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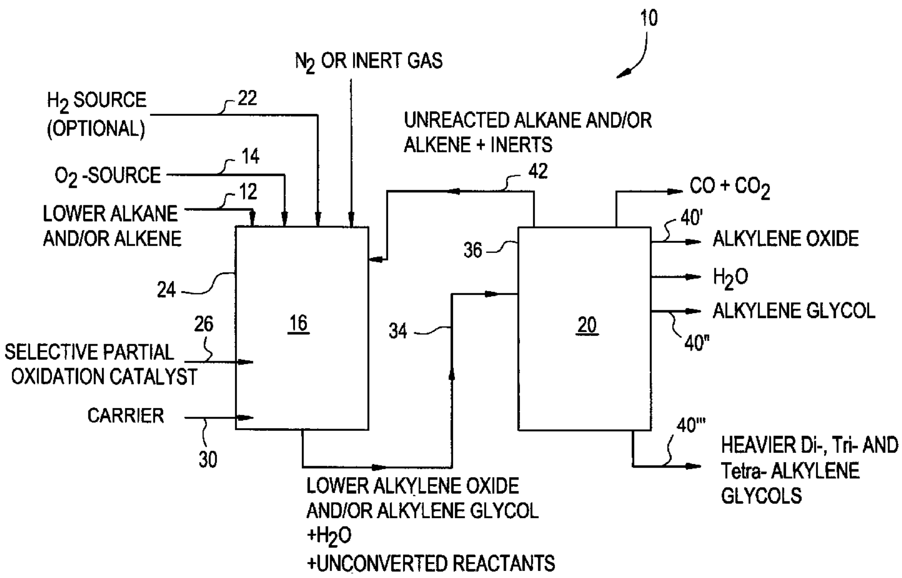
(54) **Title:** SYNTHESIS OF LOWER ALKYLENE OXIDES AND LOWER ALKYLENE GLYCOLS FROM LOWER ALKANES AND/OR LOWER ALKENES



(57) **Abstract:** A method and apparatus for synthesizing at least one of alkylene oxides and alkylene glycols from lower alkanes and/or lower alkenes. In the preferred embodiment, the apparatus included a lower alkane/alkene supply; an oxygen supply for providing a source of oxygen; and a metal oxide catalytic reactor. The metal oxide catalytic reactor included a reactor chamber; and a catalyst in the chamber for reacting the lower alkane/alkene supply with the source of oxygen to convert the lower alkane/alkene by selective partial oxidation to at least one of the alkylene oxides and alkylene glycols. Also, in the preferred embodiment, a separator, downstream form the reactor, separated the alkylene oxides and alkylene glycols from the total product stream and the unconverted reactants.

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SYNTHESIS OF LOWER ALKYLENE OXIDES AND LOWER ALKYLENE GLYCOLS FROM LOWER ALKANES AND/OR LOWER ALKENES

The invention related generally to the synthesis of lower alkylene oxides and lower alkylene glycols and, more particularly, to a method and apparatus for the synthesis of lower alkylene oxides and lower alkylene glycols from lower alkanes and/or alkenes by selective partial oxidation.

Ethylene oxide (EO) and ethylene glycol were manufactured from ethane and/or ethylene through a capital intensive, multi-step process. This conventional process utilized a thermal cracker to make ethylene and other olefin hydrocarbons from ethane, propane, butane or naphtha hydrocarbons. The ethylene was separated from other byproducts, and was then epoxidized over a silver catalyst to produce ethylene oxide and other products including water and carbon dioxide. The ethylene oxide was then separated from these other reaction products and unconverted reactants. For further conversion to ethylene glycol (1,2-ethanediol or MEG), the ethylene oxide was mixed with a ten-fold or greater ratio of water and thermally hydrolyzed, though selective catalytic routes for EO to MEG were also investigated.

Propylene glycol (1, 2 propanediol or MPG) was similarly produced by hydrolysis of propylene oxide. The production of propylene oxide from propylene first required production of a chlorohydrin intermediate by reacting propylene with chlorine and water. The chlorohydrin intermediate was then reacted with sodium hydroxide or calcium hydroxide to produce propylene oxide and sodium chloride or calcium chloride. A large volume of chloride salt byproducts was produced, and disposal of these salts was costly.

Other indirect routes were also known for producing propylene oxide. For example, isobutane could be reacted with oxygen to form t-butyl hydroperoxide, which in turn was reacted with propylene to produce propylene oxide and tert-butanol. The tert-butanol could then be reacted with methanol to produce the co-product methyl tertiary butyl ether (MTBE), a common gasoline additive. In another process, ethyl benzene was used as a starting material, and styrene was a resultant co-product. In each of these known processes for production of propylene oxide, a co-product resulted. Even though these co-products were sometimes beneficial, they must always be handled and disposed of, and added accordingly to the cost of propylene oxide production.

Therefore, a process which could produce ethylene oxide, ethylene glycol, propylene oxide, propylene glycol, and other lower alkylene oxides and lower alkylene glycols directly from lower alkanes and/or lower alkenes as the starting hydrocarbon raw materials provided a desirable advantage over the prior art. For example, capital costs were reduced by as much as fifty percent by eliminating the need for thermal crackers and associated equipment. A simpler manufacturing process also reduced production costs and cycle times by eliminating intermediate steps in the conversion processes.

The present invention was accordingly directed to a method and apparatus for producing lower alkylene oxides and lower alkylene glycols by reacting at least one of a lower alkane and/or lower alkene with a source of oxygen and, optionally, a source of hydrogen to convert the lower alkane and/or lower alkene to at least one of the desired end products.

The necessary oxygen may be obtained from any suitable source, including without limitation, oxygen, ozone, and oxides of nitrogen. Preferably, oxygen was used to carry out the reaction. The O_2 may be fed at any concentration by mixing with N_2, He, or other inert gases. A convenient and safe source of oxygen was air. The required oxygen may also be provided by a suitable metal oxide catalyst or by the reaction of a metal oxide catalyst with N_2O, NO_x or sulfur oxides which may be generated in situ or supplied to the reaction system indirectly. The term metal oxide as used herein included oxides of single metals or multiple metals. In a preferred embodiment of the invention, the oxygen was supplied by one or more reducible metal oxide catalysts that were regenerated by exposure to air, O_2, other oxygen containing gases, or other suitable oxygen sources.

Additionally, a source of hydrogen may be directly or indirectly provided, for example, H_2 gas. The necessary hydrogen may also be provided by one or more hydrogenation/dehydrogenation metal catalysts.

In the preferred embodiment, the invention included a metal or mixed metal oxide catalyst, which provided a favorable standard free energy for the selective partial oxidation reactions. Metal oxide catalysts have been found to be particularly suitable for synthesizing ethylene oxide or ethylene glycol by epoxidation and dihydroxylation, respectively. These types of metal oxides (referred to herein as "red-ox" catalysts) allowed for the ready accessibility of lattice oxygen to promote the oxidation of the feed materials, which resulted in a corresponding reduction of the metal oxide. This was followed by re-oxidation of the catalyst by another oxygen source, such as O_2 or an oxygen-containing gas. Examples of effective red-ox catalysts included but were not limited to the oxides of cerium, iron, copper, nickel, lead, cadmium, molybdenum. vanadium, bismuth, manganese, barium, cobalt, strontium, tungsten, samarium, osmium, rhenium, rare earth elements, and mixtures of these oxides.

Those metals, which were generally known as hydrogenation/dehydrogenation metals, were also effective for carrying out the reaction, either alone or in combination with above-mentioned metal oxide catalysts. As explained in more detail below, it was believed that these catalysts generated highly reactive hydroperoxo and/or peroxo species from O_2 and H_2 and provided the oxygen and hydrogen necessary for the dihydroxylation or epoxidation reaction. These catalysts included but were not limited to nickel, palladium, platinum, cobalt, rhodium, iridium, iron, ruthenium, copper, zinc, gold, silver and mixtures of these metals.

Typically, both the red-ox and hydrogenation/dehydrogenation catalysts were supported on suitable carriers such as cerias, titanias, zirconias, silicas, aluminas, α-alumina, silicon carbide, aluminum phosphate molecular sieves (AlPO's), high silica molecular sieve zeolites, MCM-type large pore zeolites, mixtures of these carriers, and other catalyst support materials well-known in the art.

Thus, in the preferred embodiment, the apparatus included a lower alkane/alkene supply; an oxygen supply for providing a source of oxygen; and a metal oxide catalytic reactor. The metal oxide catalytic reactor included a reactor chamber; and a phosphate modified catalyst in the chamber for reacting the lower alkane/alkene supply with the source of oxygen to convert the lower alkane/alkene by selective partial oxidation to at least one of the ethylene oxide and ethylene glycol.

Both the red-ox and hydrogenation/dehydrogenation catalysts can be modified with a phosphorus containing salt. While not wishing to be bound by theory, it was believed that this phosphate modification provided for isolation of metal sites which makes the both the red-ox and hydrogenation/dehydrogenation catalysts more active and selective for the dihydroxylation or epoxidation of ethane to produce ethylene glycol and ethylene oxide, respectively. The phosphate-modified catalyst may be prepared by adding a phosphorus containing salt (for example, phosphoric acid, ammonium dihydrogen phosphate, sodium phosphate, etc.) using techniques familiar to one skilled in the art. Alternatively, the phosphate may be incorporated during the forming of the re-dox or hydrogenation/dehydrogenation by coprecipitation, sol gel method, or other methods known to one skilled in the art.

Also, in the preferred embodiment, the apparatus further included a separator for separating the ethylene oxide and the ethylene glycol from the total product stream and from unconverted reactants. The separator included an input line, a distillation device, and a product output line. The distillation device may be a flash evaporator or a distillation column, wherein the evaporation or distillation was carried out under conditions known in the art to obtain the desired product purity.

The apparatus may include a recycle line for returning unconverted reactants back to the reactor. In addition, the product output line may include at least two product output streams when intermediate products were desired.

In the preferred embodiment, the lower alkane/alkene supply was selected from the group consisting of butane/butylene; propane/propylene; and ethane/ethylene. Also, preferably, the lower alkane/alkene supply was substantially sulfur-free and phosphorous-free to reduce possible poisoning of the catalyst. The lower alkane/alkene supply was a two-carbon hydrocarbon, which was preferably ethane and/or ethylene.

The oxygen supply for providing a source of oxygen was at least one of oxygen, ozone and oxides of nitrogen. Preferably, the source of oxygen was O_2 or N_2O. In the preferred embodiment, the source of oxygen was provided by at least one metal oxide catalyst. The metal oxide catalyst included at least one metal oxide that was reduced by reaction with a hydrocarbon moiety to a lower oxidation state such that the metal oxide provided a lower standard free energy for the selective partial oxidation of the lower alkane/alkene. The metal oxide may be selected from the group consisting of oxides of cerium, iron, copper, nickel, lead, cadmium, molybdenum, vanadium, bismuth, manganese, barium, cobalt, strontium, tungsten, samarium, osmium, rhenium, rare earth elements, and mixtures of these oxides. The metal oxide may be selected from the group consisting of NiO, PbO, CdO, MoO_3, V_2O_4, V_2O_5, BiO, Bi_2O_3, CuO, Cu_2O, MnO_2, Mn_2O_3, Mn_3O_4 BaO2, Co_3O_4, SrO_2, WO_2, WO_3, SnO_2, CeO_2, OsO_4, Re_2O_7, FeO, Fe_2O_3, Fe_3O_4, rare earth oxides, and mixtures thereof.

The resulting alkylene oxides and alkylene glycols were substantially free of higher hydrocarbons greater than four carbon numbers.

According to the present invention, the metal oxide catalyst was regenerable. In the preferred embodiment, the metal oxide catalyst was regenerated by exposing the metal oxide catalyst to a source of oxygen, such as in a fixed bed, fluid bed, circulating fluidized bed, or other suitable reactor. Also, in the preferred embodiment, the apparatus may further include a hydrogen supply for providing a source of hydrogen in addition to the oxygen supply for providing a source of oxygen.

In the preferred embodiment, the phosphate-modified catalyst was iron phosphate. However, hydrogenation catalyst may work as well. The catalyst may further include a catalytic modifier, such as a platinum-containing compound, which improves the activity and/or selectivity of the catalyst. Other modifiers may also be used such as alkali and alkaline earth oxides. The apparatus may also include a carrier for supporting the phosphate-modified catalyst. In the preferred embodiment, the carrier was selected from the group consisting of: cerias, titanias, zirconias, silicas, aluminas, α-alumina, silicon carbide, aluminum phosphate molecular sieves (AlPO's), high silica molecular sieve zeolites, MCM-type large pore zeolites, mixtures thereof.

The present invention was operable to react the ethane/ethylene with oxygen to form at least one of ethylene oxide and ethylene glycol and preferably forms ethylene glycol. However, the ethane/ethylene may also form higher glycols selected from the group consisting of diethylene glycol (DEG), triethylene glycol (TEG), and tetraethylene glycol (T4G).

As was expected the higher glycols were also formed as a result of condensation of the formed glycols and/or ethoxylation. In general, the lower glycol was preferred, but higher glycols may be formed preferentially by running at higher alkane/alkene conversions, or by recycle of the alkylene glycols back to the reactor.

Accordingly, one aspect of the invention was to provide a method and apparatus for synthesizing at least one of alkylene oxides and alkylene glycols from lower alkanes and/or lower alkenes, the apparatus including: a lower alkane/alkene supply; an oxygen supply for providing a source of oxygen; and a metal oxide catalytic reactor for reacting the lower alkane/alkene supply with the source of oxygen to convert the lower alkane/alkene by selective partial oxidation to at least one of the alkylene oxides and alkylene glycols.

Another aspect of the present invention was to provide a metal oxide catalytic reactor for an apparatus for synthesizing at least one of alkylene oxides and alkylene glycols from lower alkanes and/or lower alkenes. the metal oxide catalytic reactor including: a reactor chamber; and a phosphate modified catalyst in the chamber for reacting the lower alkane/alkene supply with the source of oxygen to convert the lower alkane/alkene by selective partial oxidation to at least one of the alkylene oxides and alkylene glycols.

Still another aspect of the present invention was to provide a method and apparatus for synthesizing at least one of alkylene oxides and alkylene glycols from lower alkanes and/or lower alkenes, the apparatus included: a lower alkane/alkene supply; an oxygen supply for providing a source of oxygen: a metal oxide catalytic reactor, the metal oxide catalytic reactor including: a reactor chamber; and a phosphate modified catalyst in the chamber for reacting the lower alkane/alkene supply with the source of oxygen to convert the lower alkane/alkene by selective partial oxidation to at least one of the alkylene oxides and alkylene glycols; and a separator for separating the alkylene oxides and alkylene glycols from the total product stream and unconverted reactants.

These and other aspects of the present invention were apparent to those skilled in the art after a reading the following description of the preferred embodiment when considered with the drawings.

FIGURE 1 contained a series of plots illustrating the standard free energy change as a function of temperature for a number of ethane based routes to monoethanolamine.

FIGURE 2 contained a series of plots illustrating the standard free energy change as a function of temperature for a number of ethane based routes to ethylenediamine.

FIGURE 3 contained a series of plots illustrating the standard free energy change as a function of temperature for a number of ethane based routes to ethylene oxide;

FIGURE 4 contained a series of plots illustrating the standard free energy change as a function of temperature for a number of ethane based routes to ethylene glycol; and

FIGURE 5 was a block diagram illustrating an apparatus for converting ethane to ethylene oxide and ethylene glycol constructed according to the present invention;

In the following description, like reference characters designated like or corresponding parts throughout the several views. Also in the following description, it was understood that such terms as "forward," "rearward," "left," "right," "upwardly," and "downwardly" were words of convenience and are not to be construed as limiting terms.

The invention was described in connection with an explanation of the synthesis of ethylene oxide or ethylene glycol from ethane. However, as was apparent to those skilled in the art, the invention may be used to synthesize other alkylene oxides and alkylene glycols using other lower alkanes and/or lower alkenes as the hydrocarbon starting materials and other raw material feeds.

Four typical routes to ethylene glycol based on selective dihydroxylation of ethane, according to the invention, were set forth below. In certain preferred embodiments using a regenerable metal oxide catalyst, a non-limiting example of which was provided in reaction (4) by Fe2O3, all four routes were actively employed to provide ethylene glycol from ethane:

(1) $C_2H_6 + O_2 \rightarrow HOCH_2\text{-}CH_2OH$

(2) $C_2H_6 + 2N_2O \rightarrow HOCH_2\text{-}CH_2OH + 2N_2$

(3) $C_2H_6 + 2O_2 + 2H_2 \rightarrow HOCH_2\text{-}CH_2OH + 2H_2O$

(4) $C_2H_6 + 6Fe_2O_3 \rightarrow HOCH_2\text{-}CH_2OH + 4Fe_3O_4$

The reactions may be carried out in gas, liquid, supercritical, or multiphase media. As noted previously, any suitable source of oxygen may be utilized to convert ethane and/or ethylene to ethylene glycol. However, when the reactions were carried out in the vapor phase, O_2 gas or N_2O were the most preferred forms of these reactants. As to the hydrocarbon raw materials, it should also be understood that the use of ethane and ethylene were not mutually exclusive, and that a mixture of these reactants may be utilized in the synthesis of ethylene glycol.

The reactions may be carried out over a broad range of temperatures and pressures. Generally, however, conditions of relatively low temperature and relatively high pressure were preferred. Lower temperatures tended to enhance selectivity and reduce or eliminate the formation of undesirable combustion by-products, such as CO, CO_2, etc. Higher pressures generally increased the rate at which the desired end products were formed. Typically, the synthesis was carried out at temperatures ranging from 25°C to 500°C and at pressures ranging from 1 atmosphere to 200 atmospheres.

While not intending to be limited to a particular theory or mechanistic pathway, the dihydroxylation, as represented in reactions (1) - (2), was believed to proceed by the formation of highly reactive hydroperoxo and/or peroxo species. Specifically, the metal oxide appeared to react with either O_2 gas or N_2O to form peroxo intermediates by oxidation of the metal oxide. These peroxo intermediates can be either peroxo or some reactive monatomic oxygen. While the oxygen was coming from the metal oxide, it may need a catalyst to relinquish this oxide.

In the most preferred embodiment of the invention, reactions (1) - (4) proceeded over a reducible and regenerable metal oxide red-ox catalyst. Generally, metal oxides suitable for use in the invention were those metal oxides that were reduced by reaction with a hydrocarbon moiety to a lower oxidative state, such that the metal oxide provided a lower standard free energy for the selective partial oxidation reaction, in this particular case the reaction to produce ethylene glycol. Oxygen from the feed material then re-oxidized the metal oxide. For the synthesis of ethylene glycol from ethane using a metal oxide as a source of oxygen, an exemplary reaction in which the metal oxide wa re-oxidized by a source of oxygen (air) and then recycled back in a recycle reaction system, was shown as follows:

(5) $$C_2H_6 + 6Fe_2O_3 \rightarrow HOCH_2\text{-}CH_2OH + 4Fe_3O_4$$

↑———————————|

↑ O_2 (air)

Recycle

For other metal oxides, similar red-ox reactions can be depicted as shown above by balancing the appropriate valences and coefficients for the particular metal oxide selected.

It was believed that the necessary oxygen was provided by these catalysts as oxygen, which moved from the lattice to the surface (perhaps as O^{-2}, O^{-}, or O_2^{-} surface species). One possibility that accounted for the high activity of these catalysts was that the metal oxides have point defects, step defects, other types of defects or disorders, or cation vacancies within the lattice, which provides for the ready accessibility of oxygen.

Whatever the basis for their highly active nature, a number of metal oxides were particularly suitable for carrying out the selective partial oxidation of alkanes and alkenes including NiO, PbO, CdO, MoO_3, V_2O_4, V_2O_5, BiO, Bi_2O_3, CuO, Cu_2O, MnO_2, Mn_2O_3, Mn_3O_4 BaO2, Co_3O_4, SrO_2, WO2, WO_3, SnO_2, CeO_2, OsO_4, Re_2O_7, FeO, Fe_2O_3, Fe_3O_4, rare earth oxides, and mixtures of these metal oxides.

While not intending to be limited to a particular theory or mechanistic pathway, the dihydroxylation, as represented in reaction (3), also was believed to proceed by the formation of highly reactive hydroperoxo and/or peroxo species. Specifically, the metal oxide appeared to react with H_2 gas to form a hydroperoxo intermediate species with a further elimination of H_2O to produce the peroxo species.

These intermediates were also formed by reaction of a hydrogenation/ dehydrogenation metal catalyst with O_2 and then by reaction with H_2. The oxygen adsorbed on the catalyst, either as the hydroperoxo or peroxo intermediate, was capable of adding to an olefin which has been added either as a feed material, or generated in situ by oxidation of an alkane. The intermediate generated from reaction of the oxygen with the olefin was an epoxide. The epoxide then reacted with water to give the glycol.

For example, a feed of ethylene and/or ethane with H_2 and O_2 produced ethylene oxide as an intermediate which reacted with H_2O to produce ethylene glycol. Typically, reaction conditions such as O_2/H_2 mole ratios, pressure, and temperature were controlled to give the desired end product. Those hydrogenation/dehydrogenation metals that were the most active included but are not limited to nickel, palladium, platinum, cobalt, rhodium, iridium, iron, ruthenium, copper, zinc, gold, and silver and mixtures of these metals.

The red-ox and hydrogenation/dehydrogenation catalysts described herein can be prepared by conventional procedures known in the art. For example, the catalyst can be incorporated on preformed carriers or supports (these terms were used interchangeably herein) by impregnating the carrier with a liquid solution comprising a form of the element required to effect reaction. The support shape was generally not narrowly critical; accordingly, the carrier may take the form of, for example, pellets, extruded particles, spheres, rings, monoliths.

If more than one metal was to be incorporated the metals may be incorporated simultaneously or sequentially, the sequence of which was not narrowly critical. As noted above, typical supports include cerias, titanias, zirconias, silicas, aluminas, α-alumina, silicon carbide, aluminum phosphate molecular sieves (AlPO's), high silica molecular sieve zeolites, MCM-type large pore zeolites, mixtures of these carriers, and other catalyst support materials well known in the art.

Generally, the metal was in the form of a salt which can be easily dissolved in a liquid solvent for incorporation into the particles or monolith structure of the carrier. Several impregnation steps may be required depending on the amount of metal or metal oxide required and the solubility of the salt of the catalytic compound in the solvent. A drying step was generally employed between each impregnation. This was a well-known procedure in the art for incorporating metals and metal oxides onto a solid support material. After all of the impregnation steps were completed, the material was then usually heated at higher temperatures, typically from 100-900°C, to effect at least partial decomposition of the salt to the metal oxide.

Alternatively, the metal salt may be heated to 100-900°C after each impregnation and drying step. The drying and heating steps may be done incrementally at various temperatures over suitable periods of time, or these steps can be ramped up to the desired temperature fairly linearly. If desired, the metal oxide can be reduced to the metal, at least partially, with hydrogen or other reducing gases (for example carbon monoxide) using methods well known to one skilled in the art.

Alternatively, some form of the requisite metal can be fused, bonded or compressed into solid pellets or larger structures, or composited with one or more support materials, in association with one or more metal oxides and heated as above. The material may be reduced as alluded to above.

Still further, the catalyst can be provided at the time of preparing the support material. For example, one or more metal oxides may be condensed from their respective hydrolyzable monomers to the desired oxides to form oxide powders which can thereafter be blended and compressed to form pellets and larger structures of the catalyst. The materials were then heated and optionally reduced as alluded to above.

In yet another approach, the metal salt may be precipitated on a preformed carrier using methods described in the art. This procedure offered some advantages for depositing the active metal on the outside of the carrier which may lead to improved selectivity. Some further advantages may be realized by preparing the selective partial oxidative amination catalyst on zeolite-type materials. For zeolites, known ion- exchange procedures may be employed to incorporate various catalytic metal ions. This allows for shape selectivity and can enhance selective partial oxidation over complete oxidation. The procedures for incorporating metals on zeolites were well known.

The use of supports for the catalysts provided a number of significant advantages. Some of the catalysts were not structurally stable under the reaction conditions when utilized over an extended period of time. In a batch reaction, this was not a significant issue. However, when the reaction was effected with the catalyst as part of a fixed bed reactor, in a tubular reactor, or in a fluid bed reactor it was desirable that the catalyst have greater structural stability/integrity for the reaction medium.

Attrition can be a significant problem with an unsupported catalyst particularly if used in a fluidized bed reactor. Improved resistance to attrition of the catalyst can be achieved by providing an attrition resistant coating on the surface of the catalyst. The coating should be resistant to the reactants and products and must be sufficiently porous to permit free passage of the reactants and products through the coating to the catalyst site. Polysilicic acid, zinc oxide, titanium oxide, zirconium oxide, other metal oxides and mixtures of these oxides may be used to provide an outer coating on the catalyst which provides better attrition resistance. The techniques used to provide a protective coating were well known to one skilled in the art.

In one embodiment of the invention, the reducible metal oxide catalyst has a microstructure characterized by a plurality of porous microspheres. An attrition resistant coating was provided on the surface of the microspheres. In this particular example, the coating comprised polysilicic acid. However, as mentioned above the coating may be formed from other inert materials that will also provide attrition resistance, such as zinc oxide, TiO_2, ZrO_2, and other metal oxides.

Referring now to the synthesis of ethylene oxide, the conversion of ethane to form ethylene oxide was represented by the following reactions:

O

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(6) $C_2H_6 + O_2 \rightarrow CH_2 - CH_2 + H_2O$

O

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(7) $C_2H_6 + 6Fe_2O_3 \rightarrow CH_2 - CH_2 + 4Fe_3O_4 + H_2O$

O

/ \

(8) $C_2H_6 + 2N_2O \rightarrow CH_2 - CH_2 + 2N_2 + H_2O$

O

/ \

(9) $C_2H_6 + 2O_2 + 2H_2 \rightarrow CH_2 - CH_2 + 3H_2O$

As discussed above, with respect to reaction (3), it was expected that the metal oxide reacted with H_2 gas to form a hydroperoxo intermediate species with a further elimination of H_2O to produce the peroxo species. Also, the epoxidation of ethane to ethylene oxide proceeded under essentially the same reaction conditions and in essentially the same manner as that described above in connection with the synthesis of ethylene glycol. Accordingly, the reactions may be carried out in gas, liquid, supercritical or multiphase media.

Various sources of oxygen and hydrogen may be utilized to convert ethane to ethylene oxide; however, oxygen gas, preferably mixed with an inert gas, and hydrogen was preferred. Either ethane or ethylene may be used as the starting hydrocarbon raw material for the synthesis of ethylene oxide, or, a mixture of these starting materials may be employed. The epoxidation reactions may be carried out over a broad range of temperatures and pressures. In general, similar conditions discussed above for the synthesis of ethylene glycol were used for the synthesis of ethylene oxide with one notable exception. The reactants were generally diluted with an inert gas (for example, nitrogen or helium) to minimize the reaction between the coproducts ethylene oxide and water to form ethylene glycol. However, the same conditions of relatively low temperature and relatively high pressure discussed above in connection with the synthesis of ethylene glycol were preferred. Thus, the synthesis of ethylene oxide was typically carried out at temperatures ranging from 25°C to 500°C and at pressures ranging from 1 atmosphere to 200 atmospheres.

As in the case of ethylene glycol, the epoxidation of ethane and/or ethylene to produce ethylene oxide was preferably carried out over a reducible metal oxide catalyst, which provided the oxygen necessary for the reaction. The metal oxides suitable for synthesizing ethylene oxide were expected to be the same catalysts described above in connection with the synthesis of ethylene glycol.

In a preferred embodiment of the invention, the catalyst was continuously regenerated and recycled as illustrated in reactions (10) and (11):

(10) $C_2H_6 + 6Fe_2O_3 \rightarrow \overset{O}{\overbrace{CH_2 - CH_2}} + 4Fe_3O_4 + H_2O$

(11) $4Fe_3O_4 + O_2 \rightarrow 6Fe_2O_3$

For other metal oxides, similar red-ox reactions can be depicted as shown above by balancing the appropriate valences and coefficients for the particular metal oxide selected.

Turning now to the Figures, Figs. 1 and 2 corresponded to Figs. 3 and 4 in U.S. Patent Application 09/430,634, filed October 29, 1999, now U.S. Patent No. 6,281,387, entitled "Process and Catalyst for Synthesizing Aliphatic, Cyclic and Aromatic Alkanolamines and Alkyleneamines", the entire disclosure of which was hereby incorporated by reference. Fig. 1 contained a series of plots illustrating the standard free energy change as a function of temperature for a number of ethane based routes to monoethanolamine. Fig. 2 contained a series of plots illustrating the standard free energy change as a function of temperature for a number of ethane based routes to ethylenediamine. These Figures illustrated that that there were no thermodynamic barriers to the conversion of ethane to either monoethanolamine or ethylenediamine.

Similarly, Figs. 3 and 4 illustrated that there were no thermodynamic barriers to the conversion of ethane to ethylene oxide and ethylene glycol by epoxidation and dihydroxylation, respectively. The non-catalyzed reaction which utilized oxygen gas as the source of the required oxygen exhibits a highly favorable standard free energy change in all cases. Somewhat less favorable, but still thermodynamically advantageous free energy changes were provided by the use of a suitable metal oxide catalyst or a hydrogenation/dehydrogenation metal catalyst.

The chief advantages provided by the use of these catalysts were enhanced selectivity and increased conversion of the hydrocarbon starting materials to ethylene glycol and ethylene oxide. At the same time, the generally lower reaction temperatures at which highly active catalysts operate tended to minimize or eliminate the formation of combustion products. For example, Figs. 3 and 4 illustrated that a reducible MnO_2 catalyst provided a very favorable standard free energy change at a temperature of 250°K (-23.6°C) for the dihydroxylation of ethane and epoxidation of ethane to ethylene glycol and ethylene oxide, respectively.

The reaction may be effected by the incremental addition of one of the reactants to the other or by the joint addition of the reactants to the catalyst. The reaction may be carried out by slurrying the catalyst in the reactants (optionally in a solvent) or in a batch or semi-batch mode in an autoclave. Solvents may be used to provide two liquid phases one of which contains the selective partial oxidation catalyst and the other the reactants with a sufficient amount of mixing to effect reaction. A more preferred method effected the reaction in a continuous manner in a fixed bed or fluidized bed over the selective partial oxidation catalyst.

Inorganic membrane reactors may be used to control the concentration of reactants (for example, oxygen) in the metal oxide catalyst bed, and/or to provide a source of the metal oxide catalyst. The reactor may be an inert membrane packed bed reactor (IMPBR), an inert membrane fluidized bed reactor (IMFBR), a catalytic membrane reactor (CMR), a packed bed catalytic membrane reactor (PBCMR), or a fluidized bed catalytic membrane reactor (FBCMR).

In a preferred embodiment shown schematically in Fig. 5, the reaction was carried out in an apparatus 10 which included a lower alkane/alkene supply 12, an oxygen supply 14, and a metal oxide catalytic reactor 16. The apparatus 10 may further include a separator 20 for separation of multiple reaction products. The lower alkane/alkene supply 12 may supply ethane/ethylene, butane/butylene, and/or propane/propylene.

Preferably, the lower alkane/alkene supply 12 was substantially free of sulfur and phosphorous. The oxygen supply 14 may be oxygen, oxides of nitrogen, or ozone, and may additionally include a source of hydrogen 22.

The metal oxide catalytic reactor 16 included a chamber 24 and a modified phosphate catalyst 26 in the chamber 24, which was preferably iron phosphate. The catalyst may include a modifier, preferably containing platinum. A carrier 30 may also be provided for supporting the catalyst 26 in the reactor 16. The carrier 30 may be selected from the group consisting of cerias, titanias, zirconias, silicas, aluminas, ∝-alumina, silicon carbide, aluminum phosphate molecular sieves (AlPO's), high silica molecular sieve zeolites, MCM-type large pore zeolites, and mixtures thereof.

The separator 20 included an inlet 34, a distillation device 36, and a product output 40. Alternatively, the separator may have at least two output streams 40' and 40". The separator 20 may also include a recycle line 42 for transferring unconverted reactants back to the reactor 16. The distillation device 36 may be a flash evaporator that utilizes vapor pressure differentials to separate multiple products. Alternatively, the distillation device 36 may be a distillation column, which uses product temperature differentials for separation.

The use of a circulating fluidized bed reactor provided a number of advantages. The essentially plug flow characteristics of gas and catalyst particles in the riser gave high selectivity to ethylene oxide and ethylene glycol, and the absence of oxygen gas in the riser further improved selectivity by reducing destruction of the ethylene oxide and ethylene glycol as well as the ethane/ethylene. Specifically, the essentially plug flow characteristics of gas and catalyst particles in the riser gave high selectivity to ethylene oxide and ethylene glycol by minimizing backmixing, and the absence of oxygen gas in the riser further improved selectivity by reducing combustion of the ethylene oxide and ethylene glycol to CO_x and water.

Loosely bound highly active oxygen species were eliminated prior to entry into the riser, which resulted in increased conversion and the maintenance of high catalyst selectivity. The high circulation rate of the catalyst also provided a heat sink which helps control the temperature in the riser and reduced the heat transfer area that would otherwise be required to remove the heat of reaction. Accordingly, the reactor design provided economic as well as process advantages.

While the use of a circulating fluid bed reactor provided important advantages, it should be understood that the invention was not limited in this regard. It should also be understood that regardless of which type of reactor was utilized, should the metal oxide catalyst not provide sufficient oxygen small amounts of additional O_2 may be bleed into the reaction system. Typically, if additional oxygen wass required it was added in an amount less than 5 percent, and preferably less than 2 percent, based on the total feed.

As noted previously, the present invention has been described in detail in the context of producing ethylene glycol and ethylene oxide by the dihydroxylation or epoxidation of ethane. However, those skilled in the art will readily appreciate that the invention has general application for the production of other alkylene oxides and alkylene glycols from a variety of alkane and alkene starting materials. For example, propane/propylene to 1,2 propanediol; 1,3 propanediol; and propylene oxide. Also, butane to 1,2 butanediol; 1,3 butanediol; 1,4 butanediol; 2,3 butanediol; 2,4 butanediol; and butylene oxides.

Those skilled in the art also will readily appreciate that the reactions described above were not mutually exclusive. That is, either ethylene glycol or ethylene oxide may be produced, or both of these products may be produced simultaneously. The particular product(s) produced and the particular route(s) by which this was accomplished were determined by controlling the partial pressure of the raw materials, the temperature of the reactor and the choice of a suitable catalyst. Accordingly, the invention provided a practicable and economic means of producing a wide variety of alkylene oxides and alkylene glycols based on the use of alkanes and/or alkenes as the hydrocarbon starting materials.

Certain modifications and improvements will occur to those skilled in the art upon a reading of the foregoing description. It should be understood that all such modifications and improvements have been deleted herein for the sake of conciseness and readability but were properly within the scope of the following claims.

WHAT IS CLAIMED IS:

1. An apparatus for synthesizing at least one of alkylene oxides and alkylene glycols from lower alkanes and/or lower alkenes, said apparatus comprising:

   (a) a lower alkane/alkene supply;

   (b) an oxygen supply for providing a source of oxygen; and

   (c) a metal oxide catalytic reactor for reacting said lower alkane/alkene supply with said source of oxygen to convert said lower alkane/alkene by selective partial oxidation to at least one of said alkylene oxides and alkylene glycols.

2. The apparatus according to Claim 1, further including a separator for separating said alkylene oxides and said alkylene glycols from the total product stream and the unconverted reactants.

3. The apparatus according to Claim 2, wherein said separator included an input line, a distillation device, and a product output line.

4. The apparatus according to Claim 3, wherein said distillation device was a flash evaporator.

5. The apparatus according to Claim 4, wherein said flash evaporator maintained a pressure differential sufficient to separate said species of alkylene oxides and said alkylene glycols from the total product stream and unconverted reactants.

6. The apparatus according to Claim 3, wherein said distillation device was a distillation column.

7. The apparatus according to Claim 6, wherein said distillation column maintained a temperature differential sufficient to separate said species of alkylene oxides and said alkylene glycols from the total product stream and unconverted reactants.

8. The apparatus according to Claim 3, further including a recycle line for returning the unconverted reactants back to said reactor.

9. The apparatus according to Claim 3, wherein said product output line included at least two product output streams.

10. The apparatus according to Claim 1, wherein said lower alkane/alkene supply was selected from the group consisting of butane/butylene; propane/propylene; and ethane/ethylene.

11. The apparatus according to Claim 10, wherein said lower alkane/alkene supply was ethane/ethylene.

12. The apparatus according to Claim 10, wherein said lower alkane/alkene supply was propane/propylene.

13. The apparatus according to Claim 1, wherein said lower alkane/alkene supply was substantially sulfur-free.

14. The apparatus according to Claim 1, wherein said lower alkane/alkene supply was substantially phosphorus-free.

15. The apparatus according to Claim 1, wherein said oxygen supply for providing a source of oxygen was at least one of oxygen, ozone and oxides of nitrogen.

16. The apparatus according to Claim 15, wherein said oxygen supply for providing a source of oxygen was N_2O.

17. The apparatus according to Claim 1, wherein said oxygen supply for providing a source of oxygen was provided by at least one metal oxide catalyst.

18. The apparatus according to Claim 17, wherein the metal oxide catalyst included at least one metal oxide that was reduced by reaction with a hydrocarbon moiety to a lower oxidation state such that the metal oxide provides a lower standard free energy for the selective partial oxidation of the lower alkane/alkene.

19. The apparatus according to Claim 18, wherein the metal oxide was selected from the group consisting of oxides of cerium, iron, copper, nickel, lead, cadmium, molybdenum, vanadium, bismuth, manganese, barium, cobalt, strontium, tungsten, samarium, osmium, rhenium, rare earth elements, and mixtures of these oxides.

20. The apparatus according to Claim 19, wherein said metal oxide was selected from the group consisting of NiO, PbO, CdO, MoO_3, V_2O_4, V_2O_5, BiO, Bi_2O_3, CuO, Cu_2O, MnO_2, Mn_2O_3, Mn_3O_4 BaO2, Co_3O_4, SrO_2, WO2, WO_3, SnO_2, CeO_2, OsO_4, Re_2O_7, FeO, Fe_2O_3, Fe_3O_4, rare earth oxides, and mixtures thereof.

21. The apparatus according to Claim 17, wherein said metal oxide catalyst was regenerable.

22. The apparatus according to Claim 21, wherein said metal oxide catalyst was regenerated by exposing said metal oxide catalyst to a source of oxygen.

23. The apparatus according to Claim 21, wherein said metal oxide catalyst was regenerated in a circulating fluidized bed reactor.

24. The apparatus according to Claim 1, further including a hydrogen supply for providing a source of hydrogen in addition to said oxygen supply for providing a source of oxygen.

25. The apparatus according to Claim 1, wherein said lower alkane/alkene was reacted with oxygen to form said at least one of ethylene oxide and ethylene glycol.

26. The apparatus according to Claim 25, wherein said lower alkane/alkene forms ethylene glycol.

27. The apparatus according to Claim 26, wherein said lower alkane/alkene forms higher glycols selected from the group consisting of diethylene glycol (DEG), triethylene glycol (TEG), and tetraethylene glycol (T4G).

28. In an apparatus for synthesizing at least one of alkylene oxides and alkylene glycols from lower alkanes and/or lower alkenes, said apparatus including: a lower alkane/alkene supply; an oxygen supply for providing a source of oxygen; and a metal oxide catalytic reactor, said metal oxide catalytic reactor comprising:

(a) a reactor chamber; and

(b) a phosphate modified catalyst in said chamber for reacting said lower alkane/alkene supply with said source of oxygen to convert said lower alkane/alkene by selective partial oxidation to at least one of said alkylene oxides and alkylene glycols.

29. The apparatus according to Claim 28, wherein said phosphate modified catalyst was iron phosphate.

30. The apparatus according to Claim 29, further including a catalytic modifier.

31. The apparatus according to Claim 30, wherein said catalytic modifier was a platinum containing compound.

32. The apparatus according to Claim 28, further including a carrier for supporting said phosphate modified catalyst.

33. The apparatus according to Claim 32, wherein said carrier was selected from the group consisting of: cerias, titanias, zirconias, silicas, aluminas, ∝-alumina, silicon carbide, aluminum phosphate molecular sieves (AlPO's), high silica molecular sieve zeolites, MCM-type large pore zeolites, mixtures thereof.

34. An apparatus for synthesizing at least one of alkylene oxides and alkylene glycols from lower alkanes and/or lower alkenes, said apparatus comprising:

(a) a lower alkane/alkene supply;

(b) an oxygen supply for providing a source of oxygen;

(c) a metal oxide catalytic reactor, said metal oxide catalytic reactor including: a reactor chamber; and a phosphate modified catalyst in said chamber for reacting said lower alkane/alkene supply with said source of oxygen to convert said lower alkane/alkene by selective partial oxidation to at least one of said alkylene oxides and alkylene glycols; and

(d) a separator for separating said alkylene oxides and said alkylene glycols from the total product stream and the unconverted reactants.

35. The apparatus according to Claim 34, wherein said separator included an input line, a distillation device, and a product output line.

36. The apparatus according to Claim 35, wherein said distillation device was a flash evaporator.

37. The apparatus according to Claim 36, wherein said flash evaporator maintained a pressure differential sufficient to separate said species of alkylene oxides and said alkylene glycols from the total product stream and unconverted reactants.

38. The apparatus according to Claim 35, wherein said distillation device was a distillation column.

39. The apparatus according to Claim 38, wherein said distillation column maintained a temperature differential sufficient to separate said species of alkylene oxides and said alkylene glycols from the total product stream and unconverted reactants.

40. The apparatus according to Claim 35, further including a recycle line for returning unconverted reactants back to said reactor.

41. The apparatus according to Claim 35, wherein said product output line included at least two product output streams.

42. The apparatus according to Claim 34, wherein said lower alkane/alkene supply was selected from the group consisting of butane/butylene; propane/propylene; and ethane/ethylene.

43. The apparatus according to Claim 42, wherein said lower alkane/alkene supply was ethane/ethylene.

44. The apparatus according to Claim 42, wherein said lower alkane/alkene supply was propane/propylene.

45. The apparatus according to Claim 34, wherein said lower alkane/alkene supply was substantially sulfur-free.

46. The apparatus according to Claim 34, wherein said lower alkane/alkene supply was substantially phosphorus-free.

47. The apparatus according to Claim 34, wherein said oxygen supply for providing a source of oxygen was at least one of oxygen, ozone and oxides of nitrogen.

48. The apparatus according to Claim 47, wherein said oxygen supply for providing a source of oxygen was N_2O.

49. The apparatus according to Claim 34, wherein said oxygen supply for providing a source of oxygen was provided by at least one metal oxide catalyst.

50. The apparatus according to Claim 49, wherein the metal oxide catalyst included at least one metal oxide that was reduced by reaction with a hydrocarbon moiety to

a lower oxidation state such that the metal oxide provides a lower standard free energy for the selective partial oxidation of the lower alkane/alkene.

51. The apparatus according to Claim 50, wherein the metal oxide was selected from the group consisting of oxides of cerium, iron, copper, nickel, lead, cadmium, molybdenum, vanadium, bismuth, manganese, barium, cobalt, strontium, tungsten, samarium, osmium, rhenium, rare earth elements, and mixtures of these oxides.

52. The apparatus according to Claim 51, wherein said metal oxide was selected from the group consisting of NiO, PbO, CdO, MoO_3, V_2O_4, V_2O_5, BiO, Bi_2O_3, CuO, Cu_2O, MnO_2, Mn_2O_3, Mn_3O_4 BaO2, Co_3O_4, SrO_2, WO_2, WO_3, SnO_2, CeO_2, OsO_4, Re_2O_7, FeO, Fe_2O_3, Fe_3O_4, rare earth oxides, and mixtures thereof.

53. The apparatus according to Claim 49, wherein said metal oxide catalyst was regenerable.

54. The apparatus according to Claim 53, wherein said metal oxide catalyst was regenerated by exposing said metal oxide catalyst to a source of oxygen.

55. The apparatus according to Claim 53, wherein said metal oxide catalyst was regenerated in a circulating fluidized bed reactor.

56. The apparatus according to Claim 34, further including a hydrogen supply for providing a source of hydrogen in addition to said oxygen supply for providing a source of oxygen.

57. The apparatus according to Claim 34, wherein said lower alkane/alkene was reacted with oxygen to form said at least one of ethylene oxide and ethylene glycol.

58. The apparatus according to Claim 57, wherein said lower alkane/alkene formed ethylene glycol.

59. The apparatus according to Claim 58, wherein said lower alkane/alkene formed higher glycols selected from the group consisting of diethylene glycol (DEG), triethylene glycol (TEG), and tetraethylene glycol (T4G).

60. The apparatus according to Claim 34, wherein said phosphate modified catalyst was iron phosphate.

61. The apparatus according to Claim 60, further including a catalytic modifier.

62. The apparatus according to Claim 61, wherein said catalytic modifier was a platinum containing compound.

63. The apparatus according to Claim 34, further including a carrier for supporting said phosphate modified catalyst.

64. The apparatus according to Claim 63, wherein said carrier was selected from the group consisting of: cerias, titanias, zirconias, silicas, aluminas, ∝-alumina, silicon carbide, aluminum phosphate molecular sieves (AlPO's), high silica molecular sieve zeolites, MCM-type large pore zeolites, mixtures thereof.

65. A method for synthesizing at least one of alkylene oxides and alkylene glycols from lower alkanes and/or lower alkenes, said method comprising the steps of:

(a) providing a source of lower alkane/alkene;

(b) providing a source of oxygen; and

(c) reacting said source of lower alkane/alkene with said source of oxygen to convert said lower alkane/alkene by selective partial oxidation to at least one of said alkylene oxides and alkylene glycols.

66. The method according to Claim 65, wherein said catalyst was a metal oxide or mixed metal oxide catalyst.

67. The method according to Claim 65, wherein said catalyst included both metal oxide and mixed metal oxide catalysts.

68. The method according to Claim 65, wherein said catalyst was phosphate-modified.

69. The method according to Claim 65, wherein said catalyst further included a catalytic modifier including a platinum containing compound.

70. A method for synthesizing at least one of alkylene oxides and alkylene glycols from lower alkanes and/or lower alkenes, said method comprising the steps of:

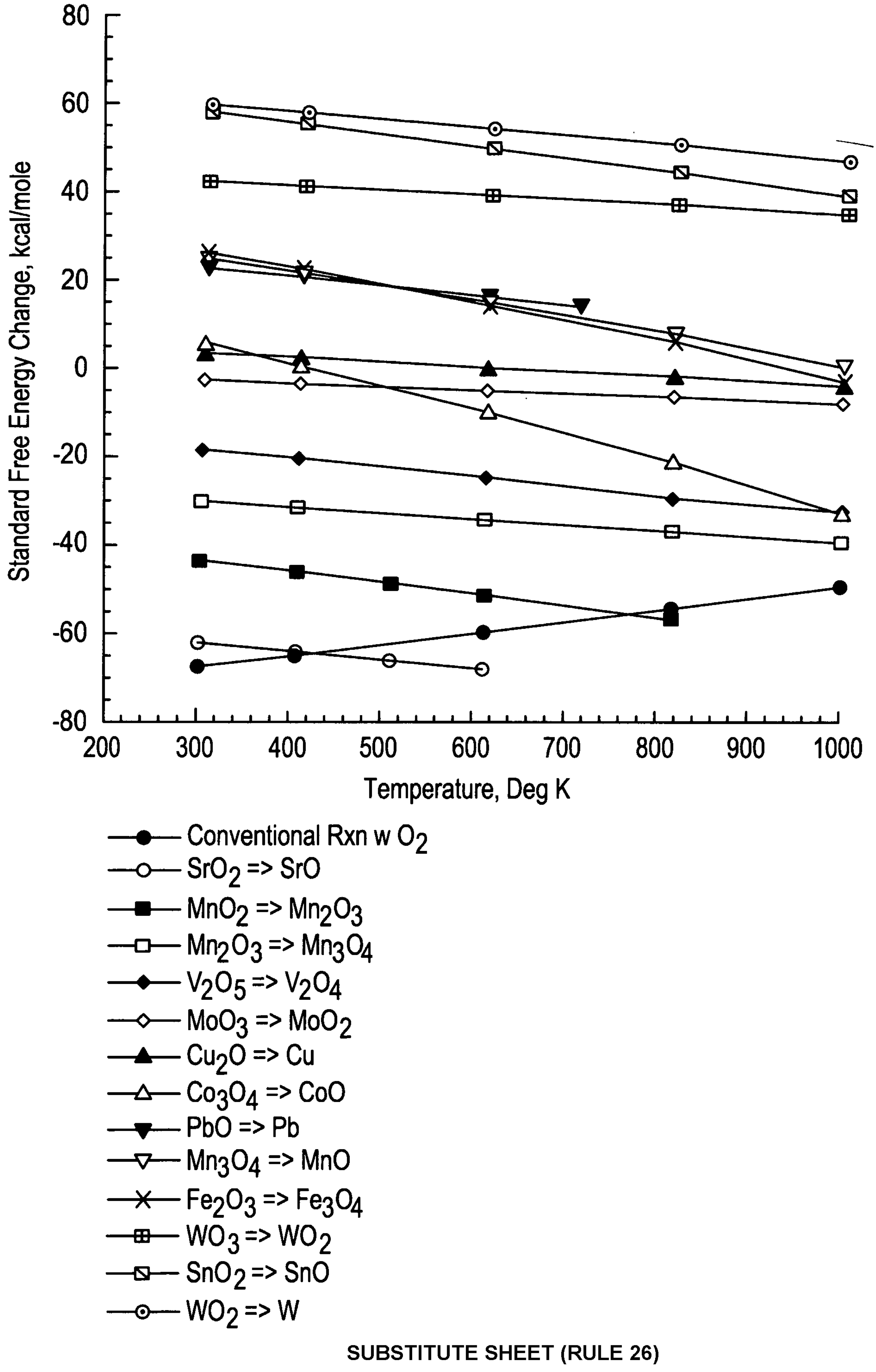
(a) providing a source of lower alkane/alkene;
(b) providing a source of oxygen; and
(c) reacting said source of lower alkane/alkene with said source of oxygen in the presence of a phosphate modified catalyst to convert said lower alkane/alkene by selective partial oxidation to at least one of said alkylene oxides and alkylene glycols.

71. A method for synthesizing at least one of alkylene oxides and alkylene glycols from lower alkanes and/or lower alkenes, said method comprising the steps of:

(a) providing a source of lower alkane/alkene;
(b) providing a source of oxygen; and
(c) reacting said source of lower alkane/alkene with said source of oxygen in the presence of a phosphate modified catalyst to convert said lower alkane/alkene by selective partial oxidation to at least one of said alkylene oxides and alkylene glycols; and
(d) separating said alkylene oxides and said alkylene glycols from the total product stream and the unconverted reactants.

72. Alkylene oxides and alkylene glycols synthesized from lower alkanes and/or lower alkenes by selective partial oxidation, said alkylene oxides and alkylene glycols being substantially free of higher hydrocarbons greater than four carbon numbers.

FIG. 1


80
60
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-20
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-60
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Standard Free Energy Change, kcal/mole
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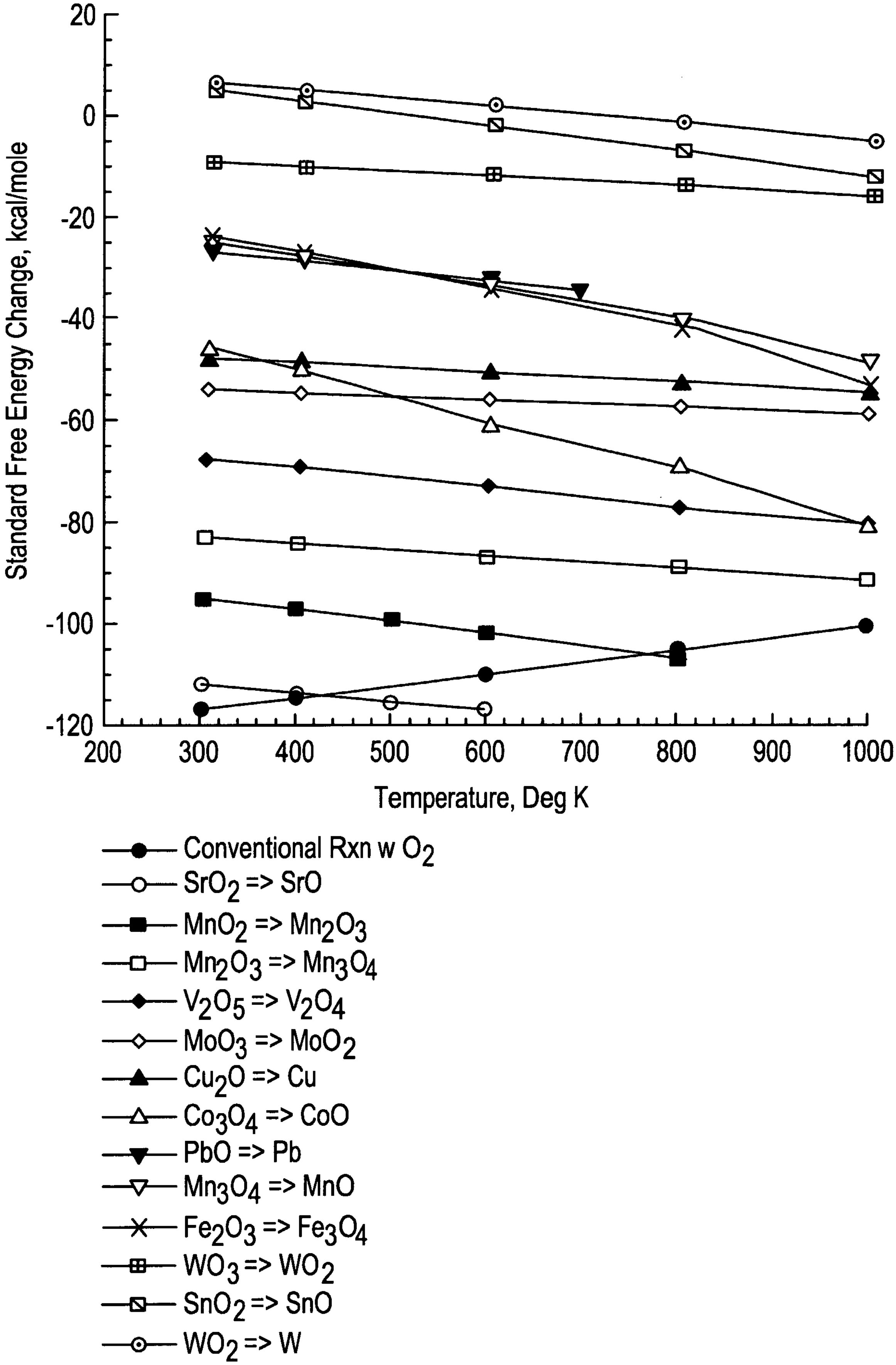
300
400
500
600
700
800
900
1000
Temperature, Deg K
Conventional Rxn w O_2
SrO_2 => SrO
MnO_2 => Mn_2O_3
Mn_2O_3 => Mn_3O_4
V_2O_5 => V_2O_4
MoO_3 => MoO_2
Cu_2O => Cu
Co_3O_4 => CoO
PbO => Pb
Mn_3O_4 => MnO
Fe_2O_3 => Fe_3O_4
WO_3 => WO_2
SnO_2 => SnO
WO_2 => W

FIG. 2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-20
-40
-60
-80
-100
-120
200
300
400
500
600
700
800
900
1000
Standard Free Energy Change, kcal/mole
Temperature, Deg K
Conventional Rxn w O2
SrO2 => SrO
MnO2 => Mn2O3
Mn2O3 => Mn3O4
V2O5 => V2O4
MoO3 => MoO2
Cu2O => Cu
Co3O4 => CoO
PbO => Pb
Mn3O4 => MnO
Fe2O3 => Fe3O4
WO3 => WO2
SnO2 => SnO
WO2 => W

FIG. 3

Ethane Based Route to Ethylene Oxide

$$C_2H_6(g) + O_2(g) \Leftrightarrow CH_2OCH_2(g) + H_2O(g)$$
$$C_2H_6(g) + 6\ Fe_2O_3(s) \Leftrightarrow CH_2OCH_2(g) + 4\ Fe_3O_4 + H_2O(g)$$
etc.

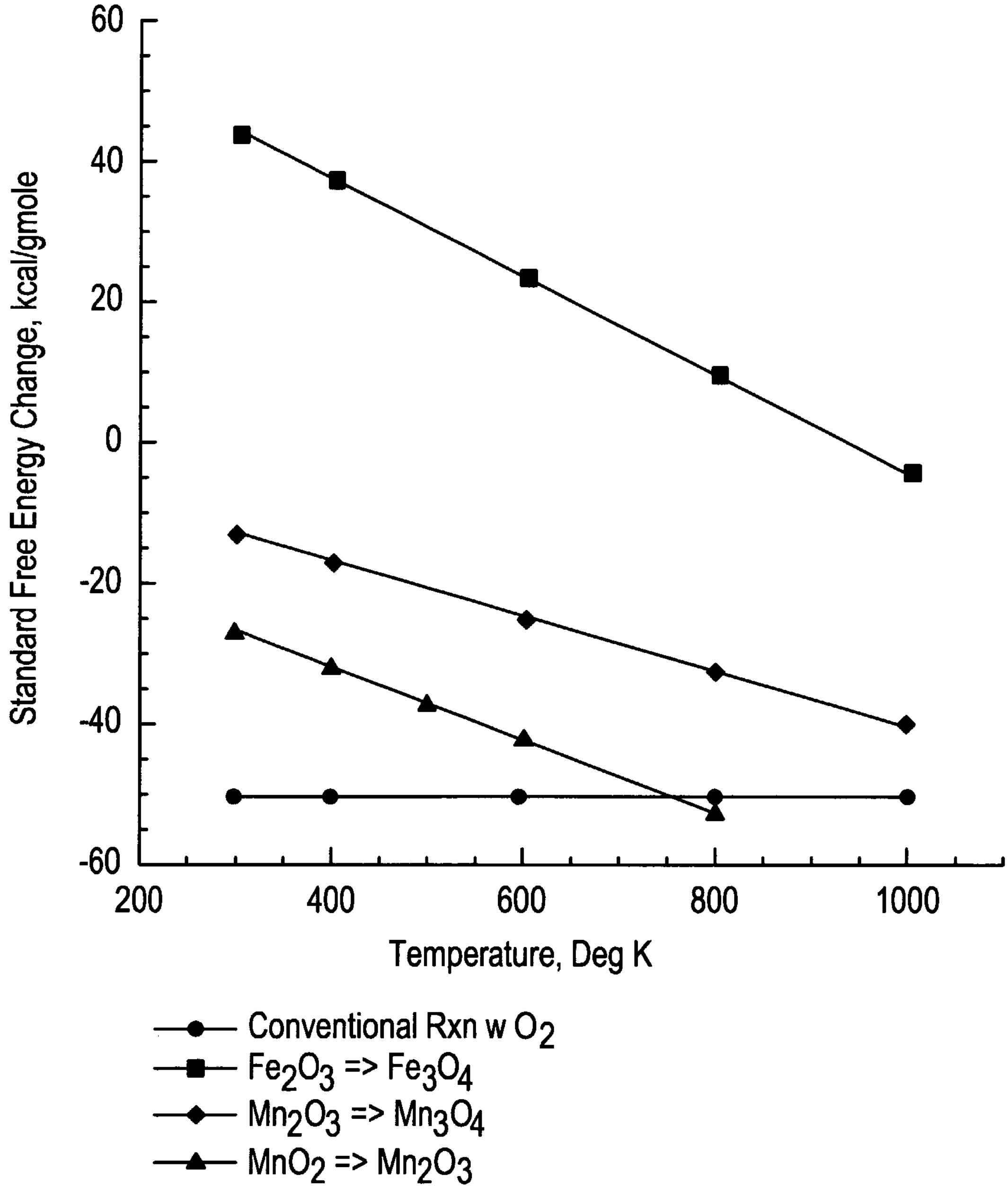


FIG. 4

Ethane Based Route to Ethylene Glycol

$C_2H_6(g) + O_2(g) <=> HOCH_2CH_2OH(g)$

$C_2H_6(g) + 6\ Fe_2O_3(s) <=> HOCH_2CH_2OH(g) + 4\ Fe_3O_4$

etc.

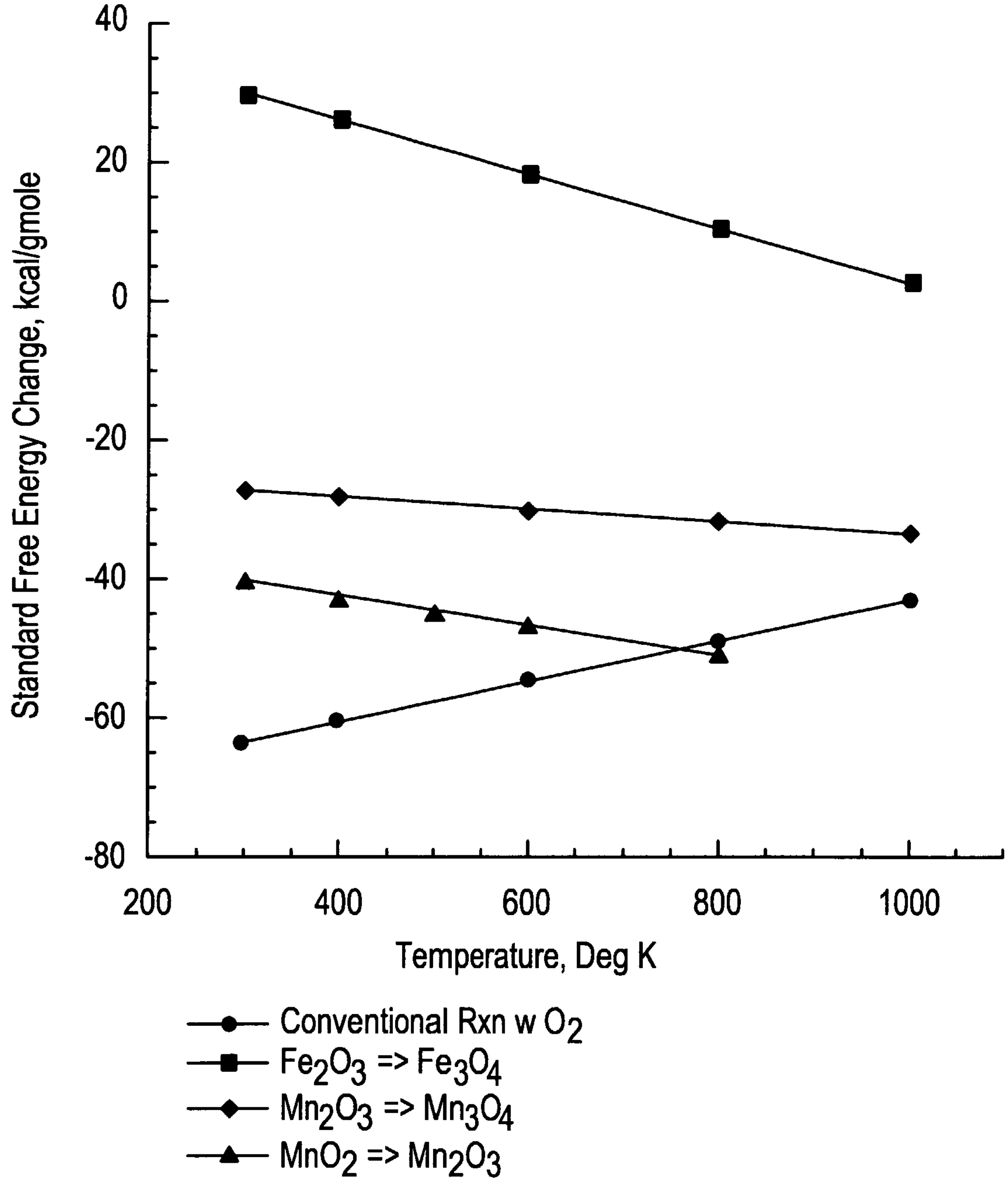
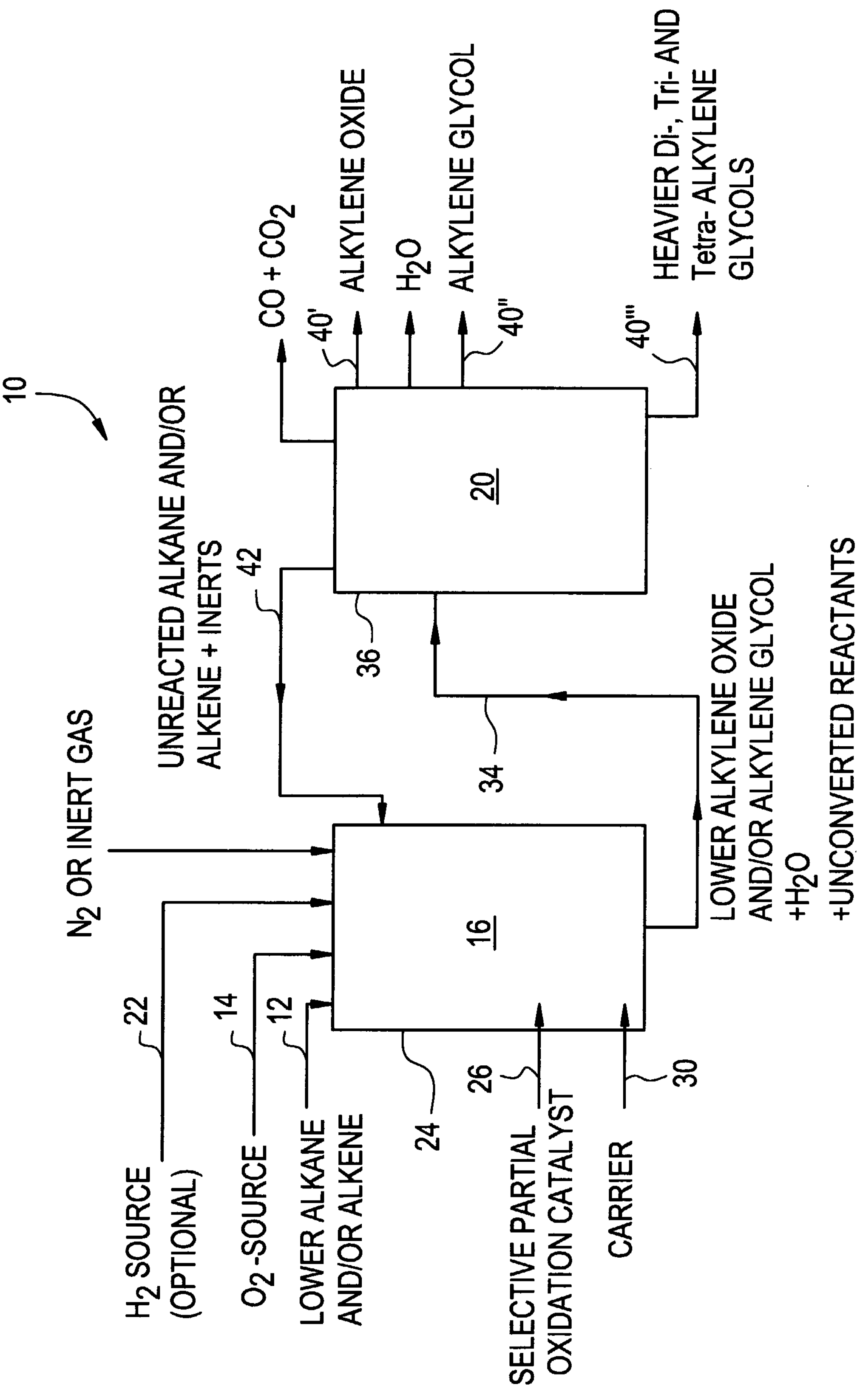


FIG. 5


10
N_2 OR INERT GAS
UNREACTED ALKANE AND/OR ALKENE + INERTS
42
$CO + CO_2$
40'
ALKYLENE OXIDE
H_2O
ALKYLENE GLYCOL
40''
40'''
HEAVIER Di-, Tri- AND Tetra- ALKYLENE GLYCOLS
20
36
34
16
22
14
12
24
26
30
H_2 SOURCE (OPTIONAL)
O_2 -SOURCE
LOWER ALKANE AND/OR ALKENE
SELECTIVE PARTIAL OXIDATION CATALYST
CARRIER
LOWER ALKYLENE OXIDE AND/OR ALKYLENE GLYCOL $+H_2O$ +UNCONVERTED REACTANTS

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 02/12526

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07D301/04 C07D301/22 C07C29/48 C07C31/20

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C07D C07C

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

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

BEILSTEIN Data, EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	US 5 344 946 A (S. WARWEL ET AL.) 6 September 1994 (1994-09-06) claims 1-24	1-72
X	US 3 987 069 A (B. J. BARONE) 19 October 1976 (1976-10-19) claim 1	1-72
X	US 4 130 570 A (G. K. BORESKOV ET AL.) 19 December 1978 (1978-12-19) claims 1-17	1-72

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
12 September 2002	25/09/2002

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Herz, C

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 02/12526

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X	US 2 125 333 A (R. M. CARTER) 2 August 1938 (1938-08-02) claims 1-12 ---	1-72
X	US 2 437 930 A (I. BERSTEINSSON, J. R. SCHEIBLI) 16 March 1948 (1948-03-16) claims 1-6 ---	1-72
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE CROSSFIRE BEILSTEIN 'Online! Beilstein Institut zur Förderung der Chemischen Wissenschaften, Frankfurt am Main, DE; Database accession no. 1895029 XP002213250 abstract & A. SEN ET AL.: J. AMER. CHEM. SOC., vol. 116, no. 3, 1994, pages 998-1003, ---	1-72
X	DATABASE CROSSFIRE BEILSTEIN 'Online! Beilstein Institut zur Förderung der Chemischen Wissenschaften, Frankfurt am Main, DE; Database accession no. 209121 XP002213251 abstract & E. P. TALSI ET AL.: J. CHEM. SOC. CHEM. COMMUN., no. 24, 1985, pages 1768-1769, ---	1-72
X	DATABASE CROSSFIRE BEILSTEIN 'Online! Beilstein Institut zur Förderung der Chemischen Wissenschaften, Frankfurt am Main, DE; Database accession no. 6798863 XP002213252 abstract & MC BEE ET AL.: IND. ENG. CHEM., vol. 37, 1945, page 434 ---	1-72
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X	DATABASE CROSSFIRE BEILSTEIN 'Online! Beilstein Institut zur Förderung der Chemischen Wissenschaften, Frankfurt am Main, DE; Database accession no. 6798867 XP002213254 abstract & WAN: IND. ENG. CHEM., vol. 45, 1953, page 234 --- -/--	1-72

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
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