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(54) **Title:** HYDRO-OXIDATION PROCESS USING A CATALYST CONTAINING GOLD AND A HALOGEN-CONTAINING COMPOUND

(57) **Abstract:** A process for the hydro-oxidation of an olefin having three or more carbon atoms, such as propylene, to form an olefin oxide, such as propylene oxide. The process involves contacting the olefin with oxygen in the presence of hydrogen and a hydro-oxidation catalyst containing gold deposited on a titanium-containing support, preferably, a titanosilicate, and in the presence of a halogen-containing compound, preferably, a promoter halide, such as a promoter chloride or a mixture of promoter chloride with one or more promoter fluorides, bromides, and/or iodides, wherein the promoter comprises a Group 1, Group 2, lanthanide rare earth, or actinide metal. The halogen-containing compound improves catalyst selectivity, hydrogen efficiency, and/or productivity, while reducing the formation of water which is formed both as a co-product and by-product of the process.

HYDRO-OXIDATION PROCESS USING A CATALYST CONTAINING GOLD AND A HALOGEN-CONTAINING COMPOUND

CROSS-REFERENCE TO RELATED APPLICATION

This application claims the benefit of US Provisional Application Serial No. 60/986024, filed November 7, 2007.

FIELD OF THE INVENTION

This invention pertains to a process and catalyst for the hydro-oxidation of an olefin, such as propylene, by oxygen in the presence of hydrogen to form an olefin oxide, such as propylene oxide.

BACKGROUND

Olefin oxides, such as propylene oxide, are used to alkoxylate alcohols to form polyether polyols, which find utility in the manufacture of polyurethanes and synthetic elastomers. Olefin oxides are also important intermediates in the manufacture of alkylene glycols, such as propylene glycol, and alkanolamines, such as isopropanolamine, which are useful as solvents and surfactants.

Propylene oxide is produced commercially via a chlorohydrin process wherein propylene is reacted with an aqueous solution of chlorine to produce a mixture of propylene chlorohydrins, which are dehydrochlorinated with an excess of alkali to produce propylene oxide. This process suffers from the production of a low concentration salt stream. (See K. Weissermel and H. J. Arpe, *Industrial Organic Chemistry*, 2nd ed., VCH Publishers, Inc., New York, NY, 1993, pp. 264-265.)

Another well-known route to olefin oxides relies on the transfer of an oxygen atom from an organic hydroperoxide or peroxycarboxylic acid to an olefin. In a first step, a peroxide generator, such as isobutane, ethylbenzene, or acetaldehyde, is autoxidized with oxygen to form a peroxy compound, such as t-butyl hydroperoxide, ethylbenzene hydroperoxide, or peracetic acid. The organoperoxy compound is used to epoxidize the olefin, typically in the presence of a transition metal catalyst, for example, a titanium, vanadium, or molybdenum compound or complex. Along with the olefin oxide, this process produces equimolar amounts of co-product alcohol, such as t-butanol or methylphenyl-carbinol, or co-product carboxylic acid, such as acetic acid. The co-products must be recycled or their value must be captured in a market place.

More recently, propylene oxide is industrially manufactured by the direct reaction of propylene with hydrogen peroxide in the presence of a titanosilicate catalyst. Water is the only stoichiometric co-product; but this process does rely on a source of hydrogen peroxide.

The direct oxidation of propylene by oxygen to propylene oxide has been the subject of numerous investigations. Recent focus turned to hydro-oxidations wherein propylene is oxidized with oxygen in the presence of hydrogen to form propylene oxide in a selectivity typically greater than 90 mole percent, as illustrated, for example, in WO 98/00413, WO 98/00415, and WO 00/59632. The catalyst for the hydro-oxidation advantageously comprises gold, silver, and/or a platinum group metal deposited on a titanium-containing support, such as, a titanosilicate or titanium dioxide. Water is produced as a co-product of the hydro-oxidation, as a by-product in the direct oxidation of hydrogen by oxygen, and as a by-product in complete combustion of partially-oxidized organic products, such as the olefin oxide itself. A measure of the efficiency of hydrogen usage is advantageously given as moles of water per mole of olefin oxide (OO) produced (H_2O/OO ratio), or for propylene oxide in particular, moles of water per mole of propylene oxide produced (H_2O/PO).

International patent publications WO 98/00414 and WO 00/59632 disclose the addition of a promoter, such as a Group 1, Group 2, lanthanide rare earth, or actinide compound, to the hydro-oxidation catalyst as providing for improved catalyst lifetime, increased catalyst activity, improved olefin oxide selectivity, and/or lower water production, as compared with the performance of an identical catalyst absent the promoter. Nevertheless, if the direct hydro-oxidation of an olefin to an olefin oxide is to be commercialized, further improvements are needed in catalyst activity and/or hydrogen efficiency with concomitant reduction in water production.

SUMMARY OF THE INVENTION

This invention provides for an improved hydro-oxidation process of preparing an olefin oxide comprising contacting an olefin having three or more carbon atoms with oxygen in the presence of hydrogen and in the presence of a hydro-oxidation catalyst comprising gold deposited on a titanium-containing support, the gold being provided to the catalyst from a source of gold, and the contacting being conducted under process conditions sufficient to produce the corresponding olefin oxide. The improvement in the aforementioned hydro-oxidation process comprises conducting the process in the presence of a halogen-containing compound such that the process employs a halogen to gold atomic ratio greater than the corresponding halogen to gold atomic ratio of the source of gold. As used herein, the term "halogen" is intended to encompass any covalently-bonded or ionically-bonded form of halogen, as detailed hereinafter. The halogen-containing compound may be supplied to the catalyst prior to use, or alternatively, may be fed to the process in a gaseous or liquid phase. As a proviso, when cesium or palladium is present in the catalyst with chloride or a chlorine-containing compound, then the catalyst comprises at least one additional halogen other than chlorine.

The novel process of this invention is drawn towards use of a halogen-containing compound in a hydro-oxidation process for improving the production of olefin oxide directly from an olefin having three or more carbon atoms and oxygen in the presence of hydrogen. Without being bound to the following advantages, a selectivity to olefin oxide of greater than about 90 mole percent, based on the moles of olefin converted, is typically achieved. Undesirable partial and complete combustion products, such as acrolein and carbon dioxide, are produced in low amounts, which mean that the total selectivity to these partially-oxidized and/or fully-oxidized by-products is less than about 10 mole percent, based on the moles of olefin converted. As a further advantage, the hydrogen efficiency of the process of this invention is improved over prior art processes, which means that the molar ratio of water to olefin oxide produced (H_2O/OO) is typically lower as compared to prior art processes. In preferred embodiments, for example, a H_2O/OO molar ratio of less than about 6:1 can be advantageously achieved over sustained periods of time, whereas the prior art exhibits ratios up to 10:1 over a comparable time frame. As a further advantage, the process of this invention achieves an improved catalyst activity with consequential improvement in productivity, as compared with prior art processes. Activity is advantageously measured as moles of olefin converted to all products; while productivity is advantageously measured in grams olefin oxide produced per kilogram catalyst per hour.

In another aspect, this invention provides for a novel catalyst composition comprising gold and a halogen-containing compound deposited on a titanium-containing support; the gold being provided to the catalyst from a source of gold such that the catalyst possesses a halogen to gold atomic ratio greater than the corresponding halogen to gold atomic ratio of the source of gold. As a proviso, when cesium or palladium is present in the catalyst with chloride or a chlorine-containing compound, then the catalyst comprises at least one additional halogen other than chlorine.

The novel composition of this invention can be effectively employed in the aforementioned hydro-oxidation process wherein an olefin having three or more carbon atoms is converted to its corresponding olefin oxide. Besides being selective for the olefin oxide, the novel catalyst of this invention exhibits improved activity, improved hydrogen efficiency, and/or improved productivity, as compared with gold catalysts of the prior art.

DETAILED DESCRIPTION

Certain phrases, terms, and words used in this Application are defined hereinafter. When interpreting a meaning of a phrase, term, or word, its definition here governs, unless for a particular use, a different meaning is stated elsewhere in this specification or unless a context of the use of the phrase, term, or word clearly indicates a different meaning is intended from the definitions provided herein.

The articles “a” and “the” refer to singular and plural forms of what is being modified by the articles. When used in front of a first member of a list of two or more members, the words “a” and “the” independently refer to each member in the list. As used herein, "a," "an," "the," "at least one," and "one or more" are used interchangeably. The term "comprises" and variations thereof do not have a limiting meaning where these terms appear in the description and claims. Thus, for example, a reactant mixture that comprises "an" olefin can be interpreted to mean that the olefin includes "one or more" olefins.

All percentages, preferred amounts or measurements, ranges and endpoints thereof are inclusive, that is, “a range from 5 to 10” includes 5 and 10. “At least” is equivalent to “greater than or equal to,” and “at most” is, thus, equivalent to “less than or equal to.” Numbers herein have no more precision than stated. Thus, “115” includes at least from 114.6 to 115.4. All ranges from a parameter described as “at least,” “greater than,” “greater than or equal to” or similarly, to a parameter described as “at most,” “up to,” “less than,” “less than or equal to” or similarly are preferred ranges regardless of the relative degree of preference indicated for each parameter. Thus, a range that has an advantageous lower limit combined with a most preferred upper limit is preferred for the practice of this invention. The term “advantageously” is used to denote a degree of preference more than required, but less than is denoted by the term “preferably.”

Unless stated otherwise, when an element, material, or step capable of causing undesirable effects is present in amounts or in a form such that it does not cause the effect to an unacceptable degree, that element, material, or step is considered substantially absent for the practice of this invention. Those skilled in the art recognize that acceptable limits vary with equipment, conditions, applications, and other variables, but are determinable without undue experimentation in each situation where they are applicable. In some instances, variation or deviation in one parameter is acceptable to achieve another desirable end.

As used herein, the phrase “having the formula” or “represented by the formula” is not intended to be limiting and is used in the same manner as the term “comprising” is commonly used.

The term "comprising," is synonymous with "including," "containing," or "characterized by," is inclusive or open-ended and does not exclude additional, unrecited elements, material, or steps. The term “consisting essentially of” indicates that in addition to specified elements, materials, or steps, unrecited elements, materials or steps are optionally present in amounts that do not unacceptably materially affect at least one basic and novel characteristic of the subject matter. The term “consisting of” indicates that only stated elements, materials or steps are present except that unrecited elements, materials or steps are optionally present to an extent that has no appreciable effect, or are substantially absent.

The word “optionally” means “with or without,” that is, not mandatory and left to one’s choice. As an example, to say “optionally, a promoter” means with or without a promoter.

The words "the process" or the words "the hydro-oxidation process" as used hereinafter refer to the process of this invention as described herein,

The number of carbon atoms or a range thereof forming a moiety or compound is defined by prefixing the moiety or compound with a formula "C_m" or "C_m-C_n," respectively, wherein m and n are integers. For example, a C_1-C_{10} hydrocarbyl means the hydrocarbyl has a number of carbon atoms in a range from one (1) to ten (10) carbon atoms.

Abbreviations and symbols "g," "h," "L," "ml," "mol," "mmol," "NMR," "°C," "psia (kPa)," and "%" are used, respectively, for "gram," "hour" "liter," "milliliter," "mole," "millimole," "nuclear magnetic resonance," "degree Celsius," "pounds per square inch absolute (kilopascals), and "percent," respectively, and plural forms thereof.

For the purposes of this invention, all citations herein to chemical Group(s) and elements are referenced with respect to the Periodic Table of the Elements, *CRC Handbook of Chemistry and Physics*, 75th ed., CRC Press, 1994.

The relevant teachings of each reference cited herein are incorporated to the maximum extent allowed by United States law. In the event of a conflict between a portion of an incorporated reference and this Application, this Application takes precedence.

Several chemical terms may be used that, for clarity, are defined hereinafter.

A "hydrocarbyl" moiety is defined as a monovalent moiety derived from a hydrocarbon by removal of one hydrogen atom from one carbon atom. A "hydrocarbon" shall have its ordinary meaning referring to a compound composed of carbon and hydrogen atoms. A hydrocarbyl can be an alkyl, alkenyl, alkynyl, or aryl, which is defined as a monovalent moiety derived from an alkane, alkene, alkyne, or arene, respectively, by removal of one hydrogen atom from one carbon atom.

The term "alkyl" refers to a saturated monovalent hydrocarbyl radical, which may be linear, branched, or cyclic (alicyclic). If linear or branched, the radical advantageously contains from 1 to about 30 carbon atoms, for example, methyl, ethyl, propyl, isopropyl, butyl, iso-butyl, tert-butyl, and the like. If cyclic (alicyclic), the radical advantageously contains from 4 to about 8 carbon atoms, such as cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, and cyclooctyl. Preferably, the linear or branched alkyl radical contains from about 1 to about 12 carbon atoms; and the alicyclic radical contains from about 5 to about 7 carbon atoms, exclusive of carbon-containing substituents. An alkyl can be a primary alkyl, secondary alkyl, or tertiary alkyl, which has two or three hydrogen atoms, one hydrogen atom, or no hydrogen atom, respectively; on the carbon atom that forms the alkyl.

The term "alkylene" as used herein refers to a linear, branched, or cyclic divalent alkyl radical.

The term "olefin" as used herein refers to a class of unsaturated aliphatic hydrocarbons having one or more carbon-carbon double bonds (C=C) (absent aromatic character as defined hereinbelow).

The term "aromatic" refers to a polyatomic, cyclic, conjugated ring system containing ($4\delta+2$) π-electrons, wherein δ is an integer greater than or equal to 1. The term "fused" as used herein with respect to a ring system containing two or more polyatomic, cyclic rings means that with respect to at least two rings thereof, at least one pair of adjacent atoms is included in both rings.

The term "aryl" refers to a monovalent aromatic radical. Examples of aryl moieties include phenyl, naphthyl, anthracenyl, and biphenyl.

As used herein, any and all of the terms "hydrocarbyl," "alkyl," "alkylene," "olefin," "aromatic," and "aryl" are intended to include substituted variants thereof. The term "substituted" or the words "substituted variants thereof" refer to replacement of one or more H or C atoms in the compound or radical by one or more heteroatoms or one or more functional groups that contain one or more heteroatoms, including but not limited to nitrogen, oxygen, sulfur, phosphorus, boron, chlorine, bromine, and iodine. For example, "halo" substitution refers to replacement of a hydrogen atom by chlorine, bromine, or an iodine atom.

As described herein, there is provided an improved hydro-oxidation process for producing an olefin oxide comprising contacting an olefin having three or more carbon atoms with oxygen in the presence of hydrogen and a hydro-oxidation catalyst comprising gold deposited on a titanium-containing support, the gold being provided to the support from a source of gold, and the contacting being conducted under process conditions sufficient to prepare the corresponding olefin oxide. Optionally, a diluent can be employed in the process. The relative molar quantities of olefin, oxygen, hydrogen, and optional diluent can be any quantities sufficient to prepare the desired olefin oxide, preferably, the quantities noted hereinafter. In a preferred embodiment of this invention, the olefin is a C_{3-12} olefin, which is converted to the corresponding C_{3-12} olefin oxide. In a more preferred embodiment, the olefin is a C_{3-8} olefin, which is converted to the corresponding C_{3-8} olefin oxide. In a most preferred embodiment, the olefin is propylene, and the olefin oxide is propylene oxide. The improvement of the aforementioned hydro-oxidation process comprises conducting the process in the presence of a halogen-containing compound such that the process employs a halogen to gold atomic ratio greater than the corresponding halogen to gold atomic ratio of the source of gold. The halogen-containing compound may be fed to the process supplied to the catalyst prior to use, or alternatively, fed to the process in a separate gas or liquid stream. As a proviso, when cesium or palladium is present in the catalyst with chloride or a chlorine-containing compound, then the catalyst comprises at least one additional halogen other than chlorine and/or chloride.

In another aspect, the catalyst employed in the hydro-oxidation process of this invention comprises gold and at least one halogen-containing compound deposited on a titanium-containing support; the gold being provided to the catalyst from a source of gold such that the catalyst possesses a halogen to gold atomic ratio greater than the corresponding halogen to gold atomic ratio of the source of gold. As a proviso, when cesium or palladium is present in the catalyst with chloride or a chlorine-containing compound, then the catalyst comprises at least one additional halogen other than chlorine.

In one preferred embodiment, the halogen of the halogen-containing compound is a selected from fluoride, chloride, bromide, and iodide, and mixtures of chloride with fluoride, bromide, and/or iodide.

In another preferred embodiment, the halogen-containing compound is selected from promoter metal halides wherein the promoter metal is selected from silver, Group 1, Group 2, the lanthanide rare earths, the actinide elements, and mixtures thereof. In a most preferred embodiment, the halogen-containing compound is a promoter metal halide selected from the fluorides, chlorides, bromides, and iodides of silver, lithium, sodium, potassium, rubidium, cesium, barium, magnesium, calcium, erbium, lutetium, and mixtures of the aforementioned chlorides with the aforementioned fluorides, bromides, and/or iodides.

Any olefin containing three or more carbon atoms or mixture of such olefins can be employed in the process of this invention. Monoolefins are suitable, as are compounds containing two or more olefinic bonds, such as dienes. The olefin can be a simple hydrocarbon containing only carbon and hydrogen atoms; or alternatively, the olefin can be substituted at any of the carbon atoms with an inert substituent. The term "inert", as used herein, requires the substituent to be substantially non-reactive in the process of this invention. Suitable inert substituents include, but are not limited to halogen, ether, ester, alcohol, and aromatic moieties; preferably, chloro, C_{1-12} ether, C_{1-12} ester, and C_{1-12} alcohol moieties, and C_{6-12} aromatic moieties. Non-limiting examples of olefins suitable for the process of this invention include propylene, 1-butene, 2-butene, 2-methylpropene, 1-pentene, 2-pentene, 2-methyl-1-butene, 2-methyl-2-butene, 1-hexene, 2-hexene, 3-hexene, and analogously, the various isomers of methylpentene, ethylbutene, heptene, methylhexene, ethylpentene, propylbutene, the octenes, including preferably 1-octene, and other higher analogues of these; as well as butadiene, cyclopentadiene, dicyclopentadiene, styrene, α-methylstyrene, divinylbenzene, allyl alcohol, allyl ether, allyl ethyl ether, allyl butyrate, allyl acetate, allyl benzene, allyl phenyl ether, allyl propyl ether, and allyl anisole. Preferably, the olefin is an unsubstituted or substituted C_{3-12} olefin, more preferably, an unsubstituted or substituted C_{3-8} olefin. Most preferably, the olefin is propylene. Many of the aforementioned olefins are available commercially; others can be prepared by chemical processes known to those skilled in the art.

The quantity of olefin employed can vary over a wide range provided that the corresponding olefin oxide is produced in the process. Advantageously, the quantity of olefin depends upon the specific process features, including for example, the design of the reactor, the specific olefin, and economic and safety considerations. Those skilled in the art will know how to determine a suitable range of olefin concentrations for the specific process features. In light of the disclosure herein, the quantity of olefin is advantageously greater than about 1, preferably, greater than about 10, and more preferably, greater than about 20 mole percent, based on the total moles of olefin, oxygen, hydrogen, and optional diluent. Advantageously, the quantity of olefin is less than about 99, preferably, less than about 85, and more preferably, less than about 70 mole percent, based on the total moles of olefin, oxygen, hydrogen, and optional diluent.

Oxygen is also required for the process of this invention. Any source of oxygen is acceptable, including air or essentially pure molecular oxygen. Other sources of oxygen may be suitable, including ozone and nitrogen oxides, such as nitrous oxide. Molecular oxygen is preferred. The quantity of oxygen employed can vary over a wide range provided that the quantity is sufficient for producing the desired olefin oxide. Advantageously, the number of moles of oxygen per mole of olefin used in the feedstream is less than 1. Preferably, the quantity of oxygen is greater than about 0.01, more preferably, greater than about 1, and most preferably greater than about 5 mole percent, based on the total moles of olefin, hydrogen, oxygen, and optional diluent. Preferably, the quantity of oxygen is less than about 30, more preferably, less than about 25, and most preferably less than about 20 mole percent, based on the total moles of olefin, hydrogen, oxygen, and optional diluent. Above about 20 mole percent, the concentration of oxygen may fall within the flammable range for olefin-hydrogen-oxygen mixtures.

Hydrogen is also required for the process of this invention. In the absence of hydrogen, the activity of the catalyst is significantly decreased. Any source of hydrogen can be used in the process of this invention, including for example, molecular hydrogen obtained from the dehydrogenation of hydrocarbons and alcohols. In an alternative embodiment of this invention, the hydrogen may be generated *in situ* in the olefin oxidation reactor, for example, by dehydrogenating alkanes, such as propane or isobutane, or alcohols, such as isobutanol. Alternatively, hydrogen may be used to generate a catalyst-hydride complex or a catalyst-hydrogen complex which can provide the necessary hydrogen to the process.

Any quantity of hydrogen can be employed in the process provided that the amount is sufficient to produce the olefin oxide. Suitable quantities of hydrogen are advantageously greater than about 0.01, preferably, greater than about 0.1, and more preferably, greater than about 3 mole percent, based on the total moles of olefin, hydrogen, oxygen, and optional diluent. Suitable quantities of hydrogen are advantageously less than about 50, preferably, less than about 30, and more preferably, less than about 20 mole percent, based on the total moles of olefin, hydrogen, oxygen, and optional diluent.

In addition to the above reagents, it may be desirable to employ a diluent with the reactants, although the use thereof is optional. Since the process of this invention is exothermic, a diluent beneficially provides a means of removing and dissipating the heat produced. In addition, the diluent provides an expanded concentration regime in which the reactants are non-flammable. The diluent can be any gas or liquid that does not inhibit the process of this invention. The specific diluent chosen will depend upon the manner in which the process is conducted. For example, if the process is conducted in a gas phase, then suitable gaseous diluents include, but are not limited to, helium, nitrogen, argon, methane, carbon dioxide, steam, and mixtures thereof. Most of these gases are essentially inert with respect to the process of this invention. If the process is conducted in a liquid phase, then the diluent can be any oxidation stable and thermally stable liquid. Examples of suitable liquid diluents include aliphatic alcohols, preferably C_{1-10} aliphatic alcohols, such as methanol and t-butanol; chlorinated aliphatic alcohols, preferably C_{1-10} chlorinated alkanols, such as chloropropanol; chlorinated hydrocarbons, preferably C_{1-10} chlorinated hydrocarbons, such as dichloroethane and chlorinated benzenes, including chlorobenzene and dichlorobenzene; aromatic hydrocarbons, preferably, C_{6-15} aromatic hydrocarbons, such as benzene, toluene, and xylenes; ethers, preferably, C_{2-20} ethers, including tetrahydrofuran and dioxane; as well as liquid polyethers, polyesters, and polyalcohols.

If a diluent is used in the gas phase, the amount of diluent is advantageously greater than about 0, preferably greater than about 0.1, and more preferably, greater than about 15 mole percent, based on the total moles of olefin, oxygen, hydrogen, and diluent. If a diluent is used in the gas phase, the amount of diluent is advantageously less than about 90, preferably, less than about 80, and more preferably, less than about 70 mole percent, based on the total moles of olefin, oxygen, hydrogen, and diluent. If a liquid diluent (or solvent) is used in the liquid phase, the amount of liquid diluent (or solvent) is advantageously greater than about 0, and preferably, greater than about 5 weight percent, based on the total weight of the olefin and diluent. If a liquid diluent is used in the liquid phase, the amount of liquid diluent is advantageously less than about 99, and preferably, less than about 95 weight percent, based on the total moles of olefin and diluent.

The concentrations of olefin, oxygen, hydrogen, and diluent disclosed hereinabove are suitably based on the reactor designs and process parameters disclosed herein. Those skilled in the art will recognize that concentrations other than those disclosed herein may be suitably employed in other various engineering realizations of the process.

The unique catalyst employed in the hydro-oxidation process of this invention comprises gold and at least one halogen-containing compound deposited on a titanium-containing support. The gold may exist as metallic gold or oxidized gold, as determined by any suitable analytical technique, for example, X-ray photoelectron spectroscopy (XPS) and/or high resolution transmission electron spectroscopy (HR-TEM), known to those of skill in the art. Mie scattering, measured on an ultraviolet-visible diffuse reflectance spectrometer (UV-VIS DRS) scanning, for example, through the 525 nm region, can also be employed to analyze for the presence or absence of metallic gold. A gold elemental analysis can confirm the presence of gold and, by implication, oxidized gold when other techniques do not reveal the presence of metallic gold particles. Preferably, the gold oxidation state ranges from 0 to about +3. Advantageously, the average size of metallic gold particles, when they are present, ranges from about 10 Å to about 500 Å, but preferably, from about 10 Å to about 35 Å, as measured by HR-TEM.

The gold loading on the support may be any amount that yields an active hydro-oxidation catalyst for the process of this invention. Advantageously, the gold loading is greater than about 0.001 weight percent (10 parts per million, ppm), and preferably, greater than about 0.005 weight percent (50 ppm), based on the total weight of the catalyst. Advantageously, the gold loading is less than about 20, preferably, less than about 10, and more preferably, less than about 5.0 weight percent, based on the total weight of the catalyst.

The titanium-containing support can be any solid wherein titanium comprises an integral component of the solid's framework structure, or wherein titanium is grafted or deposited onto a solid structure, or wherein a combination of framework and grafted or deposited titanium is present. The titanium-containing support can be crystalline, quasi-crystalline, or amorphous. The titanium is present essentially as non-metallic titanium.

Suitable supports include, without limitation, titanium-containing amorphous and crystalline silicas, such as Ti-silicalite or Ti-MCM-41; titanium-containing aluminas; titanium-containing metallosilicates, including Ti-aluminosilicates and preferably titanosilicates; titanium-containing promoter metal silicates, such as, the Ti-silicates of Groups 1 and 2 and the lanthanide and actinide elements; and other titanium-containing refractory oxides and conventional support materials.

Also suitable as the support are stoichiometric and non-stoichiometric promoter metal titanates of a crystalline or amorphous nature, having a surface area greater than about 5 m^2/g, non-limiting examples of which include such titanates of Group 1, Group 2, and the lanthanide and actinide metals. Suitably, the promoter metal titanate is selected from the group consisting of magnesium titanate, calcium titanate, barium titanates, strontium titanate, sodium titanate, potassium titanate, lithium titanate, cesium titanate, rubidium titanate, and the titanates of erbium, lutetium, thorium, and uranium. As a further suitable support, an amorphous or crystalline titanium oxide including anatase, rutile, and brookite phases of titanium dioxide, preferably, having a surface area greater than 5 m^2/g, can be advantageously employed.

Preferred titanium-containing supports are also described in WO 98/00413, WO 98/00414, WO 98/00415, and US-B1-6,255,499, all references incorporated herein by reference.

In those instances wherein titanium is affixed onto or into the support, the titanium loading can be any that gives rise to an active catalyst in the process of this invention. Advantageously, the titanium loading is greater than about 0.02 weight percent, preferably, greater than about 0.1 weight percent, based on the weight of the support including any binder as noted hereinafter. Advantageously, the titanium loading is less than about 35 weight percent, and preferably, less than about 10 weight percent, based on the weight of the support including any binder. It is to be understood that in cases wherein titanium is a stoichiometric component of the support, such as in promoter metal titanates, the weight percentage of titanium in the support can be higher than 35 weight percent.

A preferred titanium-containing support comprises a nanoporous material. The word “nanoporous” as used in this context refers to the presence of channels, pores and/or cavities within the support’s framework structure, of a width (or largest dimension) ranging from about 0.5 nm to about 50 nm. Such porous structures possess micropores, taken as pore widths not exceeding about 2 nm, and mesopores, taken as pore widths between about 2 nm and 50 nm. Larger void spaces, between particles or interior to a particle, of a width greater than 50 nm are not included in the term “nanoporous.” The distribution of the channels, pores, and/or cavities can be regular or irregular; and the pores and/or channels may be one, two, or three dimensional.

The distribution of pore widths in the titanium-containing support can be determined from adsorption isotherms using, for example, nitrogen gas at the temperature of the boiling point of nitrogen at ambient atmospheric pressure. The surface area of the support can be determined by the Brunauer-Emmett-Teller (BET) gas adsorption method. For a more complete discussion of these techniques, refer to American National Standard Testing Method, ASTM D 3663-78 and to IUPAC, K. S. W. Sing, et al., "Reporting Physisorption Data for Gas/Solid Systems – with special Reference to the Determination of Surface Area and Porosity," Pure & Applied Chemistry, Vol. 57, No. 4 (1985), pp. 603-619, incorporated herein by reference. Advantageously, the nanoporous titanium-containing support possesses a surface area greater than about 5 m^2/g, preferably, greater than about 50 m^2/g, more preferably, greater than about 150 m^2/g, as determined by the BET method.

In a more preferred embodiment, the support comprises a nanoporous titanosilicate, even more preferably, a titanosilicate zeolite. An even more preferred titanium-containing support comprises a nanoporous titanosilicate selected from TS-1, TS-2, Ti-beta, Ti-MCM-41, Ti-MCM-48, Ti-SBA-15, and Ti-SBA-3. A most preferred titanosilicate comprises a quasi-crystalline titanosilicate having an MFI structure, which is orthorhombic at room temperature (21°C), as determined by X-ray diffraction (XRD). Such a support and its method of preparation are disclosed in US 6,255,499, incorporated herein by reference.

The silicon to titanium atomic ratio (Si:Ti) of the preferred nanoporous titanosilicate support can be any ratio that provides for an active hydro-oxidation catalyst in the process of this invention. An advantageous Si:Ti atomic ratio is greater than about 5:1, preferably, greater than about 35:1, more preferably, greater than about 50:1. An advantageous Si:Ti atomic ratio is less than about 2000:1, preferably, less than about 1000:1, and more preferably, less than about 250:1. Even more preferably, the titanosilicate support is essentially free of anatase phase titania, as determined by Raman spectroscopy as known to the skilled person.

Any combination or mixture of titanium-containing supports described hereinabove can be employed in the catalyst of this invention.

The titanium-containing support may be shaped into any form suitable for catalyst particles, for example, beads, pellets, spheres, honeycombs, monoliths, extrudates, and films. Optionally, the titanium-containing support can be extruded with, bound to, or supported on a second support for the purpose of binding together the catalyst particles and/or improving the catalyst's strength and/or attrition resistance. For example, it may be desirable to prepare a thin film of the titanium-containing support on a secondary support which is shaped into a bead, pellet, or extrudate. Suitable secondary supports include carbon and any refractory oxide, such as, silica, titania, alumina, aluminosilicates, and magnesia; ceramics, including ceramic carbides and nitrides, as well as any metallic support. Advantageously, the quantity of second support ranges from about 0 to about 95 weight percent, based on the combined weight of the catalyst (comprising gold, halogen-containing compound, and titanium-containing support) and the secondary support, however, with the following proviso. When the binder or secondary support is titania, then advantageously, the total titania is present in an amount not greater than about 35 weight percent, based on the total weight of the catalyst and secondary support. Unless otherwise noted, any binder added to, physically mixed with, extruded with, or incorporated into the titanium-containing support shall be considered to be a component of the titanium-containing support.

The particles of the preferred nanoporous titanium-containing support, excluding binder, are preferably greater than about 50 nm and less than about 2 microns (μm) in diameter (or largest dimension). More preferably, the particles of the preferred nanoporous titanium-containing support, including binder, are greater than about 50 nm and less than about 1 μm in diameter (or largest dimension).

There is no limitation on the method of incorporating gold onto the titanium-containing support, so long as the catalyst produced exhibits activity in the hydro-oxidation process of this invention. Non-limiting examples of suitable preparation methods include deposition-precipitation, impregnation, spray-drying, ion-exchange, vapor deposition, and solid-solid reaction. Impregnation and deposition-precipitation are preferred. In the deposition-precipitation method the titanium-containing support is contacted with a solution containing a source of gold at a temperature and pH sufficient to deposit a gold compound onto the support. The synthesis conditions can be varied as a function of several parameters, for example, the specific source of gold, the concentration of the gold source in solution, the nature and concentration of other ionic species, such as, sodium ions and silicate; the specific support, pH, temperature, the specific base selected, and contacting time. In the impregnation method, the support is wetted with a solution or suspension containing a source of gold to the point of incipient wetness or to a point of lesser or greater wetness, as desired. Here too, the impregnation conditions can vary, for example, with the specific gold compound, its concentration in the solution or suspension, the particular support, and the impregnation temperature. The support may be treated with multiple impregnations, if desired.

The temperature of the deposition-precipitation and impregnation techniques (or the ion-exchange technique, if that is used) advantageously ranges from about ambient, taken as 21°C, to about 100°C, but other temperatures may be suitable. Any gold compound can be used as the source of gold to prepare the gold solution or suspension for the deposition-precipitation and impregnation methods, or the ion-exchange method, if that is used. The source of gold may or may not contain halogen, e.g., in the form of halide.

Non-limiting examples of suitable gold compounds that can function as the source of gold include sodium gold oxide ($NaAuO_2$), cesium gold oxide ($CsAuO_2$), chloroauric acid, gold chloride, gold fluoride, sodium fluoroaurate, potassium fluoroaurate, sodium chloroaurate, potassium chloroaurate, gold cyanide, potassium gold cyanide, gold acetate, diethylamine auric acid trichloride, alkyl gold halides, preferably, alkyl gold chlorides and alkyl gold fluorides, and alkali aurates, such as lithium aurate, sodium aurate, potassium aurate, rubidium aurate, and cesium aurate; as well as gold cluster complexes, including preferably, the following clusters Au_3, Au_4, Au_5, Au_6, Au_7, Au_8, Au_9, Au_{10}, Au_{11}, Au_{12}, Au_{13}, Au_{20}, Au_{55}, and Au_{101}. (Some variation is expected in the number of gold atoms. For clusters of 20 or more gold atoms, a variation of +/- 10 percent may be expected in the number of gold atoms.) Such clusters can be found in the following non-limiting list of complexes: $(Ph_3PAu)_3OBF_4$, $[(AuPPh_3)_3O]PF_6]$, $Au_5(PPh_3)_4Cl$, $Au_6(PPh_3)_6(BF_4)_2$, $Au_6(PPh_3)_6(NO_3)_2$, $Au_6(PPh_3)_6(PF_6)_2$, $Au_8(PPh_3)_8(NO_3)_2$, $Au_8(PPh_3)_7(NO_3)_2$, $Au_9(PPh_3)_8(NO_3)_3$, $Au_{10}(PPh_3)_5(C_6F_5)_4$, $Au_{11}Cl_3\{(m\text{-}CF_3C_6H_4)_3P\}_7$, $Au_{11}(PPh_3)_7(PF_6)_3$, $[Au_{13}(PMe_2Ph)_{10}Cl_2](PF_6)_3$, $Au_{13}(PPh_3)_4[S(CH_2)_{11}(CH_3)]_4$, $[Au_{13}(PPh_2CH_2PPh_2)_6](NO_3)_4$, $Au_{55}(Ph_2PC_6H_4SO_3Na\cdot 2H_2O)_{12}Cl_6$, and $Au_{55}(PPh_3)_{12}Cl_6$, wherein "Ph" is phenyl and "Me" is methyl; as well as gold-ligand cluster compounds and complexes available commercially, for example, from Strem Chemicals and Nanoprobes, Incorporated, preferably, Nanoprobes brand gold-ligand cluster complexes of Catalog numbers

2010, 2022, and 2023. More preferably, the gold-ligand cluster complex comprises a Nanogold® brand gold-ligand cluster complex having an average gold particle size of about 1.4 nm.

Other suitable gold cluster species comprise gold-noble metal-ligand cluster complexes including, for example: $[(PPh_3)Pt(AuPPh_3)_6](NO_3)_2$, $[(PPh_3)(CO)Pt(AuPPh_3)_6](PF_6)_2$, $[Pd(AuPPh_3)_8](NO_3)_2$, $[H_4(PPh_3)_2Re(AuPPh_3)_5](PF_6)_2$, $[PPh_3Pt(AuPPh_3)_6](PF_6)_2$, $[H(PPh_3)Pt(AuPPh_3)_7](NO_3)$, $[Pt(AuPPh_3)_7(Ag)_2](NO_3)_3$. $[Pd(AuPPh_3)_8](PF_6)_2$, $[Pt(AuPPh_3)_8](NO_3)_2$, $[Pt(AuPPh_3)_8](PF_6)_2$, $[(PPh_3)Pt(AuPPh_3)_8(Ag)](NO_3)_2$, $[Pt_2(AuPPh_3)_{10}(Ag)_{13}]Cl_7$, wherein "Ph" is phenyl. Mixtures of any of the aforementioned gold-ligand cluster complexes, including gold-only, gold-silver, gold-noble metal, and gold-noble metal-silver ligand cluster complexes, may also be suitably employed. Of course, the phosphine ligands in the aforementioned formulas can be replaced with any other equivalent triorganophosphine ligand, such as tri(tolyl)phosphine or bis(diphenylphosphino)methane. Moreover, any of the anions in the aforementioned preferred formulas can be replaced with an equivalently charged anion. Organo-gold compounds can also be employed.

Suitable solvents for the deposition solution include, but are not limited to, water and organic solvents, the latter including alcohols (for example, methanol, ethanol, and isopropanol), esters, ketones, and aliphatic and aromatic hydrocarbons. Mixtures of water and organic solvents are also suitably employed. Advantageously, where a solution is used, the molarity of the soluble gold compound ranges from about 0.0001 M to the saturation point of the soluble gold compound, preferably, from about 0.0005 M to about 0.5 M. If an aqueous solution is used, the pH of the gold solution may be adjusted to any value between 1 and 14. The pH selected depends to some extent upon the subsequent heat treatment implemented. Preferably, the pH ranges from greater than about 5 to less than about 13, particularly when it is desired to pretreat the catalyst in helium prior to use. If the catalyst is to be pretreated under hydrogen, then the pH is less critical and may range from 2 to about 13. The pH can be adjusted to the desired value with any suitable base selected, for example, from hydroxides, carbonates, borates, carboxylates, silicates, and/or mixtures thereof.

As seen in the above discussion, the source of gold may or may not contain a halogen, which if present, is advantageously in the form of halide. Either way, a halogen to gold atomic ratio can be determined for the source of gold. For example, sodium gold oxide ($NaAuO_2$) has a halogen to gold atomic ratio of 0. Chloroauric acid ($HAuCl_4$) has a Cl/Au atomic ratio of 4/1. $Au_{55}(PPh_3)_{12}Cl_6$ has a Cl/Au atomic ratio of 6/55 or 0.11. In contrast, $Au_6(PPh_3)_6(BF_4)_2$ has a F/Au atomic ratio of 8/6 or 1.3. Where a mixture of sources is employed, the ratio of total halogen to total gold atoms is calculated based on relative quantities of each source present. As an example, in an equimolar mixture of $HAuCl_4$ and $Au_{55}(PPh_3)_{12}Cl_6$, the ratio of Cl/Au is the total 10/56 or 0.18. As a requirement of this invention, the halogen to gold atomic ratio used in the hydro-oxidation process exceeds the corresponding halogen to gold atomic ratio derived from the source(s) of gold. For such a requirement, it is necessary to add a halogen-containing compound directly to the process or during preparation of the catalyst, in addition to whatever halogen is provided by the source(s) of gold. Quantitatively, at least a 10 percent excess in halogen/gold atomic ratio is employed in the process and/or catalyst, as compared with the corresponding ratio in the source of gold; but the excess may go much higher.

It should be mentioned that if the deposition-precipitation or other precipitation method is used to deposit gold onto the titanium-containing support, the method advantageously adjusts pH to a desired value. Such a method can displace halide in the source of gold, e.g., $HAuCl_4$, by hydroxide or other ions. If such a displacement takes place, the actual quantity of halide deposited onto the support may be less than the quantity found in the source of gold. This invention prefers to calculate the halogen/gold atomic ratio from the source of gold employed, instead of the actual quantity of halogen deposited onto the titanium-containing support resulting from catalyst preparation and/or pH adjustments.

The halogen-containing compound may be any organic or inorganic halogen-containing compound known to the skilled person. The term "halogen" broadly includes halogen atoms that are covalently bonded to a central atom, such as carbon, phosphorus, or boron, as well as halogen atoms that are negatively-charged ions, i.e., halides, that are ionically associated with a positively-charged cation (e.g., M^{n+} or NH_4^+ or NR_4^+, wherein M is any metal ion having valence n^+ and each R is independently any monovalent hydrocarbyl radical, advantageously having from 1 to 20 carbon atoms). The halides are selected from fluorides, chlorides, bromides, iodides, and mixtures thereof, preferably, mixtures of chlorides with fluorides, bromides, and/or iodides. In any of the aforementioned covalent or ionically-bonded forms, the halogen functions to improve the performance of the hydro-oxidation catalyst. Factors contributing to improved performance include, but are not limited to, increased conversion of the olefin, increased selectivity to the olefin oxide, decreased productivity to water (correlating with improved hydrogen efficiency), increased catalyst productivity, and/or increased catalyst lifetime.

Suitable non-metallic halogens include elemental halogens, such as chlorine (Cl_2) and fluorine (F_2); ammonium halides, such as ammonium chloride, ammonium bromide, ammonium iodide and ammonium fluoride (noting that care should be taken when handling ammonium ions in the presence of gold(III) compounds); quaternary organo-ammonium halides, preferably, tetra-(C_{1-10}) organo-ammonium halides, such as tetramethylammonium fluoride, tetramethyl ammonium chloride, tetramethylammonium bromide, tetramethylammonium iodide, tetraethylammonium fluoride, tetraethylammonium chloride, tetraethylammonium bromide, and tetraethylammonium iodide; as well as boron halides, such as boron trifluoride and boron tetrafluoride ion; phosphorus halides, such as phosphorus trichloride and phosphorus hexafluoride ion; and organic halides, including preferably, C_{1-20} alkyl halides, such as, methyl chloride, dichloromethane, chloroform, and ethylchloride, and halogen-substituted C_{1-20} carboxylic acid salts, preferably, sodium trifluoroacetate and cesium trifluoroacetate.

Preferably, the halogen-containing compound is provided to the process as a metallic halide. Suitable metallic halides include any metallic halide from Groups 1 through 15 of the Periodic Table, as well as the lanthanide rare earths and actinide metals. Preferably, the metal of the metallic halide is selected from silver, Group 1 metals including lithium, sodium, potassium, rubidium, and cesium; Group 2 metals, including beryllium, magnesium, calcium, strontium, and barium; the platinum group metals, including ruthenium, rhodium, palladium, osmium, iridium, and platinum; the lanthanide rare earth metals, including lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium; and the actinide metals, specifically, thorium and uranium. The halides of such metals are advantageously supplied to the catalyst during catalyst preparation. It is noted however, that when cesium or palladium is present in the catalyst with chloride or a chlorine-containing compound, then at least one additional halogen other than chlorine or chloride should also be present, such as an ionic fluoride or a covalently-bonded fluorine-containing compound. Gold-containing halides, such as those noted hereinabove, including chloroauric acid and halogen-containing gold cluster complexes, may be employed to introduce halogen into the catalyst.

The quantity of halogen-containing compound provided to the catalyst and/or process is determined from the halogen/gold atomic ratio chosen for use. Advantageously, the halogen/gold atomic ratio is greater than 0, preferably, greater than about 1/1, and more preferably, greater than 4/1. The halogen/gold atomic ratio is advantageously less than about 32/1, preferably, less than about 16/1, and more preferably, less than about 12/1. The actual range for any given catalyst is limited to a range greater than the halogen/gold atomic ratio provided by the source(s) from which the gold is derived, such that the halogen functions to promote a beneficial effect above and beyond what the source(s) of gold may already accomplish.

Optionally, the catalyst of this invention may contain one or more metal-containing promoters that improve one or more performance features of the catalyst, including activity, selectivity, hydrogen efficiency, and/or productivity. Advantageously, such compounds comprise metal salts or organometallic complexes or coordination compounds wherein the valence of the metal ranges from +1 to +7; but zerovalent metal species may also be present. Non-limiting examples of suitable promoter metals include the metals of Groups 1 through 12 of the Periodic Table of the Elements as well as the rare earth lanthanides and actinides. Preferably, the promoter(s) is(are) selected from silver, Group 1 metals including lithium, sodium, potassium, rubidium, and cesium; Group 2 metals, including beryllium, magnesium, calcium, strontium, and barium; the lanthanide rare earth metals, including lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium; and the actinide metals, specifically, thorium and uranium. More preferably, the promoter is selected from silver, lithium, sodium, potassium, rubidium, cesium, barium, magnesium, calcium, erbium, lutetium, and combinations thereof.

If the promoter is a metal salt or mixture thereof, it may comprise any known anion(s) including halides (F, Cl, Br, I), nitrates, borates, silicates, sulfates, phosphates, carbonates, and carboxylates, particularly the acetates, oxylates, cinnamates, lactates, maleates, and citrates; or any mixture of the aforementioned anions. Consistent with the process of this invention, halides are particularly preferred, more preferably, chloride, fluoride, and mixtures thereof. In the instance wherein the metal-containing promoter is a metal halide, the metal halide simultaneously provides for both the required halogen-containing compound and the promoter.

If one or more metal promoters are used, the total quantity thereof advantageously is greater than about 0.001 and, preferably, greater than about 0.01 weight percent, based on the total weight of the catalyst. The total quantity of metal promoter(s) is advantageously less than about 20 and, preferably, less than about 15 weight percent, based on the total weight of the catalyst.

The halogen-containing compound(s) and the metal promoter compound(s) can be deposited onto the titanium-containing support simultaneously with the titanium deposition, if applicable; or alternatively, in a separate step either before or after titanium deposition, or simply directly onto a pre-formed titanium-containing support. The halogen-containing compound(s) and the metal promoter(s) can be deposited onto a preformed titanium-containing support simultaneously with the gold, or alternatively, in a separate step either before or after gold is deposited. For the purposes of this discussion, the word "deposit" includes all of the methods of deposition-precipitation, ion-exchange, and impregnation. Advantageously, the halogen-containing compound and any optional metal promoter(s) are deposited from an aqueous or organic solution or suspension containing one or more of these materials. Ordinarily, the support is contacted with the solution of the promoter(s) and halogen-containing compound(s) under conditions similar to those used for contacting the support with the gold solution. Afterwards, washing is optional; but preferably, washing is not performed.

The as-synthesized catalyst may be used without further treatment, or alternatively, may be calcined under air, or heated under hydrogen, or heated under an inert atmosphere, such as helium. The calcination/heating temperature is advantageously varied from about 100°C to about 800°C, preferably, from about 120°C to about 750°C. Preferably, when the catalyst is heated under helium, the solution from which gold and/or promoter(s) and/or halogen-containing compound(s) is deposited onto the titanium-containing support has a pH ranging from about 6 to about 13. Preferably, when the catalyst is heated under hydrogen, the pH of the solution from which gold and/or promoter(s) and/or halogen-containing compound(s) is deposited is not so critical and may range from 2 to 14.

The process of this invention can be conducted in a reactor of any conventional design suitable for gas or liquid phase processes. These designs broadly include batch, fixed-bed, transport bed, fluidized bed, moving bed, trickle bed, and shell and tube reactors, as well as continuous and intermittent flow and swing reactor designs. The olefin, hydrogen, and oxygen can be contacted together. Alternatively, the process can be conducted step-wise wherein the catalyst is first contacted with oxygen and thereafter the oxygenated catalyst is contacted with a mixture of propylene and hydrogen. Preferably, the process is conducted in the gas phase, and the reactor is designed with heat transfer features for the removal of the heat produced. Preferred reactors designed for these purposes include fixed-bed, shell and tube, fluidized bed, and moving bed reactors, as well as swing reactors constructed from a plurality of catalyst beds connected in parallel and used in an alternating fashion.

The process conditions for the oxidation described herein can vary considerably over a nonflammable and flammable regime. It is beneficial, however, to recognize the conditions which distinguish between nonflammable and flammable mixtures of the olefin, hydrogen, and oxygen. Accordingly, a composition diagram can be constructed or consulted which for any given process temperature and pressure shows the flammable and non-flammable range of reactant compositions, including the diluent, if used. The more preferred reactant mixtures specified hereinabove are believed to lie outside the flammable regime when the process is operated at the more preferred temperatures and pressures specified hereinbelow. Nevertheless, operation within the flammable regime is possible, as designed by one skilled in the art.

Advantageously, the process is conducted at a temperature which is greater than about ambient, taken as 21°C, preferably, greater than about 70°C, more preferably greater than about 130°C. Advantageously, the process is conducted at a temperature less than about 300°C, preferably less than about 260°C. Advantageously, the pressure ranges from about 1 psia (6.89 kPa) to about 400 psia (2,758 kPa), preferably, from about 100 psia (690 kPa) to about 300 psia (2,069 kPa).

In flow reactors, the residence time of the reactants and the molar ratio of reactants to catalyst will be determined by the space velocity. For a gas phase process the gas hourly space velocity (GHSV) of the olefin can vary over a wide range, but advantageously is greater than about 10 ml olefin per ml catalyst per hour (h^{-1}), preferably greater than about 100 h^{-1}, and more preferably, greater than about 1,000 h^{-1}. Advantageously, the GHSV of the olefin is less than about 50,000 h^{-1}, preferably, less than about 35,000 h^{-1}, and more preferably, less than about 20,000 h^{-1}. Also, for a gas phase process the total gas hourly space velocity (GHSV) of the feedstream (olefin, oxygen, hydrogen, and optional diluent) can vary over a wide range, but advantageously is greater than about 10 ml gas per ml catalyst per hour (h^{-1}), preferably, greater than about 100 h^{-1}, and more preferably, greater than about 1,000 h^{-1}. Advantageously, the GHSV of the feedstream is less than about 50,000 h^{-1}, preferably, less than about 35,000 h^{-1}, and more preferably, less than about 20,000 h^{-1}. Likewise, for a liquid phase process the weight hourly space velocity (WHSV) of the olefin component can vary over a wide range, but advantageously is greater than about 0.01 g olefin per g catalyst per hour (h^{-1}), preferably, greater than about 0.05 h^{-1}, and more preferably, greater than about 0.1 h^{-1}. Advantageously, the WHSV of the olefin is less than about 100 h^{-1}, preferably, less than about 50 h^{-1}, and more preferably, less than about 20 h^{-1}. The gas and weight hourly space velocities of the oxygen, hydrogen, and diluent components can be determined from the space velocity of the olefin taking into account the relative molar ratios desired.

When an olefin having at least three carbon atoms is contacted with oxygen in the presence of hydrogen and the catalyst described hereinabove, the corresponding olefin oxide (epoxide) is produced in good productivity. A preferred olefin oxide is propylene oxide.

The conversion of olefin in the process of this invention can vary depending upon the specific process conditions employed, including the specific olefin, temperature, pressure, mole ratios, and form of the catalyst. For the purposes of this invention, the term “conversion” is defined as the mole percentage of olefin that reacts to form products.

Advantageously, an olefin conversion of greater than about 0.25 mole percent is achieved. Preferably, the olefin conversion is greater than about 1.0 mole percent, more preferably, greater than about 1.5 mole percent, and most preferably, greater than about 2.0 mole percent.

The selectivity to olefin oxide can vary depending upon the specific process conditions employed. For the purposes of this invention, the term "selectivity" is defined as the mole percentage of reacted olefin that forms a particular product, desirably the olefin oxide. The process of this invention produces olefin oxides in a high selectivity. Advantageously the selectivity to olefin oxide is greater than about 70, preferably, greater than about 80, and more preferably, greater than about 90 mole percent.

The hydrogen efficiency in the process of this invention is advantageously improved as compared with prior art processes. Improved hydrogen efficiency correlates with lower production of water and consequently lower molar ratio of water to olefin oxide (H_2O/OO) produced. More specifically, the water to olefin oxide molar ratio is greater than about 1:1, but advantageously less than about 6:1, preferably, less than about 5:1, and more preferably, less than 4:1, over a period of time greater than 70 hours, and preferably, up to 100 hours of operation.

The productivity of the catalyst, measured as grams of olefin oxide per kilogram catalyst per hour (g OO/kg cat-h), more particularly, grams propylene oxide per kg catalyst per hour (g PO/kg cat-h), depends upon the specific catalyst used and process conditions, such as, temperature, pressure, and feed rates. The productivity is advantageously greater than about 50 g PO/kg cat-h, preferably, greater than about 100 g PO/kg cat-h, and more preferably, greater than about 300 g PO/kg cat-h.

The invention will be further clarified by a consideration of the following examples, which are intended to be purely exemplary of the use of the invention. Other embodiments of the invention will be apparent to those skilled in the art from a consideration of this specification or practice of the invention as disclosed herein. Unless otherwise noted, all percentages are given on a mole percent basis.

Titanosilicate Support

The titanosilicate for the following examples is prepared as follows. Nanometer size crystals of a titanosilicate are prepared using tetraethylorthosilicate (TEOS), titanium n-butoxide, and tetrapropylammonium hydroxide (TPAOH), in an aqueous reaction mixture having the following molar composition: 1.0 SiO_2 : 0.015 TiO_2 : 35 H_2O : 0.33 TPA. A solution containing TEOS and isopropyl alcohol in a ratio of 5:1 is added with vigorous stirring to a solution of TPAOH (20 weight percent). After 20 min of agitation a solution of titanium tetra(n-butoxide) in dry isopropyl alcohol (1:5 ratio) is added to the first solution slowly with vigorous stirring. The clear solution is stirred for 1 hour followed by a slow addition of cooled deionized water. The synthesis mixture is sealed in an autoclave with stirring at 170°C under autogenous pressure for 4 days. A crystalline solid is recovered by centrifugation at 2,000 RPM for 3 hours. The crystalline solid is washed twice with hydrochloric acid (0.1 M), washed with deionized water, and dried at 70°C for 2 hours. The solid is thereafter calcined at 550°C in air for 8 hours. The resulting titanosilicate product comprises orthorhombic crystals of an average size of 100 nm, as measured by TEM, with an MFI structure type, as determined by powder XRD. No bulk titanium dioxide is found. Si:Ti atomic ratio is 90:1. In some examples, the titanosilicate is extruded to form an extrudate (1/8 inch or 3 mm particles).

General Procedure for Hydro-Oxidation Process

Each hydro-oxidation catalyst is evaluated in the hydro-oxidation of propylene to propylene oxide as follows. The catalyst (0.5 g) and an equal volume of quartz chips are loaded into a fixed-bed, continuous flow reactor [0.25 inch (6 mm) diameter x 12 inches (30 cm) length)] and activated as follows. The catalyst is heated under helium or hydrogen for 1 hour at a starting temperature of between 120°C and 140°C, then heated under a flow of propylene and hydrogen for 10 min, then oxygen is added. Feedstream composition and pressure are listed by each table below. After a constant rate of propylene oxide production is obtained for at least 1 hour, the temperature is ramped in 10°C intervals up to the operating temperature. Products are analyzed using either on-line gas chromatography (Chrompack^{TM} Poraplot^{TM} S column, 25 m) or mass spectrometry.

Examples 1 to 6

Sodium gold oxide ($NaAuO_2$) (8.0333 g, 20.39 mmol) is dissolved in water (20.15 g). Sodium hydroxide (2.5693 g, 6.42 mmol) is dissolved in water (15.31 g). The sodium hydroxide solution is added to the gold solution. The combined gold-NaOH solution is red in color with a pH 6.5 at 42°C. A solution of sodium hydroxide (50 weight percent) is added to the combined gold solution until a pH 8.0 is reached, and then the solution is heated to 60°C. An orange precipitate forms and the resulting mixture is stirred for 1 h at 60°C. The mixture is filtered and a gold-containing precipitate is collected and washed with water 5 times (150 ml H_2O) until it is chloride free, as determined by dropping test samples of wash filtrate into silver nitrate ($AgNO_3$) solution until no precipitation occurs. The gold-containing precipitate is dried in a vacuum oven at 60°C to recover gold hydroxide [$Au(OH)_3$, 4.0 g]. A sample of the gold hydroxide (0.5007 g, 2.02 mmol) is added to water (45 g), and sodium hydroxide (0.1400 g, 3.5 mmol) is added to form an orange slurry. The slurry is heated at 83°C at which temperature a yellow solution of sodium gold oxide forms ($NaAuO_2$, 0.40 g Au/100 ml).

Example 1: A portion of the $NaAuO_2$ solution is treated with an aqueous sodium chloride (NaCl) solution to obtain an aqueous solution with a Cl:Au atom ratio of 1:1. The solution is impregnated onto a titanosilicate of the MFI crystallographic structure (extrudate 1/8", previously calcined at 550°C).

Example 2: A catalyst is prepared as in Example 1, with the exception that the amount of NaCl is adjusted to yield a Cl:Au atom ratio of 2:1.

Example 3: A catalyst is prepared as in Example 1, with the exception that the amount of NaCl is adjusted to yield a Cl:Au atom ratio of 4:1.

Example 4: A catalyst is prepared as in Example 1, with the exception that the amount of NaCl is adjusted to yield a Cl:Au atom ratio of 8:1.

Example 5: A catalyst is prepared as in Example 1, with the exception that the amount of NaCl is adjusted to yield a Cl:Au atom ratio of 16:1.

Example 6: A catalyst is prepared as in Example 1, with the exception that the amount of NaCl is adjusted to yield a Cl:Au atoms ratio of 32:1.

In Examples 1 to 6, the catalysts each contain essentially 1,000 ppm Au. Each catalyst is heated in helium at 140°C for 1 hour, then evaluated in the hydro-oxidation of propylene starting at 140°C and then raising the temperature by 10°C up to 170°C. Results showing the effect of chloride on the $NaAuO_2$/TS catalyst are shown in Table 1.

Table 1: $NaAuO_2$ + Cl on Titanosilicate[1,2]

Example	Cl / Au	PP Conversion (Mole %)	PO Selectivity (Mole %)	H_2O/PO
1	1	0.57	80.4	7.80
2	2	0.83	84.4	6.65
3	4	0.71	89.9	5.74
4	8	0.51	91.3	5.27
5	16	0.59	91.9	5.14
6	32	0.62	90.8	5.63

1. PP = propylene; PO = propylene oxide
2. Data taken at 170°C, 1 atm (101 kPa), total flow 160 cc/min; feed composition 20% PP, 10% O_2, 10% H_2 and balance He.

From Table 1, it is seen that as the chloride content of the catalyst increases, the selectivity to propylene oxide increases and the ratio of water produced to propylene oxide produced beneficially decreases.

Examples 7 to 10

A gold hydroxide sample is prepared as in Examples 1-6. A sample of the gold hydroxide (0.5085 g, 2.05 mmol) is added to water (45 g). Cesium hydroxide (0.4503 g, 3.0 mmol) is added to form an orange slurry. The slurry is heated at 82°C, at which temperature the orange slurry clears and a orange-yellow solution is formed comprising cesium gold oxide ($CsAuO_2$, 0.41 g Au/100 ml).

Example 7: A portion of the cesium gold oxide solution is treated with sodium chloride to obtain a solution comprising a Cl:Au atom ratio of 1:1. The solution is impregnated onto a titanosilicate (extrudate 1/8” previously calcined at 550°C).

Example 8: A catalyst is prepared as in Example 7, with the exception that the quantity of chloride is adjusted to yield a Cl:Au atom ratio of 2:1.

Example 9: A catalyst is prepared as in Example 7, with the exception that the quantity of chloride is adjusted to yield a Cl:Au atom ratio of 4:1.

Example 10: A catalyst is prepared as in Example 7, with the exception that the quantity of chloride is adjusted to yield a Cl:Au atom ratio of 8:1.

In Examples 7 to 10, the catalysts contain essentially 1000 ppm Au. Each of the catalysts is heated in helium at 140°C for 1 hour, then evaluated in the hydro-oxidation of propylene with oxygen in the presence of hydrogen at a temperature starting at 140°C and increasing every 10° to 180°C. Results showing the effect of chloride on the $CsAuO_2$/TS catalyst are set forth in Table 2.

Table 2. $CsAuO_2$ + Cl on Titanosilicate[1,2]

Example	Cl / Au	PP Conversion (Mole %)	PO Selectivity (Mole %)	H_2O/PO
7	1	1.04	82.3	7.80
8	2	1.25	85.7	6.93
9	4	0.81	87.8	5.77
10	8	0.32	88.8	6.33

1. PP = propylene; PO = propylene oxide
2. Data taken at 180°C, 1 atm (101 kPa), total flow 160 cc/min; feed composition 20% PP, 10% O_2, 10% H_2 and balance He.

From Table 2, it is seen that as the quantity of chloride increases the propylene oxide selectivity increases, and in Examples 7, 8, and 9 the water to propylene oxide molar ratio also favorably decreases.

Examples 11 to 15

Example 11: Gold acetate (Au $(acetate)_3$, 0.2265 g, 0.606 mmol) is dissolved in water (50.0 g) to which is added sodium acetate (1.0666 g, 13.01 mmol) to form an aqueous gold solution. Sodium chloride (0.0168 g, 0.287 mmol) is added to the gold solution. The solution (2.1 g) is impregnated onto a titanosilicate support (3.0 g, 14/30 U.S. mesh, 595-1420 μm, previously calcined at 550°C). The impregnated titanosilicate is vacuum dried at 105°C for 1 h. The resulting catalyst has atomic ratios of Na:Au = 21.9 and Cl:Au = 0.47.

Example 12: Sodium chloride (0.0182 g (0.311 mmol) is added to the aqueous gold acetate solution from Example 11. The resulting solution (2.1 g) is impregnated onto the titanosilicate support (3.0), which is then dried in the manner of Example 11. The resulting catalyst has an atomic ratio of Na:Au = 22.5 and Cl:Au = 0.99.

Example 13: Sodium chloride (0.0359 g, 0.614 mmol) is added to the aqueous gold acetate solution from Example 12. The resulting solution (2.1 g) is impregnated onto a sample of the titanosilicate support (3.0), which is then dried as in Example 11. The resulting catalyst has an atomic ratio of Na:Au = 23.5 and Cl:Au = 2.0.

Example 14: Sodium chloride (0.0711 g, 1.22 mmol) is added to the aqueous gold acetate solution from Example 13. The resulting solution (2.1 g) is impregnated onto a sample of the titanosilicate support (3.0), which is then dried as in Example 11. The resulting catalyst has an atomic ratio of Na:Au = 25.5 and Cl:Au = 4:1.

Example 15: Sodium chloride (0.1458 g, 2.49 mmol) is added to the aqueous gold acetate solution from Example 14. The resulting solution (2.1 g) is impregnated onto a sample of the titanosilicate support (3.0), which is then dried as in Example 11. The resulting catalyst has an atomic ratio of Na:Au = 29.6 and Cl:Au = 8:1.

Each of the above catalysts is heated in helium at 130°C for 1 h then evaluated in the hydro-oxidation of propylene with oxygen in the presence of hydrogen starting at a temperature of 130°C and increasing every 10° to 160°C with the results shown in Table 3.

Table 3. Au(Acetate)$_3$ and Cl on Titanosilicate[1,2]

Example	Na/Au	Cl / Au	PP Conversion (Mole %)	PO Selectivity (Mole %)	H_2O/PO (Molar Ratio)
CE-1	0	0	0.05	84.0	3.90
CE-2	22.0	0	0.39	97.8	2.94
11	21.9	0.47	0.40	98.2	3.11
12	22.5	0.99	0.60	98.6	2.95
13	23.5	2	1.07	99.1	3.32
14	25.5	4	1.56	98.2	3.32
15	20.6	8	1.46	98.3	3.46

1. PP = propylene; PO = propylene oxide
2. Data taken at 160°C, 100 psia (689 kPa), total flow 250 cc/min; feed composition 30% PP, 10% O_2, 10% H_2, balance He

Comparative Experiments CE-1 and CE-2

CE-1: Gold acetate [Au(acetate)3)] (0.2204g, 0.589 mmol) is dissolved in water (50.0 g). The resulting gold acetate solution (2.1 g) is impregnated onto a titanosilicate support (3.60 g, 14/30 U.S. mesh, 595-1420 μm, calcined at 550°C), which is then vacuum dried at 105°C for 1 hour. The resulting comparative catalyst has Na:Au = 0 and Cl:Au = 0.

CE-2: Gold acetate [Au(acetate)3)] (0.2204g, 0.589 mmol) is dissolved in water (50.0 g). Sodium Acetate (1,0631 g, 12.93 mmol) is added to the aqueous gold solution. The resulting gold-sodium solution (2.1 g) is impregnated onto a titanosilicate support (3.60 g, 14/30 U.S. mesh, 595-1420 μm, calcined at 550°C), which is then vacuum dried at 105°C for 1 hour. The resulting comparative catalyst has Na:Au = 22.0/1 and Cl:Au = 0.

The comparative materials are evaluated in the manner described in Examples 11 to 15 with the results shown in Table 3. When Examples 11 to 15 are compared with Comparative Experiments 1 and 2, it is seen that the presence of sodium and chloride favorably increase propylene conversion, propylene oxide selectivity, and hydrogen efficiency as measured by a lower H_2O/PO molar ratio. Conversion increases from 0.40 to 1.46 mole percent with increasing chloride concentration.

Examples 16 and 17

Example 16: Chloroauric acid ($HAuCl_4 \cdot 3H_2O$, 0.2138 g, 0.543 mmol) is dissolved in water (40.0 g). Tetramethylammonium hydroxide (0.816 g, $N(CH_3)_4OH$, 25% in H_2O) is added, and then water is added to a total of 50.0 g water. The pH of the solution is 12. To a portion of the foregoing solution (15.0 g) is added 0.1424 g (2.44 mmol) sodium chloride. The resulting solution (2.167 g) is impregnated onto a titanosilicate support (3.04 g, 14/30 U.S. mesh, 595-1420 μm), and then the impregnated support is vacuum dried at 105°C for 1 hour. The resulting catalyst has an atomic ratio of Na:Au of 15:1 and Cl:Au of 19:1.

Example 17. To a sample (15.0 g) of the gold solution of pH 12 is added sodium chloride (0.0762 g, 1.30 mmol) and sodium nitrate (0.1310 g, 1.54 mmol), and the resulting solution (2.157 g) is impregnated onto the titanosilicate support (3.03 g, 14/30 U.S. mesh, 595-1420 μm). The impregnated support is vacuum dried as in Example 16. The resulting catalyst has an atomic ratio Na:Au of 17:1 and a Cl:Au of 12/1.

Each of the above catalysts is heated in hydrogen (10 vol percent) in helium at 250°C for 1 h then evaluated in the hydro-oxidation of propylene with oxygen in the presence of hydrogen starting at a temperature of 140°C for 6 hours and increasing every 2.5° per hour to 160°C. Results are set forth in Table 4.

Table 4. $HAuCl_4$ with Cl on Titanosilicate[1,2]

Ex.	Cl / Au	Na/Au	PP Conversion (mole %)	PO Selectivity (mole %)	H_2O/PO (Molar Ratio
CE-3	4	0	0.95	96.8	3.80
17	12	15/1	1.92	98.0	3.04
16	19	17/1	2.25	97.9	2.38

1. PP = propylene; PO = propylene oxide
2. Data taken at 160°C, 100 psia (689 kPa), total flow 250 cc/min; feed composition 30% PP, 10% O_2, 10% H_2 and balance He

Comparative Experiment CE-3

Example 16 is repeated, with the exception that sodium chloride is excluded from the preparation. The resulting comparative catalyst contains no sodium promoter and the Cl:Au is 4:1. The comparative catalyst is evaluated in the manner described in Examples 16 and 17. Results are shown in Table 4. When Examples 16 and 17 are compared with Comparative Experiment CE-3, it is seen that sodium increases activity. Also, at substantially constant sodium content, the selectivity to propylene oxide increases with increasing chloride content.

Examples 18 to 22

Five catalysts are prepared using a titanosilicate support [1/4" extrudates (3 mm), pre-calcined for 10 hours at 550°C]. Each of the catalysts is evaluated in the hydro-oxidation of propylene by heating in helium at 140°C for 1 hour then starting the run at 140°C and raising temperature 10°C increments up to 170°C.

Example 18. An aqueous solution of chloroauric acid ([$HAuCl_4 \cdot 3H_2O$)], 1.66 g, 0.05 M, 0.083 mmol), an aqueous solution of sodium hydroxide (3.75 g, 2.0 M, 7.5 mmol), phosphoric acid (2.0 M, 1.25 g, 2.5 mmol), sodium fluoride (0.17 g, 0.5 M, 0.085 mmol) are mixed for 30 minutes with water to make a 10.0 g total of solution. The solution (2.0 g) is impregnated onto the titanosilicate (3.0 g), held for 30 min, and vacuum dried at 100°C for 1 hour. The resulting catalyst has a Na:Au ratio = 91/1, a PO_4:Au = 30/1 and F/Au = 1/1.

Example 19. The procedure of Example 18 is repeated, with the exception that 0.34 g sodium fluoride (0.5 M, 0.17 mmol) replaces the amount in Example 18. The resulting catalyst has Na:Au = 92/1, PO_4:Au = 30/1, and F:Au = 2/1.

Example 20. The procedure of Example 18 is repeated, with the exception that 0.68 g of sodium fluoride (0.5M, 0.34 mmol) replaces the amount in Example 18. The resulting catalyst has Na:Au = 94/1, PO_4:Au = 30/1, and F:Au = 4/1.

Example 21. The procedure of Example 18 is repeated, with the exception that 1.36 g sodium fluoride (0.5 M 0.68 mmol) replaces the amount in Example 18. The resulting catalyst has a Na:Au = 98/1, PO_4:Au = 30/1 and F:Au = 8/1.

Example 22. The procedure of Example 18 is repeated, with the exception that 2.72 g of sodium fluoride (0.5 M, 0.68 mmol) replaces the amount in Example 18. The resulting catalyst has Na:Au = 106/1, PO_4:Au = 30/1, and F:Au = 16/1.

Results are shown in Table 5.

Table 5. $HAuCl_4$ with High Na Content and Added F[1,2]

Example	Na/Au	Cl/Au	F / Au	PP Conversion (mole %)	PO Selectivity (mole %)	H_2O/PO (Molar Ratio
CE-4	90	4	0	2.39	87.0	7.79
18	91	4	1	2.31	88.7	6.71
19	92	4	2	2.38	90.2	6.02
20	94	4	4	2.43	90.9	6.03
21	98	4	8	2.25	91.2	5.88
22	106	4	16	2.67	88.5	6.02

1. PP = propylene; PO = propylene oxide
2. Data taken at 170°C, 1 atm (101kPa), 160 cc/min; feed composition 20% PP, 10% O_2, 10% H_2 and balance He.

Comparative Experiment 4

Example 18 is repeated, with the exception that no sodium fluoride is used in the catalyst preparation. The resulting catalyst has Na/Au = 90/1; PO_4/Au = 30/1; and F/Au = 0. The comparative catalyst is evaluated in the manner described in Examples 18-22 with the results shown in Table 5. By comparing Examples 18 – 22 and Comparative Experiment 4, it can be seen that all samples start with a high sodium content and the addition of sodium from NaF does not increase the Na:Au ratio significantly. Moreover, all samples have a constant Cl:Au ratio of 4 obtained from the starting gold compound ($HAuCl_4 \cdot 3H_2O$). All samples also have a high constant concentration of phosphate anion. The main difference between samples resides in the fluoride content in a F:Au ratio from 0 to 16. It is found that increasing the fluoride content, at constant phosphate and chloride concentrations, increases PO selectivity and decreases the H_2O/PO ratio, while keeping catalyst activity nearly constant.

Examples 23 to 25

Three catalysts are prepared as follows and evaluated in the hydro-oxidation of propylene to propylene oxide. A stock aqueous gold solution is used in the catalyst preparations. The stock solution is prepared as follows. Chloroauric acid ($HAuCl_4 \cdot 3H_2O$, 0.856 g, 2.17 mmol) is dissolved in water (160.0 g) and tetramethylammonium hydroxide [3.08 g $N(CH_3)_4OH$ (25% in H_2O] is added dropwise to a pH of 7.1; then water is added to a total of 200.0 g. The titanosilicate support in each example is prepared as in Example 1 hereinabove.

Example 23: To a sample of the stock gold solution (15.008 g) are added barium nitrate $Ba(NO_3)_2$ (0.170 g, 0.65 mmol) and barium chloride $BaCl_2 \cdot 2H_2O$ (0.159 g, 0.65 mmol). The resulting solution (2.178 g) is impregnated onto a titanosilicate support (3.0 g), previously calcined at 550°C). The impregnated support is vacuum dried at 105°C for 30 minutes. Resulting catalyst has Ba:Au = 8 and Cl:Au = 12/1.

Example 24: To a sample of the stock gold solution (15.000 g) are added lanthanum nitrate $La(NO_3)_3 \cdot 6H_2O$ (0.183 g, 0.43 mmol) and lanthanum chloride $LaCl_3 \cdot 7H_2O$ (0.162 g, 0.43 mmol). The resulting solution (2.161 g) is impregnated onto a titanosilicate support (3.03 g). The impregnated support is vacuum dried at 105°C for 30 minutes. The resulting catalyst has La:Au = 5.3/1 and Cl:Au = 12/1.

Example 25: To a sample of the stock gold solution (15.000 g) are added praseodymium nitrate $Pr(NO_3)_3 \cdot 6H_2O$ (0.189 g, 0.43 mmol) and praseodymium chloride $PrCl_3 \cdot 6H_2O$ (0.153 g, 0.43 mmol). The resulting solution (2.168 g) is impregnated onto a titanosilicate support (3.03 g). The impregnated support is vacuum dried at 105°C for 30 minutes. The resulting catalyst has Pr:Au = 5.3/1 and Pr:Au = 12/1.

Each catalyst is heated in a mixture of hydrogen (10 percent) in helium at 250°C for 1 h, then evaluated in the hydro-oxidation of propylene starting at 140°C and holding for 6 hours and then increasing temperature at 2.5°C/hr to 160°C. Results are shown in Table 6.

Table 6. $HAuCl_4$ with Added Cl[1,2]

Example	P	P/Au	Cl/Au	PP Conversion (mole %)	PO Selectivity (mole %)	H_2O/PO (Molar Ratio
CE-5	Ba	8/1	4/1	0.60	92.7	9.0
23	Ba	8/1	12/1	0.67	94.6	6.45
CE-6	La	5.3/1	4/1	0.72	93.1	8.42
24	La	5.3/1	12/1	0.64	96.3	4.53
CE-7	Pr	5.3/1	4/1	0.66	93.1	8.87
25	Pr	5.3/1	12/1	0.60	95.9	4.87

1. PP = propylene; PO = propylene oxide
2. Data taken at 160°C, 100 psia (689 kPa), total flow 250 cc/min; feed composition 30% PP, 10% O_2, 10% H_2 and balance He

Comparative Experiments CE-5 to CE-7

CE-5: Example 23 is repeated, with the exception that 0.340 g barium nitrate (1.3 mmol) replaces the 0.170 g barium nitrate and 0.159 g barium chloride used in Example 23. The resulting catalyst has a Ba:Au = 8/1 and Cl:Au = 4/1.

CE-6: Example 24 is repeated, with the exception that 0.372 g lanthanum nitrate (0.86 mmol) replaces the 0.183 g lanthanum nitrate and 0.162 g lanthanum chloride used in Example 24. The resulting catalyst has a La:Au = 5.3/1 and Cl:Au = 4/1.

CE-7: Example 25 is repeated, with the exception that 0.374 g praseodymium nitrate (0.86 mmol) replaces the 0.189 g of praseodymium nitrate and 0.153 g of praseodymium chloride used in Example 25. The resulting catalyst has a Pr:Au = 5.3/1 and Cl:Au = 4/1.

The comparative catalysts are evaluated in the manner described in Examples 23-25 with the results shown in Table 6. When Example 23 is compared with Comparative

Experiment 5, it is seen that at constant promoter metal content (Ba), the PO selectivity increases and the H_2O/PO molar ratio decreases with increasing chloride content. The same is found when comparing Example 24 versus Comparative Experiment 6, and Example 25 versus Comparative Experiment 7, wherein the promoter metals are lanthanum and praseodymium, respectively.

Example 26

Example 26: To 10.00 g deionized water, cesium acetate (0.1004 g) and cesium chloride (0.0030 g) are added. The cesium acetate/chloride solution (4.197 g) is added to 6.00 g of a titanosilicate support. The material is vacuum dried at 70°C for 60 minutes; then calcined at 550°C for 10 hours. A gold cluster compound (0.010 g) $[Au_9(PPh_3)_8(NO_3)_3]$ is dissolved in acetone (7.455 g) and methanol (2.35 g). The gold cluster solution (1.010 g) is deposited onto the calcined support (1.50 g). The resulting material is vacuum dried at 100°C for 30 minutes to yield a catalyst having Cl:Au_9 = 1.

The catalyst is heated in 10 vol. percent hydrogen in helium at 250°C for 1 hour, then evaluated in the hydro-oxidation of propylene starting at 140°C, then at 160°C, then at 220°C, and finally at 240°. Results are shown in Table 7.

Table 7. Au_9 Cluster with Added Halide[1,2]

Example	P	P/Au	Halide (H)	H/Au_9	Productivity (g PO/kg cat . hr)
CE-8	Cs	25/1	Cl	0	354
26	Cs	25/1	Cl	1/1	364
CE-9	Cs	25/1	F	0	443
27	Cs	25/1	F	1/1	476

1. PP = propylene; PO = propylene oxide; P = Promoter ion; H = Halide
2. Data taken at 240°C, 100 psia (689 kPa), total flow 250 cc/min; feed composition 30% PP, 10% O_2, 10% H_2 and balance He

Comparative Experiment 8

Example 26 is repeated, with the exception that no cesium chloride is used in the preparation. The resulting catalyst has Cl:Au_9 = 0. The comparative catalyst is evaluated in the manner described in Examples 26 with the results shown in Table 7. When Experiment 26 is compared with Comparative Experiment 8, at constant content of promoter metal (Cs), the productivity of the catalyst increases with increasing chloride content.

Example 27

To 10.00 g deionized water, cesium acetate (0.1006 g) and cesium chloride (0.0029 g) are added. The cesium acetate/fluoride solution (4.197 g) is added to 6.00 g of zeolitic titanosilicate support. The material is vacuum dried at 70°C for 60 minutes; then calcined at 550°C for 10 hours. A gold cluster compound (0.010 g $Au_9(PPh_3)_8(NO_3)_3$) is dissolved in acetone (7.466 g) and methanol (2.364 g). The gold cluster solution (1.010 g) is added to the calcined support (1.50 g). The resulting material is vacuum dried at 100°C for 30 minutes to yield a catalyst having $F:Au_9 = 1$.

The catalyst is heated in 10 vol. percent hydrogen in helium at 250°C for 1 hour, then evaluated in the hydro-oxidation of propylene starting at 140°C, then at 160°C, then at 220°C, and finally at 240°. Results are shown in Table 7.

Comparative Experiment 9

Example 27 is repeated, with the exception that no cesium fluoride is added to the preparation. The resulting catalyst has $F:Au_9 = 0$. The comparative catalyst is evaluated in the manner described in Example 27 with the results shown in Table 7. When Experiment 27 is compared with Comparative Experiment 9, at constant content of promoter metal (Cs), the productivity of the catalyst increases with increasing fluoride content.

Examples 28 to 30

A titanosilicate is prepared as in Example 1 and used as 14/30 U.S. mesh particles (595-1420 μm) in the following examples.

Example 28: Chloroauric acid [0.428 g (2.17 mmol) $HAuCl_4 \cdot 3H_2O$] is dissolved in H_2O (80.03 g) to which is added tetramethylammonium hydroxide $N(CH_3)_4OH$ [1.632 g, 25% in H_2O]. Then, sufficient water is added to bring the total water content to 100 g. The pH of the resulting solution is 8.3. To a portion (15.002 g) of the gold solution are added sodium nitrate (0.2076 g, 2.438 mmol) and sodium fluoride (0.007 g, 0.163 mmol). The resulting gold solution (2.168 g) is impregnated onto the titanosilicate support (3.0 g). The impregnated support is vacuum dried at 105°C for 30 minutes. The resulting catalyst has Na:Au = 16, Cl:Au = 4, and F:Au = 1.

Example 29: A gold and tetramethylammonium hydroxide aqueous solution of pH 8.3 is prepared as in Example 28. To a portion (14.998 g) of the gold solution are added sodium nitrate (0.194 g, 2.274 mmol) and sodium fluoride (0.0137 g, 0.326 mmol). The resulting gold solution (2.178 g) is impregnated onto the titanosilicate support (3.00 g). The impregnated support is vacuum dried at 105°C for 30 minutes. The resulting catalyst has Na:Au = 16, Cl:Au = 4, and F:Au = 2.

Example 30: A gold and tetramethylammonium hydroxide aqueous solution of pH 8.3 is prepared as in Example 28. To a portion (15.003 g) of the gold solution are added sodium nitrate (0.1657 g, 1.95 mmol) and sodium fluoride (0.0279 g, 0.65 mmol). The resulting gold solution (2.176 g) is impregnated onto the titanosilicate support (3.00 g). The impregnated support is vacuum dried at 105°C for 30 minutes. The resulting catalyst has Na:Au = 16, Cl:Au = 4, and F:Au =4.

Each of the catalysts is evaluated in the hydro-oxidation of propylene as follows. Each of the catalysts is heated in hydrogen (10 percent in helium) at 250°C for 1 hour then run the hydro-oxidation process starting at 140°C, then holding the temperature for 6 hours, and then increasing the temperature at 2.5°C/hr to 160°C. Results are shown in Table 8.

Table 8. $HAuCl_4$ with Added F[1,2]

Example	Na/Au	Cl/Au	F / Au	Conversion	Selectivity	H_2O/PO	H_2O/PO at 90 hrs
CE10	16	4	0	1.92	98.1	2.88	4.28
28	16	4	1	2.13	97.5	3.83	5.43
29	16	4	2	2.25	97.4	3.88	5.51
30	16	4	4	2.62	97.1	4.21	5.91

1. PP = propylene; PO = propylene oxide
2. Data taken at 160°C, 100 psia (689 kPa), total flow 250 cc/min; feed composition 30% PP, 10% O_2, 10% H_2 and balance He

Comparative Experiment 10

Example 28 is repeated, with the exception that no sodium fluoride is added.

The resulting material has a Na:Au = 16,. Cl:Au = 4, and F:Au = 0. The comparative catalyst is evaluated in the hydro-oxidation of propylene in the manner described for Examples 28-30 with the results shown in Table 8. It can be seen by comparing Examples 28 – 30 with CE-10 that these samples start with a moderate sodium (Na) content (Na:Au = 16), and the balancing of the sodium from the $NaNO_3$ to NaF does not change the Na:Au ratio. These samples have a constant Cl:Au ratio = 4 as obtained from the gold compound used ($HAuCl_4•3H_2O$). The main difference between the samples is an increase in the F:Au ratio from 0 to 4. With keeping the sodium and chloride contents constant, increasing the fluoride content increases catalyst activity.

Examples 31 to 36

In these examples a titanosilicate support (14/30 U.S. mesh, 595-1420 μm) is used, which has been previously calcined at 500°C. Each catalyst contains 1500 ppm gold, and an initial Na/Au atomic ratio of 22/1, and a Cl/Au ratio of 26/1.

Example 31. Sodium chloride (2.804 g, 47.98 mmol) and chloroauric acid (0.8727g, 2.21 mmol) are dissolved in water (199.945g) to form an aqueous gold solution of pH 2.10. A portion of the aqueous gold solution (2.10 g) is impregnated onto the titanosilicate support (3.0 g). The resulting material is vacuum dried at 70°C for 1 hour.

Example 32. The remainder of the solution prepared in Example 31 is treated with 135 ul of 50wt% sodium hydroxide aqueous solution, resulting in a pH of 4.22. A portion (2.10 g) of the solution is impregnated onto the titanosilicate (3.0g) and vacuum dried as in Example 31.

Example 33. The remainder of the solution prepared in Example 32 is treated with 147 ul of 50wt% sodium hydroxide aqueous solution, resulting in a pH of 5.93. A portion (2.10 g) of the solution is impregnated onto the titanosilicate (3.0g) and vacuum dried as in Example 31.

Example 34. The remainder of the solution prepared in Example 33 is treated with 220 ul of 50wt% sodium hydroxide aqueous solution, resulting in a pH of 8.17. A portion (2.10 g) of the solution is impregnated onto the titanosilicate (3.0g) and vacuum dried as in Example 31.

Example 35. The remainder of the solution prepared in Example 34 is treated with 110 ul of 50wt% sodium hydroxide aqueous solution, resulting in a pH of 10.3. A portion (2.10 g) of the solution is impregnated onto the titanosilicate (3.0g) and vacuum dried as in Example 31.

Example 36. The remainder of the solution prepared in Example 35 is treated with 190 ul of 50wt% sodium hydroxide aqueous solution, resulting in a pH of 11.97. A portion (2.10 g) of the solution is impregnated onto the titanosilicate (3.0g) and vacuum dried as in Example 31.

Each catalyst so prepared is divided into two portions. A first portion of each catalyst is heated in helium as temperature is raised from room temperature to 250°C in 120 minutes, and then held at 250°C for 1 hour. The sample thusly-treated is evaluated in the hydro-oxidation of propylene starting at 140°C and increasing temperature to 160°C. Results are shown in Table 9.

Table 9. Added Cl with pH Variation and Activation in Helium[1,2]

Example	pH	Productivity at 160°C for He Activation (g PO/kg cat-hr)	H_2O/PO for He Activation
31	2.1	50.7	2.9
32	4.2	30	4.8
33	5.9	63	3.7
34	8.2	148	2.8
35	10.3	169	2.5
36	12.0	343	2.9

1. PO = propylene oxide
2. Data taken at 160°C, 100 psia (689 kPa), total flow 250 cc/min; feed composition 30% PP, 10% O_2, 10% H_2 and balance He

A second portion of each catalyst 31-36 is heated in hydrogen (10 percent) in helium as temperature is raised from room temperature to 250°C in 120 minutes, and then held at 250°C for 1 hour. The sample thusly-treated is evaluated in the hydro-oxidation of propylene starting at 140°C and increasing temperature to 160°C. Results are shown in Table 10.

Table 10. Added Cl and Activation in H_2 vs pH[1,2]

pH	Example	Productivity With NaCl	H_2O/PO with NaCl	Comparative Exp.	Productivity No NaCl	H_2O/PO without NaCl
2.1	31	436	4.21	11	113	9.02
4.2	32	416	4.06	12	213	6.51
5.9	33	405	3.63	13	232	4.48
8.2	34	423	3.44	14	267	4.14
10.3	35	432	3.33	15	267	4.34
12	36	464	3.48	16	267	4.14

1. PO = propylene oxide
2. Data taken at 160°C, 100 psia (689 kPa), total flow 250 cc/min; feed composition 30% PP, 10% O_2, 10% H_2 and balance He

Comparative Experiments 11 to 16

Examples 31-36 are repeated, with the exception that in each case no sodium chloride is added. The pH is adjusted by adding the corresponding amounts of 50 wt% sodium hydroxide. The resulting catalysts contain 1500 ppm gold and a Cl/Au ratio of 4/1. The catalysts are each heated in hydrogen (10 percent) in helium as temperature is raised from room temperature to 250°C in 120 minutes, and then held at 250°C for 1 hour. The samples thusly-treated are evaluated in the hydro-oxidation of propylene as in Example 31-36, with the results shown in Table 10. When Examples 31-36 are compared with their corresponding Comparative Experiments 11 to 16, it is seen that the addition of sodium chloride improves both productivity and the H_2O/PO molar ratio. As the pH increases from 2 to 12, productivity and water/PO molar ratio are also improved.

Example 37

A portion of the titanosilicate support, prepared as described hereinabove, is oven dried at 136°C for 1 hour. An aqueous cesium trifluoroacetate (CsTFA) solution is prepared by mixing water (35.013 g) and CsTFA (0.304 mL of 6 M aqueous CsTFA from Fluka). An aqueous cesium acetate (CsOAc) solution is prepared by mixing water (17.500 g) and CsOAc (0.1830 g). A combined CsTFA/CsOAc solution is prepared by mixing 2.5 mL of the CsTFA solution and 2.5 mL of the CsOAc solution. The combined CsTFA/CsOAc solution (1.397 g) is added to the titanosilicate support (2.00 g). The sample is transferred to a vacuum oven, held under vacuum at room temperature for 30 minutes, heated under vacuum to 70°C, and then held under vacuum at 70°C for 1 hour. The heat is turned off and the sample is cooled to room temperature and maintained under vacuum overnight. A portion of the CsTFA/CsOAc/titanosilicate support is oven dried at 136°C for 1 hour. A gold cluster solution is prepared by mixing Nanogold® Au-ligand cluster complex (30 nmol; 1.4 nm gold particles; Nanoprobes, Incorporated; Catalog no. 2010) with cold methanol (2.180 g). The solution (0.373 g) is then added to the CsTFA/CsOAc/titanosilicate support (0.55 g). The sample is covered and held in a freezer for 30 minutes. The sample is transferred to a vacuum oven, held under vacuum at room temperature for 30 minutes, heated to 100°C, held at 100°C for 60 minutes, cooled to room temperature, and then maintained under vacuum overnight. The resulting catalyst composition is heated in the reactor and tested in the hydro-oxidation of propylene; both the heating and hydro-oxidation being conducted in the manner described in Example 1. Data are recorded after the reactor temperature is increased to 210°C. Results are shown in Table 11.

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Table 11. Gold Cluster with Added Cs and F[1,2]

Time (hrs)	Temperature (°C)	PP Conversion	PO Selectivity	Cumulative H_2O/PO
0	209	1.86	95.0	1.08
5	214	2.10	94.8	1.42
10	214	2.03	94.9	1.68
15	215	1.97	95.2	1.82
20	215	1.89	95.4	1.95
25	216	1.85	94.9	2.04
30	214	1.81	95.1	2.11
35	225	2.18	94.1	2.19
40	225	2.12	94.3	2.24
45	225	2.08	94.7	2.31
50	225	1.99	94.3	2.36
55	230	2.11	93.8	2.40
60	227	2.05	93.8	2.45
65	227	2.00	94.0	2.49
70	229	1.99	94.1	2.52

1. PP = propylene; PO = propylene oxide
2. Feed to reactor is 30% PP, 10% O_2, 10% H_2, and balance He; 100 psia (689 kPa), 250 cc/min; temperature as shown.

Examples 38 to 41

A titanosilicate is prepared as in Example 1 and used as 14/30 U.S. mesh particles (595-1420 μm) in the following examples.

Example 38: Chloroauric acid [0.429 g (2.17 mmol) $HAuCl_4•3H_2O$] is dissolved in water (79.96 g) to which is added tetramethylammonium hydroxide $N(CH_3)_4OH$ [1.633 g, 25% in H_2O]. Then, sufficient water is added to bring the contents to 100.0 g. To a portion (15.003 g) of the gold solution are added cesium nitrate (0.474 g, 2.438 mmol) and cesium fluoride (0.025 g, 0.163 mmol). The resulting gold solution (2.172 g) is impregnated onto the titanosilicate support (3.0 g). The impregnated support is vacuum dried at 105°C for 30 minutes. The resulting catalyst has Cs:Au = 16, Cl:Au = 4, and F:Au = 1.

Example 39: A gold and tetramethylammonium hydroxide aqueous solution is prepared as in Example 38. To a portion (15.007 g) of the gold solution are added cesium nitrate (0.447g, 2.274 mmol) and cesium fluoride (0.050 g, 0.326 mmol). The resulting gold solution (2.170 g) is impregnated onto the titanosilicate support (3.00 g). The impregnated support is vacuum dried at 105°C for 30 minutes. The resulting catalyst has Cs:Au = 16, Cl:Au = 4, and F:Au = 2.

Example 40: A gold and tetramethylammonium hydroxide aqueous solution is prepared as in Example 38. To a portion (15.002 g) of the gold solution are added cesium nitrate (0.382 g, 1.95 mmol) and cesium fluoride (0.099 g, 0.65 mmol). The resulting gold solution (2.179 g) is impregnated onto the titanosilicate support (3.00 g). The impregnated support is vacuum dried at 105°C for 30 minutes. The resulting catalyst has Cs:Au = 16, Cl:Au = 4, and F:Au =4.

Example 41: A gold and tetramethylammonium hydroxide aqueous solution is prepared as in Example 28. To a portion (15.010 g) of the gold solution are added cesium nitrate (0.250 g, 1.95 mmol) and cesium fluoride (0.198 g, 0.65 mmol). The resulting gold solution (2.173 g) is impregnated onto the titanosilicate support (3.00 g). The impregnated support is vacuum dried at 105°C for 30 minutes. The resulting catalyst has Cs:Au = 16, Cl:Au = 4, and F:Au =8.

Each of the catalysts is evaluated in the hydro-oxidation of propylene as follows. Each of the catalysts is heated in hydrogen (10 percent in helium) at 250°C for 1 hour then run the hydro-oxidation process starting at 140°C, then holding the temperature for 6 hours, and then increasing the temperature at 2.5°C/h to 160°C. Results are shown in Table 12.

Table 12. $HAuCl_4$ with Added F[1]

Example	Cs/Au	Cl/Au	F / Au	Conversion	Selectivity	H_2O/PO
CE17	16	4	0	2.29	96.4	3.95
38	16	4	1	2.18	96.7	3.63
39	16	4	2	2.25	96.9	3.68
40	16	4	4	2.51	96.4	3.98
41	16	4	8	2.25	96.6	3.99

1. Data taken at 160°C and 100 psia; 30% PP, 10% O_2, 10% H_2 and balance He
2. PP = propylene; PO = propylene oxide

Comparative Experiment 17

Example 38 is repeated, with the exception that no cesium fluoride is added. The resulting material has a Cs:Au = 16, Cl:Au = 4, and F:Au = 0. The comparative catalyst is evaluated in the hydro-oxidation of propylene in the manner described for Examples 38-41 with the results shown in Table 12. It can be seen by comparing Examples 38 – 41 with CE-17 that these catalyst samples start with a moderate cesium (Cs) content (Cs:Au = 16), and the balancing of the cesium from the $CsNO_3$ to CsF does not change the Cs:Au ratio. These catalyst samples have a constant Cl:Au ratio = 4 as obtained from the gold compound used ($HAuCl_4•3H_2O$). The main difference between the samples is an increase in the F:Au ratio from 0 to 8. With keeping the cesium and chloride contents constant, increasing the fluoride content increases catalyst activity and/or improves PO selectivity and/or decreases H_2O/PO ratio.

Examples 42 to 45

A titanosilicate is prepared as in Example 1 and used as 14/30 U.S. mesh particles (595-1420 μm) in the following examples.

Example 42: Chloroauric acid [0.429 g (2.17 mmol) $HAuCl_4•3H_2O$] is dissolved in H_2O (79.96 g) to which is added tetramethylammonium hydroxide $N(CH_3)_4OH$ [1.633 g, 25% in H_2O]. Then, sufficient water is added to bring the contents to 100.0 g. To a portion (15.003 g) of the gold solution are added cesium nitrate (0.474 g, 2.438 mmol) and cesium bromide (0.025 g, 0.163 mmol). The resulting gold solution (2.172 g) is impregnated onto the titanosilicate support (3.0 g). The impregnated support is vacuum dried at 105°C for 30 minutes. The resulting catalyst has Cs:Au = 16, Cl:Au = 4, and Br:Au = 1.

Example 43: A gold and tetramethylammonium hydroxide aqueous solution is prepared as in Example 42. To a portion (15.007 g) of the gold solution are added cesium nitrate (0.447g, 2.274 mmol) and cesium bromide (0.050 g, 0.326 mmol). The resulting gold solution (2.170 g) is impregnated onto the titanosilicate support (3.00 g). The impregnated support is vacuum dried at 105°C for 30 minutes. The resulting catalyst has Cs:Au = 16, Cl:Au = 4, and Br:Au = 2.

Example 44: A gold and tetramethylammonium hydroxide aqueous solution is prepared as in Example 42. To a portion (15.002 g) of the gold solution are added cesium nitrate (0.382 g, 1.95 mmol) and cesium bromide (0.099 g, 0.65 mmol). The resulting gold solution (2.179 g) is impregnated onto the titanosilicate support (3.00 g). The impregnated support is vacuum dried at 105°C for 30 minutes. The resulting catalyst has Cs:Au = 16, Cl:Au = 4, and Br:Au =4.

Example 45: A gold and tetramethylammonium hydroxide aqueous solution is prepared as in Example 42. To a portion (15.010 g) of the gold solution are added cesium nitrate (0.250 g, 1.95 mmol) and cesium fluoride (0.198 g, 0.65 mmol). The resulting gold solution (2.173 g) is impregnated onto the titanosilicate support (3.00 g). The impregnated support is vacuum dried at 105°C for 30 minutes. The resulting catalyst has Cs:Au = 16, Cl:Au = 4, and Br:Au =8.

Each of the catalysts is evaluated in the hydro-oxidation of propylene as follows. Each of the catalysts is heated in hydrogen (10 percent in helium) at 250°C for 1 hour then run the hydro-oxidation process starting at 140°C, then holding the temperature for 6 hours, and then increasing the temperature at 2.5°C/hr to 160°C. The temperatures were then adjusted to give nearly the same conversion. Results are shown in Table 13 at 160°C and then at temperatures for nearly the same conversion.

———Table 13. $HAuCl_4$ with Added Br[1]

Example	Temp	Hours on Stream	Cs/Au	Cl/Au	Br / Au	Conversion	Selectivity	H_2O/PO
CE18	160	24	16	4	0	2.11	97.0	3.58
42	160	24	16	4	1	1.46	98.2	2.81
43	160	24	16	4	2	0.92	98.8	2.63
44	160	24	16	4	4	0.31	99.3	3.04
45	160	24	16	4	8	0.10	98.9	5.87
CE18	160	64	16	4	0	1.85	95.9	5.35
42	170	64	16	4	1	1.82	97.1	3.57
43	190	64	16	4	2	1.88	96.4	3.75
44	240	64	16	4	4	1.64	90.2	4.61
45	240	64	16	4	8	0.53	90.8	4.61

1. Data taken at 100 psia; 30% PP, 10% O_2, 10% H_2 and balance He
2. PP = propylene; PO = propylene oxide

Comparative Experiment 18

Example 42 is repeated, with the exception that no cesium bromide is added. The resulting material has a Cs:Au = 16, Cl:Au = 4, and Br:Au = 0. The comparative catalyst is evaluated in the hydro-oxidation of propylene in the manner described for Examples 42-45 with the results shown in Table 13. It is seen by comparing Examples 42 – 45 with CE-18 that these samples start with a moderate cesium (Cs) content (Cs:Au = 16), and the balancing of the cesium from the $CsNO_3$ to CsBr does not change the Cs:Au ratio. These samples have a constant Cl:Au ratio = 4 as obtained from the gold compound used ($HAuCl_4•3H_2O$). The main difference between the samples is an increase in the Br:Au ratio from 0 to 8. With keeping the cesium and chloride contents constant, increasing the bromide content improves selectivity and/or decreases H_2O/PO ratio. The materials with added bromide content show higher selectivity and/or decreased H_2O/PO ratio even at higher temperature than the non-bromide containing materials.

Examples 46 to 47

A titanosilicate is prepared as in Example 1 and used as 14/30 U.S. mesh particles (595-1420 μm) in the following examples.

Example 46: Chloroauric acid [0.429 g (2.17 mmol) $HAuCl_4•3H_2O$] is dissolved in water (79.96 g) to which is added cesium hydroxide CsOH [1.403 g, 50 wt% in H_2O] up to a pH 10. Then, sufficient water is added to bring the contents to 100.0 g. To a portion (15.003 g) of the gold solution are added cesium nitrate (0.254 g, 1.3 mmol) and potassium nitrate (0.127 g, 1.26 mmol) and potassium iodide (0.007 g, 0.041 mmol). The resulting gold solution (2.172 g) is impregnated onto the titanosilicate support (3.0 g). The impregnated support is vacuum dried at 105°C for 30 minutes. The resulting catalyst has Cs/Au = 12.3; K/Au = 8; Cl/Au = 4; I/Au = 0.25.

Example 47: A gold and tetramethylammonium hydroxide aqueous solution is prepared as in Example 46. To a portion (15.003 g) of the gold solution are added cesium nitrate (0.254 g, 1.3 mmol) and potassium nitrate (0.123 g, 1.22 mmol) and potassium iodide (0.014 g, 0.082 mmol). The resulting gold solution (2.170 g) is impregnated onto the titanosilicate support (3.00 g). The impregnated support is vacuum dried at 105°C for 30 minutes. The resulting catalyst has Cs/Au = 12.3; K/Au = 8; Cl/Au = 4; I/Au = 0.50.

Each of the catalysts is evaluated in the hydro-oxidation of propylene as follows. Each of the catalysts is heated in hydrogen (10 percent in helium) at 250°C for 1 hour then run the hydro-oxidation process starting at 140°C, then holding the temperature for 6 hours, and then increasing the temperature at 2.5°C/hr to 160°C. Results are shown in Table 14.

Table 14. $HAuCl_4$ with Added I[1]

Example	Temp	Hours on Stream	Cs/Au	K/Au	Cl/Au	I / Au	Conversion	Selectivity	H_2O/PO
CE19	250	160	12.3	8	4	0	0.88	82.6	7.4
46	250	160	12.3	8	4	0.25	0.68	84.9	6.6
47	250	160	12.3	8	4	0.5	0.58	85.6	6.1

1. Data taken at 100 psia; 30% PP, 10% O_2, 10% H_2 and balance He
2. PP = propylene; PO = propylene oxide

Comparative Experiment 19

Example 46 is repeated, with the exception that no potassium iodide is added. The resulting material has a Cs/Au =12.3; K/Au = 8; Cl/Au = 4; I/Au = 0. The comparative catalyst is evaluated in the hydro-oxidation of propylene in the manner described for Examples 46 – 47 with the results shown in Table 14. It can be seen by comparing Examples 46 – 47 with CE-19 that these samples start with a moderate cesium (Cs) content (Cs:Au = 12.3) and a moderate potassium (K) content (K:Au = 8), and the balancing of the potassium from the KNO_3 to KI does not change the Cs:Au ratio nor the K:Au ratio. These samples have a constant Cl:Au ratio = 4 as obtained from the gold compound used ($HAuCl_4 \cdot 3H_2O$). The main difference between the samples is an increase in the I:Au ratio from 0 to 0.5. With keeping the cesium and potassium and chloride contents constant, increasing the iodide content improves selectivity and/or decreases H_2O/PO ratio.

Example 48

A portion of the titanosilicate support, prepared as described hereinabove, is oven dried at 136°C for 1 h. An aqueous cesium fluoride (CsF) solution is prepared by mixing water (4.955 g) and CsF (0.0411 g). The CsF solution (1.398 g) is added to the titanosilicate support (2.00 g). The sample is transferred to a vacuum oven, heated under vacuum to 70°C, and then held under vacuum at 70°C for 1 h. The heat is turned off and the sample is cooled to room temperature and maintained under vacuum overnight. A portion of the CsF/titanosilicate support is oven dried at 136°C for 1 h. A gold cluster solution is prepared by mixing Nanogold® Au-ligand cluster complex (0.0050 g; 1.4 nm gold particles; Nanoprobes, Incorporated; Catalog no. 2010) with cold methanol (12.148 g). The gold cluster solution

(0.378 g) is added to the CsF/titanosilicate support (0.55 g). The sample is covered and held in a freezer for 40 minutes. The sample is transferred to a vacuum oven, heated to 100°C, held at 100°C for 60 minutes, cooled to room temperature, and then maintained under vacuum overnight. The resulting catalyst composition is heated in the reactor and tested in the hydro-oxidation of propylene; both the heating and the hydro-oxidation being conducted in the manner described in Example 37. Results are shown in Table 15.

Table 15.

Time (hrs)	Temperature (°C)	PP Conversion	PO Selectivity	H_2O/PO
5	139	0.22	100.0	3.39
10	143	0.20	100.0	3.32
15	150	0.27	100.0	2.85
20	219	1.74	95.7	2.28
25	227	1.96	95.0	2.39
30	227	1.87	95.1	2.45
35	226	1.80	95.0	2.48
40	227	1.70	95.4	2.52
46	229	1.69	95.0	2.52
51	228	1.65	94.8	2.56
56	237	1.96	93.8	2.69
59	237	1.91	94.2	2.69
65	237	1.88	94.1	2.72
70	238	1.84	93.8	2.81
75	238	1.82	94.0	2.81
80	237	1.84	93.9	2.88
85	237	1.83	94.0	2.91

1. PP = propylene; PO = propylene oxide
2. Feed to reactor is 30% PP, 10% O_2, 10% H_2, and balance He; 100 psia (689 kPa), 250 cc/min; temperature as shown.

Example 49

A portion of the titanosilicate support, prepared as described hereinabove, is oven dried at 136°C for 1 hour. An aqueous cesium fluoride (CsF) solution is prepared by mixing water (17.779 g) and CsF (0.0730 g). A combined CsF/cesium chloride (CsCl) solution is prepared by mixing the CsF solution (5.079 g) and CsCl (0.0230 g). The combined CsF/CsCl solution (1.404 g) is added to the titanosilicate support (2.00 g). The sample is transferred to a vacuum oven, heated under vacuum to 70°C, and then held under vacuum at 70°C for 1 h. The heat is turned off and the sample is cooled to room temperature and maintained under vacuum overnight. A portion of the CsF/CsCl/titanosilicate support is oven dried at 136°C for 1 h. A gold cluster solution is prepared by mixing Nanogold® Au-ligand cluster complex (0.0050 g; 1.4 nm gold particles; Nanoprobes, Incorporated; Catalog no. 2010) with cold methanol (12.148 g). The gold cluster solution (0.362 g) is then added to the CsF/CsCl/titanosilicate support (0.55 g). The sample is covered and held in a freezer for 30 minutes. The sample is transferred to a vacuum oven, heated to 100°C, held at 100°C for 60 minutes, cooled to room temperature, and then maintained under vacuum overnight. The resulting catalyst composition is heated in the reactor and tested in the hydro-oxidation of propylene; both the heating and the hydro-oxidation being conducted in the manner described in Example 37. Results are shown in Table 16.

Table 16.

Time (hrs)	Temperature (°C)	PP Conversion	PO Selectivity	H_2O/PO
5	139	0.13	100.0	4.83
10	139	0.11	100.0	5.26
15	155	0.17	100.0	3.71
20	214	1.14	95.1	2.71
25	249	2.03	91.7	3.02
30	249	2.00	91.9	3.06
35	244	1.97	91.9	3.09
40	252	1.94	92.1	3.13
46	243	1.94	92.1	3.16
51	248	1.90	92.1	3.20
56	253	2.09	91.2	3.34
59	253	2.04	91.0	3.34
65	254	2.02	91.1	3.37
70	253	1.99	91.2	3.40
75	253	2.00	90.8	3.43
80	250	2.02	91.0	3.49
85	254	2.04	91.1	3.50

1. PP = propylene; PO = propylene oxide
2. Feed to reactor is 30% PP, 10% O_2, 10% H_2, and balance He; 100 psia (689 kPa), 250 cc/min; temperature as shown.

Example 50

A portion of the titanosilicate support, prepared as described hereinabove, is oven dried at 136°C for 1 h. An aqueous cesium fluoride (CsF) solution is prepared by mixing water (17.779 g) and CsF (0.0730 g). A combined CsF/cesium bromide (CsBr) solution is prepared by mixing the CsF solution (5.085 g) and CsBr (0.0296 g). The combined CsF/CsBr solution (1.408 g) is added to the titanosilicate support (2.00 g). The sample is transferred to a vacuum oven, heated under vacuum to 70°C, and then held under vacuum at 70°C for 1 h. The heat is turned off and the sample is cooled to room temperature and maintained under vacuum overnight. A portion of the CsF/CsBr/titanosilicate support is oven dried at 136°C for 1 h. A gold cluster solution is prepared by mixing Nanogold® Au-ligand cluster complex (0.0050 g; 1.4 nm gold particles; Nanoprobes, Incorporated; Catalog no. 2010) with cold methanol (12.148 g). The gold cluster solution (0.366 g) is added to the CsF/CsBr/titanosilicate support (0.55 g). The sample is covered and held in a freezer for 30 minutes. The sample is transferred to a vacuum oven, heated to 100°C, held at 100°C for 60 minutes, cooled to room temperature, and then maintained under vacuum overnight. The resulting catalyst composition is heated in the reactor and tested in the hydro-oxidation of propylene; both the heating and the hydro-oxidation being conducted in the manner described in Example 37. Results are shown in Table 17.

Table 17.

Time (hrs)	Temperature (°C)	PP Conversion	PO Selectivity	H_2O/PO
5	139	0.03	100.0	14.20
10	142	0.07	100.0	7.38
15	153	0.11	100.0	5.00
20	220	0.91	94.9	2.96
25	260	2.18	89.6	3.45
30	260	2.19	89.6	3.52
35	260	2.18	89.8	3.58
40	260	2.17	89.4	3.62
46	260	2.17	89.8	3.67
51	260	2.15	89.7	3.66
56	260	2.14	89.6	3.70
59	260	2.14	89.4	3.71
65	260	2.12	89.6	3.72
70	263	2.11	89.6	3.82
75	260	2.11	89.4	3.85
80	260	2.13	89.4	3.85
85	260	2.17	89.3	3.88

1. PP = propylene; PO = propylene oxide
2. Feed to reactor is 30% PP, 10% O_2, 10% H_2, and balance He; 100 psia (689 kPa), 250 cc/min; temperature as shown.

Example 51

A portion of the titanosilicate support, prepared as described hereinabove, is oven dried at 136°C for 1 h. A combined CsBr/CsOAc solution is prepared by mixing water (5.05 g), CsBr (0.0285 g), and CsOAc (0.0261 g). The combined CsBr/CsOAc solution (1.402

g) is added to the titanosilicate support (2.00 g). The sample is transferred to a vacuum oven, held at room temperature under vacuum for 30 minutes, heated under vacuum to 70°C, and then held under vacuum at 70°C for 1 h. The heat is turned off and the sample is cooled to room temperature and maintained under vacuum overnight. A portion of the CsBr/CsOAc/titanosilicate support is oven dried at 136°C for 1 h. A gold cluster solution is prepared by mixing Nanogold® Au-ligand cluster complex (0.0050 g; 1.4 nm gold particles; Nanoprobes, Incorporated; Catalog no. 2010) with cold methanol (6.082 g). The gold cluster solution (0.370 g) is added to the CsBr/CsOAc/titanosilicate support (0.55 g). The sample is covered and held in a freezer for 80 minutes. The sample is transferred to a vacuum oven, heated to 100°C, held at 100°C for 60 minutes, cooled to room temperature, and then maintained under vacuum overnight. The resulting catalyst composition is heated in the reactor and tested in the hydro-oxidation of propylene; both the heating and the hydro-oxidation being conducted in the manner described in Example 37. Results are shown in Table 18.

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Table 18.

Time (hrs)	Temperature (°C)	PP Conversion	PO Selectivity	H_2O/PO
10	141	0.10	92.3	4.96
20	220	1.30	93.9	2.99
31	240	2.13	92.2	3.59
40	240	2.11	92.2	3.65
50	240	2.08	92.6	3.77
60	240	2.09	92.5	3.66
70	240	2.08	92.2	3.87
80	240	2.08	92.0	3.88
90	240	2.06	92.3	3.95
100	240	2.04	92.2	4.02
110	244	2.17	91.6	4.09
120	244	2.15	91.5	3.99
130	244	2.15	91.7	4.03
140	244	2.17	91.4	4.06
150	244	2.19	91.3	4.16
160	244	2.16	91.5	4.17
171	247	2.20	91.4	4.23
180	246	2.17	91.2	4.25
190	246	2.15	91.2	4.27
200	246	2.14	91.1	4.26
210	246	2.13	91.1	4.31
220	246	2.13	90.9	4.32
230	246	2.10	91.1	4.36
240	246	2.08	91.1	4.42
250	246	2.07	91.2	4.44
261	246	2.06	91.0	4.50
270	246	2.06	91.1	4.48
280	246	2.04	90.9	4.51

1. PP = propylene; PO = propylene oxide
2. Feed to reactor is 30% PP, 10% O_2, 10% H_2, and balance He; 100 psia (689 kPa), 250 cc/min; temperature as shown.

EMBODIMENTS OF THE INVENTION

1. An improved hydro-oxidation process of preparing an olefin oxide comprising contacting an olefin having three or more carbon atoms with oxygen in the presence of hydrogen and in the presence of a hydro-oxidation catalyst comprising gold deposited on a titanium-containing support, the gold being provided to the catalyst from a source of gold, and the contacting being conducted under process conditions sufficient to produce the corresponding olefin oxide; the improvement comprising conducting the process in the

presence of a halogen-containing compound such that the process employs a halogen to gold atomic ratio greater than the corresponding halogen to gold atomic ratio of the source of gold; with the proviso that when cesium or palladium is present in the catalyst with chloride or a chlorine-containing compound, then the catalyst comprises at least one additional halogen other than chlorine.

2. The aforementioned embodiment wherein the olefin is an unsubstituted or substituted C_{3-12} olefin, more preferably, an unsubstituted or substituted C_{3-8} olefin; most preferably, propylene.

3. Any one of the aforementioned embodiments wherein the olefin is selected from propylene, 1-butene, 2-butene, 2-methylpropene, 1-pentene, 2-pentene, 2-methyl-1-butene, 2-methyl-2-butene, 1-hexene, 2-hexene, 3-hexene, and analogously, the various isomers of methylpentene, ethylbutene, heptene, methylhexene, ethylpentene, propylbutene, the octenes, including preferably 1-octene, and other higher analogues of these; as well as butadiene, cyclopentadiene, dicyclopentadiene, styrene, α-methylstyrene, divinylbenzene, allyl alcohol, allyl ether, allyl ethyl ether, allyl butyrate, allyl acetate, allyl benzene, allyl phenyl ether, allyl propyl ether, and allyl anisole.

4. Any one of the aforementioned embodiments wherein the quantity of olefin is advantageously greater than about 1, preferably, greater than about 10, and more preferably, greater than about 20 mole percent, and advantageously, the quantity of olefin is less than about 99, preferably, less than about 85, and more preferably, less than about 70 mole percent, based on the total moles of olefin, oxygen, hydrogen, and optional diluent.

5. Any one of the aforementioned embodiments wherein the quantity of oxygen advantageously is greater than about 0.01, preferably, greater than about 1, and more preferably greater than about 5 mole percent, and advantageously less than about 30, preferably, less than about 25, and more preferably less than about 20 mole percent, based on the total moles of olefin, hydrogen, oxygen, and optional diluent.

6. Any one of the aforementioned embodiments wherein the quantity of hydrogen is advantageously greater than about 0.01, preferably, greater than about 0.1, and more preferably, greater than about 3 mole percent, and advantageously less than about 50,

preferably, less than about 30, and more preferably, less than about 20 mole percent, based on the total moles of olefin, hydrogen, oxygen, and optional diluent.

7. Any one of the aforementioned embodiments wherein a diluent is employed selected from aliphatic alcohols, preferably C_{1-10} aliphatic alcohols, such as methanol and t-butanol; chlorinated aliphatic alcohols, preferably C_{1-10} chlorinated alkanols, such as chloropropanol; chlorinated hydrocarbons, preferably C_{1-10} chlorinated hydrocarbons, such as dichloroethane and chlorinated benzenes, including chlorobenzene and dichlorobenzene; aromatic hydrocarbons, preferably, C_{6-15} aromatic hydrocarbons, such as benzene, toluene, and xylenes; ethers, preferably, C_{2-20} ethers, including tetrahydrofuran and dioxane; as well as liquid polyethers, polyesters, and polyalcohols.

8. The aforementioned embodiment 7 wherein the diluent is used in a gas phase, and the amount of diluent is advantageously greater than about 0, preferably greater than about 0.1, and more preferably greater than about 15 mole percent, and advantageously less than about 90, preferably less than about 80, and more preferably less than about 70 mole percent, based on the total moles of olefin, oxygen, hydrogen, and diluent.

9. The aforementioned embodiment 7 wherein a diluent (or solvent) is used in the liquid phase, the amount of liquid diluent (or solvent) is advantageously greater than about 0, and preferably greater than about 5 weight percent, and advantageously less than about 99, and preferably less than about 95 weight percent, based on the total moles of olefin and diluent.

10. Any one of the aforementioned embodiments wherein the average size of metallic gold particles, when they are present, advantageously ranges from about 10 Å to about 500 Å, and preferably, from about 10 Å to about 35 Å, as measured by HR-TEM.

11. Any one of the aforementioned embodiments wherein gold loading is advantageously greater than about 0.001 weight percent (10 parts per million, ppm), and preferably, greater than about 0.005 weight percent (50 ppm), but advantageously less than about 20, preferably, less than about 10, and more preferably, less than about 5.0 weight percent, based on the total weight of the catalyst.

12. Any one of the aforementioned embodiments wherein the titanium-containing support is selected from titanium-containing amorphous and crystalline silicas, such as Ti-silicalite or Ti-MCM-41; titanium-containing aluminas; titanium-containing

metallosilicates, including Ti-aluminosilicates and preferably titanosilicates; titanium-containing promoter metal silicates, such as, the Ti-silicates of Groups 1 and 2 and the lanthanide and actinide elements; and titanium-containing refractory oxides and conventional support materials, as well as stoichiometric and non-stoichiometric promoter metal titanates of a crystalline or amorphous nature, having a surface area greater than about 5 m^2/g, non-limiting examples of which include such titanates of Group 1, Group 2, and the lanthanide and actinide metals, preferably, magnesium titanate, calcium titanate, barium titanates, strontium titanate, sodium titanate, potassium titanate, lithium titanate, cesium titanate, rubidium titanate, and the titanates of erbium, lutetium, thorium, and uranium; as well as amorphous or crystalline titanium oxides including anatase, rutile, and brookite phases of titanium dioxide, preferably, having a surface area greater than 5 m^2/g.

13. Any one of the aforementioned embodiments wherein advantageously, the titanium loading on the titanium-containing support is greater than about 0.02, preferably, greater than about 0.1, and advantageously less than about 35, and preferably, less than about 10 weight percent, based on the weight of the support including any binder.

14. Any one of the aforementioned embodiments wherein the titanium-containing support comprises a titanosilicate selected from TS-1, TS-2, Ti-beta, Ti-MCM-41, Ti-MCM-48, Ti-SBA-15, and Ti-SBA-3; preferably comprises a quasi-crystalline titanosilicate having an MFI structure, which is orthorhombic at room temperature (21°C) as determined by X-ray diffraction (XRD).

15. Any one of the aforementioned embodiments wherein the silicon to titanium atomic ratio (Si:Ti) of a preferred nanoporous titanosilicate support is advantageously greater than about 5:1, preferably, greater than about 35:1, more preferably, greater than about 50:1, but advantageously less than about 2000:1, preferably, less than about 1000:1, and more preferably, less than about 250:1.

16. Any one of the aforementioned embodiments, wherein the titanium-containing support is in the form of beads, pellets, spheres, honeycombs, monoliths, extrudates, and films.

17. Any one of the aforementioned embodiments, wherein the titanium-containing support is extruded with, bound to, or supported on a second support selected from

carbon, silica, titania, alumina, aluminosilicates, and magnesia; ceramics, including ceramic carbides and nitrides, as well as any metallic support; in a quantity of second support from about 0 to about 95 weight percent, based on the combined weight of the catalyst (comprising gold, halogen-containing compound, and titanium-containing support) and the secondary support.

18. Any of the aforementioned embodiments wherein particles of a preferred nanoporous titanium-containing support, excluding binder, are preferably greater than about 50 nm and less than about 2 microns (μm) in diameter (or largest dimension); and preferably, particles of the preferred nanoporous titanium-containing support, including binder, are greater than about 50 nm and less than about 1 μm in diameter (or largest dimension).

19. Any one of the aforementioned embodiments wherein the source of gold is selected from one or more of the following compounds: sodium gold oxide ($NaAuO_2$), cesium gold oxide ($CsAuO_2$), chloroauric acid, gold chloride, gold fluoride, sodium fluoroaurate, potassium fluoroaurate, sodium chloroaurate, potassium chloroaurate, gold cyanide, potassium gold cyanide, gold acetate, diethylamine auric acid trichloride, alkyl gold halides, preferably, alkyl gold chlorides and alkyl gold fluorides, and alkali aurates, such as lithium aurate, sodium aurate, potassium aurate, rubidium aurate, and cesium aurate; as well as gold cluster complexes, including preferably, the following clusters Au_3, Au_4, Au_5, Au_6, Au_7, Au_8, Au_9, Au_{10}, Au_{11}, Au_{12}, Au_{13}, Au_{20}, Au_{55}, and Au_{101}, $(Ph_3PAu)_3OBF_4$, $[(AuPPh_3)_3O]PF_6]$, $Au_5(PPh_3)_4Cl$, $Au_6(PPh_3)_6(BF_4)_2$, $Au_6(PPh_3)_6(NO_3)_2$, $Au_6(PPh_3)_6(PF_6)_2$, $Au_8(PPh_3)_8(NO_3)_2$, $Au_8(PPh_3)_7(NO_3)_2$, $Au_9(PPh_3)_8(NO_3)_3$, $Au_{10}(PPh_3)_5(C_6F_5)_4$, $Au_{11}Cl_3\{(m\text{-}CF_3C_6H_4)_3P\}_7$, $Au_{11}(PPh_3)_7(PF_6)_3$, $[Au_{13}(PMe_2Ph)_{10}Cl_2](PF_6)_3$, $Au_{13}(PPh_3)_4[S(CH_2)_{11}(CH_3)]_4$, $[Au_{13}(PPh_2CH_2PPh_2)_6](NO_3)_4$, $Au_{55}(Ph_2PC_6H_4SO_3Na \cdot 2H_2O)_{12}Cl_6$, and $Au_{55}(PPh_3)_{12}Cl_6$, wherein "Ph" is phenyl and "Me" is methyl; as well as gold-ligand cluster compounds, preferably, Nanoprobes brand gold-ligand cluster complexes of Catalog numbers 2010, 2022, and 2023; $[(PPh_3)Pt(AuPPh_3)_6](NO_3)_2$, $[(PPh_3)(CO)Pt(AuPPh_3)_6](PF_6)_2$, $[Pd(AuPPh_3)_8](NO_3)_2$, $[H_4(PPh_3)_2Re(AuPPh_3)_5](PF_6)_2$, $[PPh_3Pt(AuPPh_3)_6](PF_6)_2$, $[H(PPh_3)Pt(AuPPh_3)_7](NO_3)$, $[Pt(AuPPh_3)_7(Ag)_2](NO_3)_3$. $[Pd(AuPPh_3)_8](PF_6)_2$, $[Pt(AuPPh_3)_8](NO_3)_2$, $[Pt(AuPPh_3)_8](PF_6)_2$, $[(PPh_3)Pt(AuPPh_3)_8(Ag)](NO_3)_2$, $[Pt_2(AuPPh_3)_{10}(Ag)_{13}]Cl_7$, wherein "Ph" is phenyl.

20. Any one of the aforementioned embodiments wherein the halogen-containing compound comprises halogen atoms that are covalently bonded to a central atom, such as carbon, phosphorus, or boron; or comprises halogen atoms that are negatively-charged ions, i.e., halides, that are ionically associated with a positively-charged cation (e.g., M^{n+} or NH_4^+ or NR_4^+, wherein M is any metal ion having valence n^+ and each R is independently any monovalent hydrocarbyl radical, advantageously having from 1 to 20 carbon atoms).

21. Any one of the aforementioned embodiments wherein the halogen-containing compounds are halide-containing compounds selected from fluorides, chlorides, bromides, iodides, and mixtures of chlorides with fluorides, bromides, and/or iodides.

22. Any one of the aforementioned embodiments wherein the halogen-containing compounds are non-metallic halogens selected from elemental halogens, such as chlorine (Cl_2) and fluorine (F_2); ammonium halides, such as ammonium chloride, ammonium bromide, ammonium iodide and ammonium fluoride; or quaternary organo-ammonium halides, preferably, tetra-(C_{1-10}) organo-ammonium halides, such as tetramethylammonium fluoride, tetramethyl ammonium chloride, tetramethylammonium bromide, tetramethylammonium iodide, tetraethylammonium fluoride, tetraethylammonium chloride, tetraethylammonium bromide, and tetraethylammonium iodide; as well as boron halides, such as boron trifluoride and boron tetrafluoride ion; phosphorus halides, such as phosphorus trichloride and phosphorus hexafluoride ion; and organic halides, including preferably, C_{1-20} alkyl halides, such as, methyl chloride, dichloromethane, chloroform, and ethylchloride, and halogen-substituted C_{1-20} carboxylic acid salts, preferably, sodium trifluoroacetate and cesium trifluoroacetate.

23. Any one of the aforementioned embodiments wherein the halogen-containing compound is provided to the process as a metallic halide selected from halides of silver, Group 1 metals including lithium, sodium, potassium, rubidium, and cesium; Group 2 metals, including beryllium, magnesium, calcium, strontium, and barium; the platinum group metals, including ruthenium, rhodium, palladium, osmium, iridium, and platinum; the lanthanide rare earth metals, including lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium; and the actinide metals, specifically, thorium and uranium.

24. Any one of the aforementioned embodiments wherein the quantity of

halogen-containing compound provided to the catalyst and/or process is determined from the halogen/gold atomic ratio chosen for use; and the halogen/gold atomic ratio is advantageously greater than 0, preferably, greater than about 1/1, and more preferably, greater than 4/1, but advantageously less than about 32/1, preferably, less than about 16/1, and more preferably, less than about 12/1.

25. Any one of the aforementioned embodiments wherein one or more promoter(s) are employed in the catalyst and is(are) selected from silver, Group 1 metals including lithium, sodium, potassium, rubidium, and cesium; Group 2 metals, including beryllium, magnesium, calcium, strontium, and barium; the lanthanide rare earth metals, including lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium; and the actinide metals, specifically, thorium and uranium.

26. Any one of the aforementioned embodiments wherein one or more promoters are present in the catalyst, and the total quantity thereof advantageously is greater than about 0.001, and preferably, greater than about 0.01 weight percent, but advantageously less than about 20, and preferably, less than about 15 weight percent, based on the total weight of the catalyst.

27. Any one of the aforementioned embodiments wherein the catalyst is heated under helium, and the pH of the solution from which gold and/or promoter(s) and/or halogen-containing compound(s) is deposited onto the support ranges from 5 to 14.

28. Any one of the aforementioned embodiments wherein the catalyst is heated under hydrogen, and the pH of the solution from which gold and/or promoter(s) and/or halogen-containing compound(s) is deposited onto the support ranges from 2 to 14.

29. Any one of the aforementioned embodiments wherein the process is conducted in a reactor selected from batch, fixed-bed, transport bed, fluidized bed, moving bed, trickle bed, shell and tube, continuous flow, intermittent flow, and swing reactors.

30. Any one of the aforementioned embodiments wherein the process is conducted advantageously at a temperature greater than about ambient, taken as 21°C, preferably, greater than about 70°C, more preferably greater than about 130°C, and advantageously less than about 300°C, preferably less than about 260°C.

31. Any one of the aforementioned embodiments wherein the process is conducted at a pressure advantageously ranging from about 1 psia (6.89 kPa) to about 400 psia (2,758 kPa), preferably, from about 100 psia (690 kPa) to about 300 psia (2,069 kPa).

32. Any one of the aforementioned embodiments wherein the process is conducted in a gas phase at a gas hourly space velocity (GHSV) of the olefin advantageously greater than about 10 ml olefin per ml catalyst per hour (h^{-1}), preferably greater than about 100 h^{-1}, and more preferably, greater than about 1,000 h^{-1}, and advantageously less than about 50,000 h^{-1}, preferably, less than about 35,000 h^{-1}, and more preferably, less than about 20,000 h^{-1}.

33. Any one of the aforementioned embodiments wherein olefin conversion is advantageously greater than about 0.25 mole percent, preferably, greater than about 1.0 mole percent, more preferably, greater than about 1.5 mole percent, and most preferably, greater than about 2.0 mole percent.

34. Any one of the aforementioned embodiments wherein selectivity to olefin oxide is advantageously greater than about 70, preferably, greater than about 80, and more preferably, greater than about 90 mole percent.

35. Any one of the aforementioned embodiments wherein a water to olefin oxide molar ratio of the effluent stream is greater than about 1:1, but advantageously less than about 6:1, preferably, less than about 5:1, and more preferably, less than 4:1, over a period of time greater than 70 hours, and preferably, up to 100 hours of operation.

36. Any of the aforementioned embodiments wherein productivity of the catalyst, measured as grams of olefin oxide per kilogram catalyst per hour (g OO/kg cat-h), more particularly, grams propylene oxide per kg catalyst per hour (g PO/kg cat-h), is advantageously greater than about 50 g OO/kg cat-h, preferably, greater than about 100 g OO/kg cat-h, and more preferably, greater than about 300 g OO/kg cat-h.

37. A novel catalyst composition comprising gold and a halogen-containing compound deposited on a titanium-containing support; the gold being provided to the catalyst from a source of gold such that the catalyst possesses a halogen to gold atomic ratio greater than the corresponding halogen to gold atomic ratio of the source of gold; with the proviso that when cesium or palladium is present in the catalyst with chloride or a chlorine-containing compound,

then the catalyst comprises at least one additional halogen other than chlorine; the catalyst being more specifically and preferably defined as stated in any of the aforementioned applicable embodiments.

38. The embodiment of 37 wherein the halogen is selected from fluoride, chloride, bromide, iodide, and mixtures of chloride with fluoride, bromide, and/or iodide.

WHAT IS CLAIMED IS:

1. An improved hydro-oxidation process of preparing an olefin oxide comprising contacting an olefin having three or more carbon atoms with oxygen in the presence of hydrogen and in the presence of a hydro-oxidation catalyst comprising gold deposited on a titanium-containing support, the gold being provided to the catalyst from a source of gold, and the contacting being conducted under process conditions sufficient to produce the corresponding olefin oxide; the improvement comprising conducting the process in the presence of a halogen-containing compound such that the process employs a halogen to gold atomic ratio greater than the corresponding halogen to gold atomic ratio of the source of gold; and with the proviso that when cesium or palladium is present in the catalyst with chloride or a chlorine-containing compound, then the catalyst comprises at least one additional halogen other than chlorine.

2. The process of Claim 1 wherein the olefin is a C_{3-12} monoolefin or diolefin.

3. The process of Claim 1 or Claim 2 wherein the olefin is selected from propylene,

4. The process of any one of Claims 1 to 3 wherein gold is loaded onto the support in an amount greater than 0.001 and less than 20 weight percent, based on the total weight of the catalyst.

5. The process of any one of Claims 1 to 4 wherein the halogen-containing compound is selected from elemental halogens, phosphorus halides, boron halides, ammonium halides, quaternary C_{1-20} organo-ammonium halides, C_{1-20} alkyl halides, and halogen-substituted C_{1-20} carboxylic acid salts, and mixtures thereof.

6. The process of any one of Claims 1 to 4 wherein the halogen-containing compound is selected from the halides of silver, Group 1, Group 2, the lanthanide rare earths and actinide elements, and combinations thereof.

7. The process of Claim 6 wherein the halogen-containing compound is selected from the halides of lithium, sodium, potassium, rubidium, cesium, magnesium, calcium, barium, erbium, lutetium, and combinations thereof.

8. The process of any one of Claims 1 to 7 wherein the halogen is a halide selected from fluoride, chloride, bromide, iodide, and mixtures of chloride with fluoride, bromide, and/or iodide.

9. The process of any one of Claims 1 to 8 wherein the atomic ratio of halogen to gold provided to the process ranges from greater than 1/1 to less than 32/1.

10. The process of any one of Claims 1 to 9 wherein the titanium-containing support comprises a nanoporous titanosilicate.

11. The process of any one of Claims 1 to 10 wherein the process is conducted at a temperature greater than 20°C and less than 300°C, and at a pressure ranging from 1 psia to 400 psia (6.89 to 2758 kPa).

12. The process of any one of Claims 1 to 11 wherein the process is conducted in a gaseous phase at a gas hourly space velocity of the olefin greater than 10 h^{-1} and less than 50,000 h^{-1}.

13. The process of any one of Claims 1 to 12 wherein a diluent is employed selected from helium, nitrogen, argon, methane, carbon dioxide, steam, and mixtures thereof.

14. The process of any one of Claims 1 to 13 wherein the catalyst is bound to or supported on a second support selected from silica, titania, alumina, aluminosilicates, magnesia, ceramic carbides and nitrides.

15. The process of any one of Claims 1 to 14 wherein propylene is contacted with oxygen and hydrogen in a gas phase in the presence of a hydro-oxidation catalyst comprising gold and a promoter metal halide deposited onto a nanoporous titanosilicate, wherein the halide is selected from chloride, fluoride, bromide, iodide, and mixtures of chloride with fluoride, bromide, and/or iodide, and the promoter metal is selected from silver, lithium, sodium, potassium, rubidium, cesium, barium, magnesium, calcium, erbium, lutetium, and mixtures thereof.

16. A catalyst comprising gold and at least one halogen-containing compound deposited on a titanium-containing support, the gold being provided to the catalyst from a source of gold; such that the catalyst has a halogen to gold atomic ratio greater than the corresponding halogen to gold atomic ratio of the source of gold; and with the proviso that

when cesium or palladium is present in the catalyst with chloride or a chlorine-containing compound, then the catalyst comprises at least one additional halogen other than chlorine.

. 17. The composition of Claim 16 wherein the gold loading is greater than 0.001 and less than 20 weight percent, based on the total weight of the catalyst.

18. The composition of Claim 16 or 17 wherein if gold particles are present, the particles have an average size less than 1 nm.

19. The composition of any one of Claims 16 to 18 wherein the halogen is a halide selected from chloride, fluoride, bromide, iodide, and mixtures of chloride with fluoride, bromide, and/or iodide.

20. The composition of any one of Claims 16 to 19 wherein the halogen-containing compound is selected from the halides of silver, Group 1, Group 2, the lanthanide rare earths and actinide elements, and combinations thereof.

21. The composition of any one of Claims 16 to 20 wherein the halogen-containing compound is selected from the fluorides, chlorides, bromides and iodides of silver, lithium, sodium, potassium, rubidium, cesium, magnesium, calcium, barium, erbium, lutetium, and combinations thereof, as well as mixtures of the aforementioned chlorides with the aforementioned fluorides, bromides, and/or iodides.

22. The composition of any one of Claims 16 to 21 wherein the source of gold is selected from the following compounds: sodium gold oxide, cesium gold oxide, chloroauric acid, gold chloride, gold fluoride, sodium fluoroaurate, potassium fluoroaurate, sodium chloroaurate, potassium chloroaurate, gold cyanide, potassium gold cyanide, gold acetate, diethylamine auric acid trichloride, alkyl gold compounds, alkali aurates, $(Ph_3PAu)_3OBF_4$, $[(AuPPh_3)_3O]PF_6]$, $Au_5(PPh_3)_4Cl$, $Au_6(PPh_3)_6(BF_4)_2$, $Au_6(PPh_3)_6(NO_3)_2$, $Au_6(PPh_3)_6(PF_6)_2$, $Au_8(PPh_3)_8(NO_3)_2$, $Au_8(PPh_3)_7(NO_3)_2$, $Au_9(PPh_3)_8(NO_3)_3$, $Au_{10}(PPh_3)_5(C_6F_5)_4$, $Au_{11}Cl_3\{(m\text{-}CF_3C_6H_4)_3P\}_7$, $Au_{11}(PPh_3)_7(PF_6)_3$, $[Au_{13}(PMe_2Ph)_{10}Cl_2](PF_6)_3$, $Au_{13}(PPh_3)_4[S(CH_2)_{11}(CH_3)]_4$, $[Au_{13}(PPh_2CH_2PPh_2)_6](NO_3)_4$, $Au_{55}(Ph_2PC_6H_4SO_3Na\cdot 2H_2O)_{12}Cl_6$, $Au_{55}(PPh_3)_{12}Cl_6$, wherein “Ph” is phenyl and “Me” is methyl; and gold-ligand cluster complexes having an average gold particle size of about 1.4 nm; $[(PPh_3)Pt(AuPPh_3)_6](NO_3)_2$, $[(PPh_3)(CO)Pt(AuPPh_3)_6](PF_6)_2$, $[Pd(AuPPh_3)_8](NO_3)_2$, $[H_4(PPh_3)_2Re(AuPPh_3)_5](PF_6)_2$, $[PPh_3Pt(AuPPh_3)_6](PF_6)_2$, $[H(PPh_3)Pt(AuPPh_3)_7](NO_3)$, $[Pt(AuPPh_3)_7(Ag)_2](NO_3)_3$, $[Pd(AuPPh_3)_8](PF_6)_2$,

$[Pt(AuPPh_3)_8](NO_3)_2$, $[Pt(AuPPh_3)_8](PF_6)_2$, $[(PPh_3)Pt(AuPPh_3)_8(Ag)](NO_3)_2$, $[Pt_2(AuPPh_3)_{10}(Ag)_{13}]Cl_7$, wherein “Ph” is phenyl, and mixtures of any of the aforementioned compounds and complexes.

23. The composition of any one of Claims 16 to 22 wherein an atomic ratio of halogen to gold in the catalyst composition ranges from greater than 1/1 to less than 32/1.

24. The composition of any one of Claims 16 to 23 wherein the titanium-containing support comprises a nanoporous titanosilicate.

25. The composition of any one of Claims 16 to 24 wherein the catalyst is prepared at a pH ranging from 5 to 13 and the catalyst is pretreated under helium prior to use, or wherein the catalyst is prepared at a pH ranging from 2 to 13 and the catalyst is pretreated under hydrogen prior to use.