM PROMOTERS

**(57) Abstract**

Direct oxidation of propylene oxide is accomplished using calcium–carbonate silver catalysts containing both a potassium promoter derived from potassium nitrate or the like and a magnesium promoter. The addition of iron as a co–promoter helps to further enhance the performance of the catalyst.

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# PROPYLENE OXIDE PROCESS USING CALCIUM CARBONATE-SUPPORTED SILVER CATALYSTS CONTAINING POTASSIUM AND MAGNESIUM PROMOTERS

## FIELD OF THE INVENTION

This invention relates to a process for the direct oxidation of propylene to propylene oxide in the vapor phase using molecular oxygen. In particular, the invention pertains to the use of compositions comprised of silver supported on calcium carbonate to selectively catalyze the formation of epoxides. The performance of the catalysts is improved by incorporating a potassium promoter derived from a potassium salt comprising potassium cation and a nitrogen oxyanion or precursor thereof together with a magnesium promoter. Further catalytic enhancement is realized using a combination of magnesium and iron promoters.

## BACKGROUND OF THE INVENTION

The direct oxidation of ethylene to ethylene oxide by molecular oxygen is well-known and is, in fact, the method used currently for commercial production of ethylene oxide. The typical catalyst for such purpose contains metallic or ionic silver, optionally modified with various promoters and activators. Most such catalysts contain a porous, inert support or carrier such as alpha alumina upon which the silver and promoters are deposited. A review of the direct oxidation of ethylene in the presence of supported silver catalysts is provided by Sachtler et al. in Catalyst Reviews: Science and Engineering, 23 (1&2), 127-149 (1981).

It is also well-known, however, that the catalysts and reaction conditions which are best suited for ethylene oxide production do not give comparable results in the direct oxidation of higher olefins such as propylene. The discovery of processes capable of providing propylene oxide by vapor phase direct oxidation in higher yields than are presently attainable thus would be most desirable.

Canadian Patent No. 1,282,772 proposes a direct epoxidation process using a supported silver catalyst wherein the support is an alkaline earth carbonate such as calcium carbonate. U.S. Patent No. 5,625,084 also describes a calcium carbonate-supported silver catalyst useful for converting propylene to propylene oxide, wherein the catalyst contains a molybdenum promoter. Neither of the aforementioned publications, however, teaches or recognizes that the incorporation of magnesium could significantly improve the performance, and in particular the activity, of such catalysts.

Magnesium and iron have from time to time in the patent literature been proposed as promoters for certain specific types of silver-containing olefin oxidation catalysts. See, for example, the disclosures of U.S. Pat. Nos. 2,424,083, 2,605,239, 3,962,285, 4,242,235, 4,400,308, 4,410,453, 4,783,786 and 4,859,786. On the other hand, iron contaminants have been implicated in the explosion of commercial ethylene oxide production units (see Viera et al., Chemical Engineering Progress, August 1993, pp. 66-75).

## SUMMARY OF THE INVENTION

A process for propylene epoxidation is provided wherein a feedstream comprising propylene and oxygen is contacted with a particular type of promoted silver catalyst. The catalyst is comprised of (a) a support comprised of calcium carbonate; (b) a catalytically effective amount of silver; (c) a promoting amount of a potassium promoter, and (d) a promoting amount of a magnesium promoter. A synergistic enhancement of catalytic activity is obtained using a magnesium promoter in combination with the calcium carbonate. This beneficial effect of the magnesium promoter on catalyst performance was unexpected, since silver catalysts prepared using magnesium carbonate rather than calcium carbonate as a support have much lower epoxidation activity. The potassium promoter is derived from a potassium salt such as potassium nitrate which comprises potassium cation and a nitrogen oxyanion or precursor thereof. An iron co-promoter may additionally be present in order to further enhance the performance of the catalyst.

The process described herein is capable of producing propylene oxide at remarkably high selectivity and productivity.

## DETAILED DESCRIPTION OF THE INVENTION

The present invention is directed to a process for the vapor phase oxidation of propylene to propylene oxide, i.e., an epoxidation process performed in the presence of an oxygen-containing gas and a particular class of supported silver catalysts.

The support material used in the present invention is comprised of calcium carbonate. Any of the physical forms of calcium carbonate supports described in Canadian Pat. No. 1,282,772 or U.S. Pat. No. 5,625,084 may be utilized in the present invention.

Such support materials are capable of providing exceptionally high propylene oxide selectivities and have been found to be surprisingly superior to other support materials in this respect. The carriers of the present invention may exist in various forms. In one embodiment, the carrier is one in which calcium carbonate is the predominate (i.e., at least 50% by weight) or, preferably, substantially the exclusive component of the support (i.e., the support consists essentially of calcium carbonate). In other embodiments of the invention, the calcium carbonate is used in conjunction with a solid substrate, i.e., a subsupport or substructure composed of a more conventional support material, such as alumina (preferably, alpha-alumina). However, the calcium carbonate will normally comprise at least 25 weight percent (in most embodiments, at least 35 weight percent) of the finished catalyst.

A granular form of calcium carbonate is preferred in the present invention, particularly when used as the exclusive or predominant component of the support. Calcium carbonate suitable for use in the present invention may be commercially obtained as a powder which can be converted to the preferred granular form by conventional methods. As described in greater detail below, the granular support may then be impregnated, or coated, with a solution containing a silver compound which is thereafter reduced to elemental (metallic) silver.

Alternatively, as described below, the powdered calcium carbonate may be combined with an appropriate silver compound-containing solution, such as that used conventionally to impregnate solid supports to form a slurry or paste. This material may then be spread on a suitable surface and dried and calcined at an appropriate temperature, such as about 500°C. This results in a calcium carbonate support with silver being supported thereon in its elemental state. The catalyst may then be impregnated with solutions of the compounds serving as sources of the magnesium, iron and potassium promoters described in more detail hereafter, if so desired, and thereafter dried. As an alternative, the iron compound, magnesium compound and potassium salt may be dissolved in the same silver-containing impregnation solution used to form the coating paste or slurry with the calcium carbonate. The iron compound, magnesium compound and the potassium salt may also be introduced at different steps of the catalyst preparation or by means other than impregnation.

Calcium carbonate may also be obtained from commercial sources having levels of magnesium and, optionally, iron “impurities” sufficiently high to render such materials directly usable as support materials in the present invention. Such levels may, of course, be supplemented by impregnating or otherwise combining the commercially obtained calcium carbonate with additional quantities of iron or magnesium compounds.

The support material, before or after incorporation of the silver, potassium salt and iron and/or magnesium compounds, can be formed into shaped composites suitable for use in propylene oxide manufacture. The composites may be formed by any suitable technique. For instance, it is possible to form the composites by compressing the support materials into a mold having a desired configuration. The size of the particles may be selected to be appropriate for the formation of the composite and are often in the range of about 0.001 to about 5 millimeters in major dimension.

When coated catalysts, i.e., those catalysts in which calcium carbonate coated on a substructure are employed, a slurry of said material, in either powder or granular form, may be mixed with the particles of substructure support material and thereafter dried. As with the predominant or exclusive calcium carbonate support materials described above, the coated catalysts may also be prepared by using a solution of a silver compound, iron and/or magnesium compounds, and potassium salt or separate solutions of silver compound, iron and/or magnesium compounds and potassium salt to form the slurry, followed by suitable drying and calcination.

The surface area of the calcium carbonate support material generally is at least 0.6 $m^2/g$, preferably at least 1.5 $m^2/g$. However, calcium carbonate support materials having relatively high surface areas (e.g., 50 to 100$m^2/g$) are also effective for the purposes of this invention. This result was sur-prising in view of the preference generally expressed in the direct olefin oxidation field for low surface area supports (typically, 0.03 to 10 $m^2/g$). The surface area is measured by the conventional B. E. T. method using nitrogen or krypton described by Brunauer, Emmett and Teller in J. Am. Chem. Soc. 60, 309-16 (1938).

The support materials used in the present invention may generally be described as porous or microporous and typically have water pore volumes of about 0.05 to 0.80 cc/g.

The supported silver catalysts are typically used as individual particles of irregular shape and size. This is true both for the predominate or exclu-sive calcium carbonate supports as well as the calcium carbonate-coated supports. However, in some instances the supports, particularly the coated supports, may have a particular shape and size and this is especially true of the subsupports used with the calcium carbonate. Typically the subsupports are formed into aggregates or "pills" of a size and configuration to be usable in tubular reactors. These pills may be formed by conventional extrusion and firing techniques. The pills generally range in size from about 2 mm to about 15 mm, preferably about 3 mm to about 12 mm. The size is chosen to be consistent with the type of reactor employed. For example, in fixed bed reactor applications, sizes ranging from about 3 mm to about 10 mm have been found to be most suitable in the tubular reactors commonly utilized. The shapes of the carrier aggregates useful for purposes of the present invention can vary widely and can be any of the forms conventionally used in the heterogeneous catalyst art.

The calcium carbonate- and calcium carbonate-coated supports may be prepared as indicated above or obtained commercially. The supported catalyst of the present invention may be prepared by any known method of introducing silver and/or a promoter in soluble form to a support. A preferred method of introducing silver to the calcium carbonate support is by an impregnation process in which a solution of a silver compound (which can be a salt or complex of silver) in an amount sufficient to deposit the desired weight of silver upon the support is dissolved in a suitable solvent or "complexing/solubilizing" agent. The solution may be used to impregnate the support by immersing the support in the silver compound-containing impregnating solution and forming a pasty mixture or slurry. The slurry is then dried and calcined by placing the mixture in an oven or furnace at about 100 to about 120°C for 0.5 to 6 hours and then heating the mixture at a temperature of from about 250 to about 600°C for another 1 to 6 hours. This procedure accomplishes drying of the calcium carbonate/silver mixture, removes volatile components and reduces the silver present to its elemental form.

The potassium salt, optional iron compound, and magnesium compound may be introduced to the catalyst, either simultaneously or separately, as impregnation solutions in a separate impregnation step or steps. The order in which the promoters are added is not considered to be critical. Again, this may be done by any known manner of impregnating a porous material. Conveniently, this may be carried out by placing the catalyst material in a container, evacuating the container and thereafter introducing the solution(s). Alternatively, the support may be sprayed or sprinkled with the impregnating solution(s). The excess solution may then be allowed to drain off or the solvent may be removed by evaporation under reduced pressure at a suitable temperature. The catalyst may then be dried at a moderate temperature (e.g., 100 to 150°C) in an oven for one-half to five hours. Such a procedure is known as a "sequential" or "consecutive" method of preparation. The calcium carbonate-supported catalyst may also be prepared by a "simultaneous" or "coincidental" method of preparation. With this method, the potassium salt, iron compound (if used) and the magnesium compound are included in the silver compound-containing solution used to impregnate the support.

The choice of silver compound used to form the silver-containing impregnating solution in a solvent or a complexing/solubilizing agent is not particularly critical and any silver compound generally known to the art which is preferably both soluble in and does not react with the solvent or complexing/ solubilizing agent to form an unwanted product may be employed. Thus, the silver may be introduced to the solvent or complexing/solubilizing agent as an oxide or a salt, such as nitrate, carbonate, or carboxylate, for example, an acetate, propionate, butyrate, oxalate, malonate, malate, maleate, lactate, citrate, phthalate, fatty acid ester, and the like or combinations thereof. In one embodiment, silver (I) oxide is utilized. Insoluble forms of silver such as, for example, silver chloride may also be used if so desired.

A large number of solvents or complexing/solubilizing agents may be suitably used to form the silver compound-containing impregnating solution. Besides adequately dissolving the silver compound or converting it to a soluble form, a suitable solvent or complexing/solubilizing agent should be capable of being readily removed in subsequent steps, either by a washing, volatilizing or oxidation procedure, or the like. The complexing/solubilizing agent, preferably, should also permit solution to provide silver in the finished catalyst to the extent of preferably about 10 to about 60 percent silver, based on the total weight of the catalyst. It is also generally preferred that the solvents or complexing/solubilizing agents be readily miscible with water since aqueous solutions may be conveniently employed. Among the materials found suitable as solvents or complexing/solubilizing agents for the preparation of the silver compound-containing solutions are alcohols, including glycols, such as ethylene glycol, amines (including alkanolamines such as ethanolamine and alkyldiamines such as ethylene-diamine) and carboxylic acids, such as lactic acid and oxalic acid, as well as aqueous mixtures of such materials.

Typically, a silver compound-containing solution is prepared by dissolving a silver compound in a suitable solvent or complexing/solubilizing agent such as, for example, a mixture of water, ethylenediamine, oxalic acid, silver oxide, and monoethanolamine. The solution is then mixed with support particles and drained. Thereafter the particles are suitably dried.

As indicated above, after impregnation, the silver compound-impregnated support particles are treated to convert the silver compound to silver metal and thereby effect deposition of metallic silver on the surface of the support. As used herein, the term "surface", as applied to the support, includes not only the external surfaces of the support but also the internal surfaces, that is, the surfaces defining the pores or internal portion of the support particles. This may be done by treating the impregnated particles with a reducing agent, such as hydrogen or hydrazine and/or by roasting, at an elevated temperature to decompose the silver compound and reduce the silver to its free metallic state. Certain solubilizing agents such as alkanolamines, alkyldiamines, and the like may also function as reducing agents.

Although at least a catalytically effective amount of silver must be present in the finished catalyst (meaning an amount that provides a measurable conversion of propylene to propylene oxide), the silver concentration preferably is from about 2 percent to 70 percent, by weight, based on the total weight of the catalyst. More preferably, the silver concentration ranges from about 10 to 60 percent by weight.

It has been unexpectedly discovered that the presence of potassium in the preparation of the supported silver catalyst significantly enhances the efficiency of said catalyst as a propylene epoxidation catalyst. Surprisingly, other alkali metals such as cesium which are well-known as promoters in the ethylene oxide art fail to improve catalyst performance to an appreciable extent. The potassium is introduced by means of a potassium salt, with the selection of particular anions as counter ions to the potassium cation being found to be critical to the attainment of optimum catalyst performance. The anion is preferably a nitrogen oxyanion (i.e., an anion or negative ion which contains both nitrogen and oxygen atoms) such as nitrate or nitrite. Potassium nitrate is the preferred potassium salt. Potassium compounds containing species capable of being converted to nitrogen oxyanions under the catalyst preparation or epoxidation conditions (i.e., which are nitrogen oxyanion precursors) are also suitable for use. For example, potassium salts containing carbon oxyanions (e.g., carbonate or bicarbonate) may be employed. Conversion of such species to the corresponding nitrogen oxyanions may be accomplished, for example, by exposing the catalyst to a nitrogen oxide species such as NO at an elevated temperature (e.g., 180°C to 350°C).

The efficiency-enhancing potassium salt may be introduced to the catalyst in any known manner. Thus, impregnation and deposition of silver and the potassium salt may be effected coincidentally or sequentially. For example, the support could be impregnated with a solution or solutions of the magnesium compound, potassium salt and silver compound, dried, and then calcined to reduce the silver compound and generate the active supported silver catalyst.

In order to perform coincidental impregnation, the potassium salt must be soluble in the same solvent or complexing/solubilizing agent used with the silver impregnating solution. With a sequential procedure in which the silver is added first, any solvent capable of dissolving the salt which will neither react with the silver nor leach it from the support is suitable. Aqueous solutions are generally preferred, but organic liquids, such as alcohols, may also be employed. Suitable procedures for effecting introduction of a potassium salt to a solid support are well known in the art.

The potassium salt is used in an amount sufficient to provide a potassium promoter concentration which results in an improvement in one or more of the catalytic properties (e.g., selectivity, activity, conversion, stability, yield) of the supported silver catalyst as compared to a catalyst not con-taining the potassium promoter. The precise amount will vary depending upon such variables as the composition in the feed stream, the amount of silver contained in the catalyst, the surface area of the support, the process conditions, e.g., space velocity and temperature, and morphology of support. It has been found, however, that a minimum of at least 0.5 percent by weight of the potassium promoter, calculated as cation, based on the total weight of the catalyst must be present for the catalyst to exhibit a significant advantage over an analogous catalyst containing no potassium promoter. Potassium concentrations as high as 10 percent by weight may be utilized, although generally little additional benefit is realized beyond a concentration of 5 weight percent. More preferably, the potassium promoter level is an amount corresponding to about 1 to about 3 weight percent K.

The other necessary component of the calcium carbonate-supported silver catalysts of this invention is a promoting amount of a magnesium promoter. An iron co-promoter may optionally also be present. Such additional promoter or promoters are sometimes referred to herein generally as the "secondary" promoter(s) to distinguish said component from the potassium promoter. "Promoting amount" means an amount that works effectively to provide an improvement in one or more catalytic properties of a catalyst as compared to a catalyst not containing a secondary promoter. The exact form(s) of the secondary promoter(s) under epoxidation operating conditions is (are) not known. The secondary promoter(s), it is believed, is (are) not present on the catalyst in the elemental form since the promoter(s) is (are) applied to the catalyst in the form of compounds (including ions, salts and/or complexes) and the reducing conditions generally used to reduce the silver to metallic silver are not usually sufficient to reduce such compounds to the elemental form.

While a magnesium secondary promoter may be used individually, it is particularly desirable to use both Mg and Fe promoters simultaneously as it has been unexpectedly found that such combination tends to improve catalyst performance synergistically. That is, the presence of both iron and magnesium promoters in the catalyst generally results in a greater than additive enhancement in catalyst selectivity and/or activity.

It is thought that the secondary promoter(s) deposited on the support or present on the catalyst during actual epoxidation conditions is (are) in the compound form, most probably in the form of an oxygen-containing or oxidic compound(s). However, the secondary promoter may be derived from a non-oxygen containing compound. The compound used to introduce the secondary promoter to the catalyst should be selected to avoid the introduction of other substances which poison or otherwise adversely affect catalyst selectivity or activity. Suitable types of iron and magnesium compounds include, but are not limited to, the oxides, halides (especially chlorides), nitrates, sulfates, carbonates, hydroxides, carboxylates (e.g., acetates) and the like.

The support is impregnated or otherwise combined with one or more secondary promoter compounds, including at least one magnesium compound. This may be done at the same time that the other components of the catalyst are added or before and/or later. In one advantageous and convenient embodiment of the invention, the secondary promoter compound(s), potassium salt and silver compound are incorporated into the catalyst simultaneously. In another desirable embodiment, the potassium salt is introduced after calcination of an impregnated support containing the silver compound and the secondary promoter compound(s).

The secondary promoter compound may be applied to the catalyst in the form of a solution or, alternatively, as a solid. Where the secondary promoter compound is soluble in the same solvent used to form impregnating solutions of the silver compound and/or potassium salt, for example, it will often be convenient to use an impregnation technique to introduce the secondary promoter compound into the catalyst. Such impregnation may be performed in either a sequential or coincidental manner with respect to silver compound or potassium salt impregnation. When the compound is applied as a solid, it is generally desirable to use a finely divided form of the secondary promoter compound and/or to grind, ball mill or otherwise intimately admix the components of the catalyst so as to achieve a relatively disperse and uniform distribution of the secondary promoter compound with the support.

The amount of secondary promoter is selected so as to provide an improvement in catalyst epoxidation performance (e.g., epoxide selectivity, activity, productivity) as compared to an analogous catalyst lacking such a promoter. Generally speaking, it will be desirable to have from 50 to 5000 ppm (more preferably, 100 to 2000 ppm) Fe in the supported silver catalyst. Preferred levels of the necessary magnesium promoter are from 500 to 20,000 ppm (more preferably, 1000 to 10,000 ppm) Mg.

The degree of benefit obtained within the above-defined limits will vary depending upon particular properties and characteristics, such as, for example, reaction conditions, catalyst preparative techniques, surface area and pore structure and surface chemical properties of the support utilized, silver content of the catalyst, and potassium content of the catalyst.

The presence of the indicated and claimed amounts of secondary promoter(s) in this specification and claims does not preclude the use of other activators, promoters, enhancers, stabilizers, improvers, and the like. For example, one or more promoters selected from the group consisting of Mo, W and Re may be added to the catalyst using conventional impregnation techniques, preferably at a concentration of 0.1 to 5 weight percent.

In the epoxidation process of this invention, propylene and an oxygen-containing gas (i.e., a gas comprising molecular oxygen) are brought together in a reactor in the presence of the previously described catalyst under conditions effective to accomplish at least partial oxidation of the propylene to the corresponding epoxide. Typical epoxidation conditions include temperatures within the reaction zone of the reactor on the order of about 180 to 350°C (more preferably, 200 to 300°C) and pressures from about 1 to about 60 atmospheres. To favor high selectivity to epoxide, it is desirable that the feed stream contain carbon dioxide and/or an organic halide (described in more detail hereafter). A gaseous nitrogen oxide species (described in more detail hereafter) is also desirably supplied to the reaction zone within the reactor by introducing said species to the feedstream containing propylene (fresh and/or recycled) and molecular oxygen.

Examples of nitrogen oxide species suitable for introduction in the feedstream include at least one of NO, $NO_2$, $N_2O_4$ $N_2O_3$or any gaseous substance capable of forming one of the aforementioned gases, particularly NO and $NO_2$, under epoxidation conditions, and mixtures of one of the foregoing, particularly NO, with one or more of CO, $PH_3$, $SO_3$ and $SO_2$. NO is the most preferred nitrogen oxide species.

The amount of gaseous nitrogen oxide species present is not critical, although it will be highly advantageous to expose the catalyst to the nitrogen oxide species either prior to use (as a preconditioning step), particularly where a nitrogen oxyanion precursor is utilized, or while being used in the epoxidation process. The optimum amount is determined, in part, by the particular potassium salt and secondary promoter compound(s) used and the concentrations thereof, and by other factors noted above which influence the optimum amount of potassium salt and secondary promoter. Typically, a suitable concentration of the nitrogen oxide species for epoxi-dation of propylene is about 0.1 to about 2,000 ppm by volume.

The "oxygen" employed in the reaction may be defined as including pure molecular oxygen, atomic oxygen, any transient radical species derived from atomic or molecular oxygen capable of existence under epoxidation conditions, mixtures of another gaseous substance with at least one of the foregoing, and substances capable of forming one of the foregoing under epoxidation conditions. The oxygen is typically introduced to the reactor either as air, commercially pure oxygen or other substance which under epoxidation conditions both exists in a gaseous state and forms molecular oxygen.

The gaseous components which are supplied to the reaction zone, or that region of the reactor where reactants and catalyst are brought together under epoxidation conditions, are generally combined before being introduced to the reactor. If desired, however, such components may alternatively be introduced separately or in various combinations. The feedstream having the particular composition previously described thus may be formed prior to or at the time the individual components thereof enter the reaction zone. The use of the term "feedstream" herein thus is not meant to limit the present process to the embodiment where all of the gaseous components are combined prior to introduction of said components into the reaction zone. The reactors in which the process and catalyst of the present invention are employed may be of any type known to the art. A brief description of several of the reactor parameters which may be used in the present invention is presented below.

In addition to propylene and oxygen, the feedstream also desirably contains a performance-enhancing organic halide such as an alkyl halide. The organic halide is preferably a volatile compound, i.e., a substance which predominantly exists in gaseous form under the temperature and pressure conditions present in the reaction zone. The normal boiling point of the organic halide is most preferably less than about 100°C at atmospheric pressure. Compounds containing from 1 to 10 carbon atoms are preferred. Most preferably, the alkyl halide is a chloride species. The term alkyl halide includes both saturated and unsaturated halides, such as ethylene dichloride, ethyl chloride, vinyl chloride, methyl chloride and methylene chloride. Preferably, ethyl chloride is employed as the organic halide. Mixtures of different organic halides may be employed. The amount of organic halide employed will vary depending upon a variety of factors, including the concentration of propylene being oxidized, the particular potassium salts and secondary promoter compounds, the concentration of nitrogen oxide species as well as other factors noted above as influencing the optimum amount of potassium salt and nitrogen oxide species. However, a suitable range of concentration for the organic halide in the oxidation of propylene is typically about 0.1 to about 2,000 ppm, more preferably about 25 to 500 ppm by volume, of the feedstream. In addition, a hydrocarbon, particularly a saturated hydrocarbon, such as methane, propane, or ethane or mixtures thereof, may be included in the feedstream. The feedstream may also contain a ballast or diluent, such as nitrogen, or other inert gas, particularly when air is used as the source of oxygen. Varying amounts of water vapor may also be present.

Carbon dioxide is also desirable under some conditions to include as a component of the feedstream in the epoxidation process of this invention. The presence of carbon dioxide, within certain limits, has been found to provide surprising improvement in the performance of catalysts within the scope of the invention. In particular, selectivity to propylene oxide generally will increase as the carbon dioxide concentration in the feedstream is increased. Desirable enhancements are generally observed using 1 to 60 volume % $CO_2$ in the feedstream, with 5 to 50 volume % $CO_2$ being preferred.

The components of the feedstream are most suitably present in the amounts shown in the following table:

| Component | Volume in % (or ppm) for Propylene Oxidation |
|---|---|
| propylene | about 2 to about 50% |
| oxygen | about 2 to about 10% |
| organic halide | 0 to about 2,000 ppm, more preferably, about 20 to 500 ppm |
| nitrogen oxide species | 0 to about 2,000 ppm |
| hydrocarbon other than propylene | 0 to about 80% |
| carbon dioxide | 0 to 60% |
| nitrogen or other ballast gas | remainder. |

Although the present invention can be used with any size and type of vapor phase epoxidation reactor, including both fixed bed and fluidized bed reactors known to the art, it is contemplated that the present invention will find most widespread application in standard fixed bed, multi-tubular reactors such as those now in use as ethylene oxide reactors. These generally include wall-cooled as well as adiabatic or non-wall-cooled reactors. Tube lengths may typically range from about 5 to about 60 feet but will frequently be in the range of from about 15 to about 45 feet. The tubes may have internal diameters from about 0.5 to about 2.5 inches and are expected to be typically from about 0.8 to about 1.5 inches. A plurality of tubes packed with catalyst arranged in parallel within a suitable shell may be employed. GHSV generally range from about 500 to about 10,000 $hr^{-1}$. Typically GHSV values range from about 800 to about 3,000 $hour^{-1}$ at pressures from about 1 to about 60 atmospheres, commonly about 1.1 to about 30 atmospheres. Contact times should be sufficient to convert 0.5 to 70%, preferably 5 to 30%, of the propylene.

## EXAMPLES

### Comparative Example 1

This example demonstrates the epoxidation performance obtainable from a calcium carbonate-supported silver catalyst wherein the catalyst contains very low non-promoting levels of magnesium and iron. The catalyst was prepared in accordance with the procedures described in Canadian Pat. No. 1,282,772 using a sample of calcium carbonate obtained from Aldrich Chemical Company containing 10 ppm Mg and 6 ppm Fe. Potassium nitrate and a silver compound were introduced to the catalyst by co-impregnation prior to calcination. The catalyst contained 38 weight % Ag and 1.9 weight % K.

Epoxidation of propylene was performed in a back-mixed reactor using 20cc of catalyst and a feedstream containing 10 vol. % propylene, 5 vol. % oxygen, 50 ppm ethyl chloride and 200 ppm NO (1200 $hr^{-1}$ GHSV). The reaction conditions were as follows: 250°C and 30 psig. Propylene oxide selectivity was 35%, propylene conversion was 7% and 2500 ppm propylene oxide were present in the exit stream from the reactor. Propylene oxide productivity was 0.45 $lb/ft^3 \cdot hr$.

### Comparative Example 2

Comparative Example 1 was repeated using a sample of calcium carbonate obtained from Fisher Scientific containing 5 ppm Mg and 5 ppm Fe. The catalyst contained 36 weight % Ag and 2.0 weight % K. Under the same epoxidation conditions as described in Comparative Example 1, the supported silver catalyst provided 27% propylene oxide selectivity, 6% propylene conversion and 1800 ppm propylene oxide in the exit stream. PO productivity was 0.32 $lb/ft^3 \cdot hr$.

### Example 3

Comparative Example 1 was repeated using a different sample of calcium carbonate obtained from Aldrich Chemical Company containing 2400 ppm Mg and 270 ppm Fe. The silver catalyst prepared using this calcium carbonate as a support (40 wt.% Ag, 2 wt.% K) provided 38% propylene oxide selectivity, 12% propylene conversion and 4700 ppm propylene oxide in the exit stream. PO productivity was 0.84 lb/ft$^3$ • hr. Both the activity and selectivity of the catalyst thus were improved as compared to the results obtained in Comparative Example 1.

Example 4

Comparative Example 1 was repeated using a sample of calcium carbonate obtained from Mallinkrodt containing 2600 ppm Mg and 380 ppm Fe. The silver catalyst prepared using this calcium carbonate as a support (40 wt.% Ag, 2 wt.% K) provided 35 % propylene oxide selectivity, 11.5% propylene conversion and 4300 ppm propylene oxide in the feedstream. PO productivity was 0.77 lb/ft$^3$ • hr. The activity of the catalyst thus was significantly improved over the catalysts of Comparative Examples 1 and 2 where much lower levels of Mg and Fe were present, without adversely affecting selectivity to the desired epoxide.

Example 5

Comparative Example 1 was repeated, but magnesium carbonate was added to the catalyst at the same time as the $KNO_3$ and silver compound in an amount effective to obtain 3000 ppm Mg in the final catalyst (39 wt.% Ag, 2 wt.% K). Propylene epoxidation using the catalyst indicated that activity was enhanced (10% propylene conversion) without sacrificing epoxide selectivity (35%). The exit stream contained 3000 ppm PO. PO productivity was 0.54 lb/ft$^3$ • hr.

Example 6

Example 5 was repeated, except that both magnesium carbonate and Fe(II)/Fe(III) oxide were added to provide Mg and Fe levels in the catalyst of 4100 ppm and 230 ppm respectively. The catalyst contained 37 weight % Ag and 2 weight % K. Propylene oxide selectivity was 38% at a propylene conversion of 10%, suggesting that the combination of Mg and Fe in promoting amounts unexpectedly improves both the activity and selectivity of the catalyst (compared to Example 5). The exit stream contained 3900 ppm PO. PO productivity was 0.70 $lb/ft^3 \cdot hr$.

Example 7

Example 6 was repeated using still higher levels of both Mg and Fe (7900 ppm and 670 ppm, respectively). Propylene oxide selectivity remained at 38%, while the propylene conversion increased slightly to 11%. The exit stream contained 4200 ppm PO. PO productivity was 0.75 $lb/ft^3 \cdot hr$.

Comparative Example 8

This example demonstrates that the addition of Fe alone has little or no effect on the overall performance of the catalyst. Comparative Example 1 was repeated, except that Fe(II)/Fe(III) oxide was added in an amount effective to provide a catalyst containing 700 ppm Fe (38 weight % Ag, 2 weight % K). While propylene conversion increased somewhat (from 7% to 9%), propylene oxide selectivity decreased from 35% to 30%. Only 2700 ppm PO was present in the exit stream. PO productivity was 0.48 $lb/ft^3 \cdot hr$.

Comparative Example 9

This example demonstrates that replacing the calcium carbonate support entirely with magnesium carbonate has a detrimental effect on catalyst performance. Comparative Example 1 was repeated, except that magnesium carbonate was substituted for calcium carbonate (catalyst composition: 41 wt.% Ag, 2 wt.% K, 11.4 wt.% Mg, 90 ppm Fe). Although 10% propylene conversion was observed, the selectivity to propylene oxide dropped to only 18% and only 1800 ppm PO was present in the exit stream. PO productivity was 0.32 $lb/ft^3 \cdot hr$.

**We Claim:**

**1.** A process for propylene epoxidation comprising contacting a feedstream comprising propylene and oxygen with a supported silver catalyst comprised of:

(a) a support comprised of calcium carbonate;

(b) a catalytically effective amount of silver;

(c) a promoting amount of a potassium promoter derived from a potassium salt comprising potassium cation and a nitrogen oxyanion or precursor thereof; and

(d) a promoting amount of a magnesium promoter.

**2.** The process of claim **1** wherein the supported silver catalyst is additionally comprised of a promoting amount of an iron promoter.

**3.** The process of claim **1** wherein the feedstream is additionally comprised of a gaseous additive selected from the group consisting of carbon dioxide, organic halides, nitrogen oxide species, and mixtures thereof.

**4.** The process of claim **1** wherein the supported silver catalyst contains 500 to 20,000 ppm Mg.

**5.** The process of claim **1** wherein the potassium salt is selected from the group consisting of potassium carbonate, potassium bicarbonate, potassium nitrate, potassium nitrite, and mixtures thereof.

**6.** The process of claim **1** wherein said contacting is performed at a temperature of from 180°C to 330°C.

**7.** The process of claim **1** wherein the supported silver catalyst has an elemental composition corresponding to 10 to 60 weight percent Ag, 0.5 to 10 weight percent K, 500 to 20,000 ppm Mg, and 0 to 5000 ppm Fe and is comprised of at least 25 weight percent of the alkaline earth metal compound.

**8.** The process of claim **1** wherein the magnesium promoter is derived from one or more magnesium compounds selected from the group consisting of magnesium oxide, magnesium nitrate, magnesium hydroxide, magnesium carbonate, magnesium chloride, and magnesium carboxylates.

**9.** A process for propylene epoxidation comprising contacting a feedstream comprising propylene and oxygen at a temperature of from 200°C to 300°C with a supported silver catalyst comprised of:

(a) a support comprised of calcium carbonate, wherein calcium carbonate comprises at least 25 wt. % of the supported silver catalyst;
(b) 10 to 60 wt. % Ag;
(c) 1 to 3 wt. % K derived from a potassium salt selected from the group consisting of potassium carbonate, potassium bicarbonate, potassium nitrate, potassium nitrite, and mixtures thereof;
(d) 500 to 20,000 ppm Mg;
(e) 0 to 5000 ppm Fe.

**10.** The process of claim **9** wherein the feedstream is additionally comprised of carbon dioxide.

**11.** The process of claim **9** wherein the feedstream is additionally comprised of a nitrogen oxide species.

**12.** The process of claim **9** wherein the feedstream is additionally comprised of an organic halide.

**13.** The process of claim **9** wherein the supported silver catalyst contains 100 to 2000 ppm Fe and 1000 to 10,000 ppm Mg.

**14.** A supported silver catalyst suitable for direct oxidation of propylene to propylene oxide comprised of:

(a) a support comprised of calcium carbonate, wherein calcium carbonate comprises at least 25 weight percent of the supported silver catalyst;
(b) from 2 to 70 weight percent silver;
(c) from 0.5 to 10 weight percent K derived from a potassium salt comprising potassium cation and nitrogen oxyanion or precursor thereof;

(d) from 0 to 5000 ppm Fe; and

(e) from 500 to 20,000 ppm Mg.

**15.** The supported silver catalyst of claim **14** wherein the supported silver catalyst contains 100 to 2000 ppm Fe and 1000 to 10,000 ppm Mg.

**16.** The supported silver catalyst of claim **14** wherein the potassium salt is selected from the group consisting of potassium carbonate, potassium bicarbonate, potassium nitrate, potassium nitrite and mixtures thereof.

**17.** The supported silver catalyst of claim **14** which is additionally comprised of a promoting amount of a metallic promoter selected from the group consisting of rhenium, molybdenum, tungsten, and mixtures thereof.

**18.** The supported catalyst of claim **14** wherein calcium carbonate comprises at least 35 weight percent of the supported silver catalyst and the supported silver catalyst has an elemental composition corresponding to 10 to 60 weight percent Ag, at least 100 ppm Fe, at least 1000 ppm Mg. and 1 to 3 weight percent K.

# INTERNATIONAL SEARCH REPORT

Intern al Application No
PCT/EP 98/03965

**A. CLASSIFICATION OF SUBJECT MATTER**
IPC 6 C07D301/10 B01J23/66 B01J32/00

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C07D B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category ° | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| A | US 5 625 084 A (PITCHAI RANGASAMY ET AL) 29 April 1997<br>cited in the application<br>see claims<br>--- | 1-17 |
| A | CA 1 282 772 A (UNION CARBIDE CORP) 9 April 1991<br>cited in the application<br>see claims<br>--- | 1-17 |
| A | US 4 007 135 A (HAYDEN PERCY ET AL) 8 February 1977<br>see column 3, lines 1-13<br>--- | 1-17 |
| A | EP 0 480 537 A (UNION CARBIDE CHEM PLASTIC) 15 April 1992<br>see examples<br>---<br>-/-- | 1-17 |

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

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|---|---|
| Date of the actual completion of the international search<br>30 September 1998 | Date of mailing of the international search report<br>07/10/1998 |
| Name and mailing address of the ISA<br>European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,<br>Fax: (+31-70) 340-3016 | Authorized officer<br>Steendijk, M |

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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