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(54) **Title**: PROCESS FOR PRODUCING OLEFIN OXIDE

(57) **Abstract**: A process for producing an olefin oxide which comprises reacting an olefin with oxygen in the presence of a catalyst comprising (a) copper oxide, (b) tungsten oxide and (c) alkaline metal component or alkaline earth metal component.

DESCRIPTION

PROCESS FOR PRODUCING OLEFIN OXIDE

Cross-Reference to Related Applications

This application claims priority to and the benefit of U.S. Provisional Application No.61/363,225, filed July 10, 2010, incorporated by reference here in its entirely.

Technical Field

The present invention relates to a process for producing an olefin oxide.

Background Art

Olefin oxides, such as propylene oxide, are important and versatile intermediates used in the production of a large variety of valuable consumer products such as polyurethane foams, polymers, alkylene glycol, cosmetics, food emulsifiers and as fumigants and insecticides.

Previous research on olefin epoxidation involved the use of Ag-based catalysts (Appl. Catal. A. Gen. 2001, 221, 73.), as well as silica supported Cu (J. Catal. 2005, 236, 401), various metal oxides (Appl. Catal. A.Gen. 2007, 316, 142), Au-based catalysts with H_2 as a co-reactant (Ind. & Eng. Chem. Res. 1995, 34, 2298, J. Catal. 1998, 178, 566; Appl. Catal. A.

Gen. 2000, 190, 43; Angew. Chem. Int. Ed. 2004, 43, 1546), titania based catalysts that deactivated quickly (Catal. Commun. 2001, 1356; Catal. Commun. 2003, 4, 385), molten salts of metal nitrates (Appl. Catal. A. Gen. 2000, 196, 217), the use of O_3 (Appl. Catal. A. Gen. 2000, 196, 217) and nitrous oxide (Ind. & Eng. Chem. Res. 1995, 34, 2298) as reactants. Although these developments are scientifically interesting, they have serious drawbacks, such as low PO selectivities and/or low propylene conversions, short catalyst lifetimes, the use of higher pressures or the use of costly co-reactants (Appl. Catal. A.Gen. 2007, 316, 142).

Summary of Invention

The present invention provides:

[1] A process for producing an olefin oxide which comprises reacting an olefin with oxygen in the presence of a catalyst comprising (a) copper oxide, (b) tungsten oxide and (c) alkaline metal component or alkaline earth metal component.

[2] The process according to [1], wherein the catalyst comprises (d) halogen component.

[3] The process according to [1] or [2], wherein the catalyst comprises (e) composite oxide.

[4] The process according to [1], wherein (a) copper oxide, (b) tungsten oxide and (c) alkaline metal component or alkaline earth metal component are supported on a porous support.

[5] The process according to [2], wherein (a) copper oxide, (b) tungsten oxide, (c) alkaline metal component or alkaline earth metal component and (d) halogen component are supported on a porous support.

[6] The process according to [4] or [5], wherein the porous support comprises Al_2O_3, SiO_2, TiO_2 or ZrO_2.

[7] The process according to [4] or [5], wherein the porous support comprises SiO_2.

[8] The process according to any one of [1] to [7], wherein the total amount of (a) copper oxide, (b) tungsten oxide and (c) alkaline metal component or alkaline earth metal component is 0.01 to 80% by weight of the amount of the catalyst.

[9] The process according to any one of [1] to [8], wherein the copper/tungsten metal molar ratio in the catalyst is 1/99 to 99/1.

[10] The process according to any one of [1] to [9], wherein the copper/(c) component metal molar ratio in the catalyst is 1/99 to 99/1.

[11] The process according to any one of [1] to [10], wherein (a) copper oxide is CuO.

[12] The process according to any one of [1] to [11], wherein (b) tungsten oxide is WO_2 or WO_3.

[13] The process according to any one of [1] to [12], wherein (c) alkaline metal component or alkaline earth metal component is an alkaline metal-containing compound or an alkaline earth

metal-containing compound.

[14] The process according to any one of [1] to [13], wherein (c) alkaline metal component or alkaline earth metal component is a sodium-containing compound.

[15] The process according to [4], wherein the catalyst is obtained by impregnating a porous support with a solution containing a copper ion, a tungsten ion and an alkaline metal or alkaline earth metal ion to prepare a composition, followed by calcining the composition.

[16] The process according to [5], wherein the catalyst is obtained by impregnating a porous support with a solution containing a copper ion, a tungsten ion, an alkaline metal or alkaline earth metal ion and a halogen ion to prepare a composition, followed by calcining the composition.

[17] The process according to any one of [1] to [16], wherein the olefin is propylene and the olefin oxide is propylene oxide.

[18] The process according to any one of [1] to [17], which comprises reacting an olefin with oxygen at a temperature of 100 to 350°C.

[19] A catalyst for production of an olefin oxide which comprises (a) copper oxide, (b) tungsten oxide and (c) alkaline metal component or alkaline earth metal component.

[20] The catalyst according to [19] which comprises (d) halogen component.

[21] The catalyst according to [19] or [20] which comprises

(e) composite oxide.

[22] The catalyst according to [19], wherein (a) copper oxide, (b) tungsten oxide and (c) alkaline metal component or alkaline earth metal component are supported on a porous support.

[23] The catalyst according to [20], wherein (a) copper oxide, (b) tungsten oxide, (c) alkaline metal component or alkaline earth metal component and (d) halogen component are supported on a porous support.

[24] The catalyst according to [22], which is obtained by impregnating a porous support with a solution containing a copper ion, a tungsten ion and an alkaline metal or alkaline earth metal ion to prepare a composition, followed by calcining the composition.

[25] The catalyst according to [23] which is obtained by impregnating a porous support with a solution containing a copper ion, a tungsten ion, an alkaline metal or alkaline earth metal ion and a halogen ion to prepare a composition, followed by calcining the composition.

[26] The catalyst according to any one of [19] to [25], wherein (c) alkaline metal component or alkaline earth metal component is an alkaline metal-containing compound or an alkaline earth metal-containing compound.

[27] The catalyst according to any one of [22] to [26], wherein the porous support comprises Al_2O_3, SiO_2, TiO_2 or ZrO_2.

[28] The catalyst according to any one of [22] to [27], wherein

the porous support comprises SiO_2.

[29] The catalyst according to any one of [19] to [28], wherein the olefin oxide is propylene oxide.

[30] Use of a catalyst for producing an olefin oxide, said catalyst comprising (a) copper oxide, (b) tungsten oxide and (c) alkaline metal component or alkaline earth metal component.

[31] The use of a catalyst according to [30], wherein the olefin oxide is propylene oxide.

Description of Embodiment

The process of the present invention comprises reacting an olefin with oxygen in the presence of a catalyst comprising (a) copper oxide, (b) tungsten oxide and (c) alkaline metal component or alkaline earth metal component.

The components (a), (b) and (c) may be supported on a porous support or a non-porous support. Examples of the non-porous support include a non-porous support comprising SiO_2 such as CAB-O-SIL (registered trademark).

In the catalyst, the components (a), (b) and (c) are preferably supported on a porous support. This catalyst is valuable for production of olefin oxides, which is one aspect of the present invention.

The porous support has pores capable of supporting the components (a), (b) and (c). The porous support comprises preferably Al_2O_3, SiO_2, TiO_2 or ZrO_2, more preferably SiO_2.

Examples of the porous support comprising SiO_2 include mesoporous silica. Such a porous support may also comprise zeolites.

If the catalyst comprises SiO_2 as a support, olefin oxides can be prepared with good yield and good selectivity.

The catalyst may comprise one or more kinds of (a) copper oxide. The (a) copper oxide is usually composed of copper and oxygen. Examples of the copper oxide include Cu_2O and CuO. The copper oxide is preferably CuO.

The catalyst may comprise one or more kinds of (b) tungsten oxide.

The component (b) is usually composed of tungsten and oxygen. Examples of the component (b) oxide include W_3O, $W_{17}O_{47}$, W_5O_{14}, WO_x, WO_2 and WO_3, preferably WO_2 and WO_3.

The catalyst may comprise one or more kinds of (c) alkaline metal component or alkaline earth metal component.

The (c) component may be an alkaline metal-containing compound, an alkaline earth metal-containing compound, an alkaline metal ion or an alkaline earth metal ion.

Examples of the alkaline metal-containing compound include compounds containing an alkaline metal such as Na, K, Rb and Cs. Examples of the alkaline earth metal-containing compound include compounds containing an alkaline earth metal such as Ca, Mg, Sr and Ba. Examples of the alkaline metal ion include Na^+, K^+, Rb^+ and Cs^+. Examples of the alkaline earth

metal ion include Ca^{2+}, Mg^{2+}, Sr^{2+} and Ba^{2+}.

The alkaline metal component may be an alkaline metal oxide. Examples of the alkaline metal oxide include Na_2O, Na_2O_2, K_2O, KO_2, K_2O_2, Rb_2O, Rb_2O_2, Cs_2O, Cs_2O_2, CsO_2, CsO_3, Cs_2O_3, $Cs_{11}O_3$, Cs_4O and Cs_7O. The alkaline earth metal component may be alkaline metal earth oxide. Examples of the alkaline earth metal oxide include CaO, CaO_2, MgO, MgO_2, SrO, SrO_2, BaO and BaO_2.

The alkaline metal-containing compound is preferably an alkaline metal salt. The alkaline earth metal-containing compound is preferably an alkaline earth metal salt. The alkaline metal salt comprises the alkaline metal ion as mentioned above with an anion. The alkaline earth metal salt comprises the alkaline earth metal ion as mentioned above with an anion. Examples of anions in such salts include F^-, Cl^-, Br^-, I^-, OH^-, NO_3^-, SO_4^{2-}, CO_3^{2-} HCO_3^- and SO_3^{2-}. Such salts are preferably an alkaline metal salt with a halogen, such as an alkaline metal halide, or an alkaline earth metal-containing salt with a halogen, such as an alkaline earth metal halide, more preferably an alkaline metal salt with a halogen, still more preferably an alkaline metal chloride.

The component (c) is preferably an alkaline metal-containing compound or an alkaline earth metal-containing compound, more preferably a sodium-containing compound.

Particularly if the catalyst comprises NaCl as the (c)

component, it can show excellent olefin oxide selectivity.

The copper/tungsten metal molar ratio in the catalyst is preferably 1/99 to 99/1. When the metal molar ratio falls within such a range, the olefin oxide yield and selectivity can be further improved. The lower limit of the molar ratio is more preferably 2/98, still more preferably 3/97, further preferably 10/90, particularly preferably 20/80. The upper limit of the molar ratio is more preferably 98/2, still more preferably 97/3, further preferably 90/10, particularly preferably 80/20.

The copper/(c) component molar ratio in the catalyst is preferably 1/99 to 99/1. When the molar ratio falls within such a range, the olefin oxide yield and selectivity can be further improved. The lower limit of the molar ratio is more preferably 2/98, still more preferably 3/97. The upper limit of the molar ratio is more preferably 98/2, still more preferably 97/3. The "(c) component" of the molar ratio represents the alkaline metal or alkaline earth metal existing in the (c) component and the alkaline metal or alkaline earth metal ion existing in the (c) component.

When the components (a), (b) and (c) are supported on a porous support in the catalyst, the total content of the components (a), (b) and (c) is preferably 0.01 to 80% by weight of the amount of the catalyst. When the total content falls within such a range, the olefin oxide yield and selectivity can be further improved. The lower limit of the total content is

more preferably 0.05% by weight, still more preferably 0.1% by weight of the amount of the catalyst. The upper limit of the total content is more preferably 50% by weight, still more preferably 30% by weight of the amount of the catalyst.

The catalyst may comprise (d) halogen component besides the components (a), (b) and (c). The component (d) is generally a halogen-containing compound. Examples of the halogen include chlorine, fluorine, iodine and bromine.

Examples of such a halogen-containing compound include copper halides such as CuCl and $CuCl_2$, tungsten halides such as such as WCl_4 and WCl_6, cupper oxyhalides such as $CuOCl_2$, $CuClO_4$, $ClO_2Cu(ClO_4)_3$ and $Cu_2O(ClO_4)_2$, and tungsten oxyhalides such as $WO_2(ClO_4)_2$ and WCl_2O_2. The component (d) may be supported on any of the components (a), (b) and (c) or the porous support.

The catalyst may further comprise (e) composite oxides, including those composed of copper, tungsten and oxygen, such as Cu_2WO_4, $CuWO_{4-x}$, those composed of sodium, tungsten and oxygen, such as $Na_{0.1}WO_3$, Na_2WO_4, $Na_2W_2O_7$, $Na_2W_4O_{13}$, $Na_2W_6O_{19}$ and $NaWO_3$, and those composed of sodium, copper and oxygen, such as $NaCuO_2$, Na_2CuO_2, NaCuO and $Na_6Cu_2O_6$.

If the catalyst comprises the component (d) or (e), the component may be supported on the porous support as mentioned above.

Production of the catalyst is not restricted to a specific process, examples of which include the conventional methods.

When the components (a), (b) and (c) are supported on a porous support in the catalyst, the catalyst can be obtained by impregnating a porous support with a solution containing a copper ion, a tungsten ion and an alkaline metal or alkaline earth metal ion to prepare a composition, followed by calcining the composition. The support can be in form of powder, or shaped to a desired structure as necessary. If the catalyst comprises the component (c) which is an alkaline metal salt with a halogen or alkaline earth metal salt with a halogen, and the component (d) supported on the porous support, the catalyst can be obtained in the same procedure as mentioned above except that the solution contains a copper ion, a tungsten ion, an alkaline metal or alkaline earth metal-containing ion and a halogen ion.

The solution containing a copper ion, a tungsten ion and an alkaline metal or alkaline earth metal ion can be prepared by dissolving a copper metal salt or a copper oxide, a tungsten metal salt or a tungsten oxide, and an alkaline metal or alkaline earth metal salt or an alkaline metal or alkaline earth metal oxide in a solvent. The solution is preferably prepared by dissolving a copper metal salt, a tungsten metal salt and an alkaline metal or alkaline earth metal salt in a solvent. Examples of the copper metal salt include copper acetate, copper ethoxide, copper isobutyrate, copper isopropoxide, copper hydroxide, copper nitrate, copper sulfate, copper chloride, copper diammonium chloride, copper bromide and copper iodide.

Examples of the tungsten metal salt include tungsten chloride, tungsten dichloride, tungsten dioxide, and tungsten ethoxide. The alkaline metal or alkaline earth metal salt for the solution may be the same as or different from the salt of the (c) component in the catalyst. Examples of the alkaline metal or alkaline earth metal salt include alkaline metal nitrates, alkaline earth metal nitrates, alkaline metal halides, , alkaline earth metal halides, alkaline metal acetates, alkaline earth metal acetates, alkaline metal butyrates, alkaline earth metal butyrates, alkaline metal benzoates, alkaline earth metal benzoates, alkaline metal alkoxides, alkaline earth metal alkoxides, alkaline metal carbonates, alkaline earth metal carbonates, alkaline metal citrates, alkaline earth metal citrates, alkaline metal formates, alkaline earth metal formates, alkaline metal hydrogen carbonates, alkaline earth metal hydrogen carbonates, alkaline metal hydroxides, alkaline earth metal hydroxides, alkaline metal hypochlorites, alkaline earth metal hypochlorites, alkaline metal halates, alkaline earth metal halates, alkaline metal nitrites, alkaline earth metal nitrites, alkaline metal oxalates, alkaline earth metal oxalates, alkaline metal perhalates, alkaline earth metal perhalates, alkaline metal propionates, alkaline earth metal propionates, alkaline metal tartrates and alkaline earth metal tartrates, preferably alkaline metal halides and alkaline metal nitrates, more preferably $NaNO_3$ and NaCl. At least one of the

metal salts for the solvent contains preferably a halogen ion, more preferably a chloride ion. Such a halogen ion may form the (c) components such as alkaline metal halides or alkaline earth metal halides, or the (d) components such as tungsten halides and oxyhalides, and copper halides and oxyhalides. The solution may contain acidic or basic compounds in order to control its pH.

Examples of the solvent for the solution include water and alcohols such as methanol or ethanol.

The total amount of the porous support is preferably 20 to 99.99% by weight, more preferably 50 to 99.95% by weight, still preferably 70 to 99.9% by weight of the catalyst as obtained.

The composition as prepared by the impregnation is usually dried, and the drying method thereof is not limited.

The composition as prepared by the impregnation is preferably dried at a temperature of approximately 40°C to approximately 200°C before calcining the composition. Drying is prefarably performed under an atmosphere of air or also under an inert gas atmosphere (for example, Ar, N_2, He) at standard pressure or reduced pressure. A drying time is preferably in the range from 0.5 to 24 hours. After drying, the composition can be shaped to a desired structure as necessary.

The method of calcining the composition is not limited, and calcining the composition is preferably performed under a

gas atmosphere containing oxygen. Examples of such a gas stream include air, oxygen, nitrous oxide and other oxidizing gases. The gas may be used after being mixed at an appropriate ratio with a diluting gas such as nitrogen, helium, argon, and water vapor. An optimal temperature for calcination varies depending on the kind of the gas and the composition, however, a too high temperature may cause agglomeration of tungsten oxide and copper oxide. Accordingly, the calcination temperature is typically 200 to 800°C, preferably 400 to 600°C.

The catalyst can be used as powder, but it is usual to shape it into desired structures such as spheres, pellets, cylinders, rings, hollow cylinders, or stars. The catalyst can be shaped by a known procedure such as extrusion, ram extrusion, tableting. The calcination is normally performed after shaping into the desired structures, but it can also be performed before shaping them.

Next, the following explains a reaction of an olefin with oxygen in the presence of the catalyst as described above.

In the present invention, the olefin may have a linear or branched structure and contains usually 2 to 10, preferably 2 to 8 carbon atoms. Examples of the olefin include preferably ethylene, propylene, butene, pentene, hexene, heptene , octene, and butadiene, more preferably ethylene, propylene and butene, still more preferably propylene.

The reaction is generally performed in the gas phase. In

the reaction, the olefin and oxygen may be fed respectively in the form of a gas. Olefin and oxygen gases can be fed in the form of their mixed gas. Olefin and oxygen gases may be fed with diluent gases. Examples of diluent gases include nitrogen or rare gases, such as argon and helium, carbon dioxide, water vapor, methane, ethane and propane. Preferable diluent gases are nitrogen, carbon dioxide and the both thereof.

As the oxygen source, pure oxygen may be used, or a mixed gas containing pure oxygen and a gas inactive to the reaction, such as air, may be used. Examples of the gas inactive to the reaction include nitrogen, rare gases such as argon and helium, carbon dioxide, water vapor, methane, ethane and propane. Preferable gases inactive to the reaction are nitrogen, carbon dioxide and the both thereof. The amount of oxygen used varies depending on the reaction type, the catalyst, the reaction temperature or the like. The amount of oxygen is typically 0.01 to 100 mol, and preferably 0.03 to 30 mol, more preferably 0.05 to 10 mol and expecially preferably 0.25 to 10 mol, with respect to 1 mol of the olefin.

The reaction is performed at a temperature generally of 100 to 350°C, preferably of 120 to 330°C, more preferably of 170 to 310°C.

The present reaction is carried out under reaction pressure in the range of reduced pressure to increased pressure.

By carrying out the reaction under such a reaction pressure condition, the productivity and selectivity of olefin oxides can be improved. Reduced pressure means a pressure lower than atmospheric pressure. Increased pressure means a pressure higher than atmospheric pressure. The reaction pressure is typically in the range of 0.01 to 3 MPa, and preferably in the range of 0.02 to 2 MPa, in the absolute pressure.

The reaction of the present invention may be carried out as a batch reaction or a continuous reaction, preferably as a continuous reaction for industrial application. The reaction of the present invention may be carried out by mixing an olefin and oxygen and then contacting the mixture with the catalyst under reduced pressure to increased pressure.

The reactor type is not limited. Examples of the reactor types are fluid bed reactor, fixed bed reactor, moving bed reactor, and the like, preferably fixed bed reactor. In the case of using fixed bed reactor, single tube reactor or multi tube reactor can be employed. More than one reactors can be used. If the number of reactors is large, small reactors as for exmaple microreactors, can be used, which can have multiple channels. Adiabatic type or heat exchange type may be also used.

In the present invention, the olefin oxide may have a linear or branched structure and contains usually 2 to 10, preferably 2 to 8 carbon atoms. Examples of the olefin oxides include preferably ethylene oxide, propylene oxide, butene

oxide, pentene oxide, hexene oxide, heptene oxide, octene oxide, and 3,4-epoxy-1-butene, more preferably ethylene oxide, propylene oxide and butene oxide, still more preferably propylene oxide.

The olefin oxide as obtained can be collected by a method known in the art such as separation by distillation.

Examples

In Example 1, data analysis was performed according to the following method:

A reaction gas was mixed with ethane (10 Nml/min) as an external standard, and then directly introduced in the TCD-GC equipped with a column of Gaskuropack 54 (2 m). All products in the reaction gas were collected for 1 hour with double methanol traps connected in series and cooled with a dry-ice/methanol bath. The two methanol solutions were mixed together and added to anisole as external standard, and then analyzed with two FID-GCs quipped with different columns, PoraBOND U (25 m) and PoraBOND Q (25 m).

The detected products were propylene oxide (PO), acetone (AT), CO_x (CO_2 and CO), propanal(PaL), acrolein(AC)

The propylene conversion, product selectivity, and yield (calculated as selectivity of product × propylene conversion) of products were calculated on the basis of carbon balance. Propylene conversions (X_{PR}) were determined from the following:

$$X_{PR} = \{[\ PO+AC+AT+PaL+CO_2/3]_{out}/[C_3H_6]_{in}\} \times 100\%;$$

and PO selectivities (S_{PO}) were then calculated using the following expression:

$$S_{PO} = \{[PO] / [PO+AC+AT+PaL+CO_2/3]\} \times 100\%$$

Each metal weight was determined from the amounts of the metal salts used for preparation of the catalyst.

Example 1

A catalyst was prepared by a co-impregnation method. A predetermined weight (2.9 g) of amorphous silica powder (SiO_2, Japan Aerosil, 380 m^2/g) was added to an aqueous solution mixture containing 0.35 g of WCl_4 (Wako), 0.45 g of $Cu(NO_3)_2$ (Wako) and 0.15 g of NaCl (Wako), followed by stirring for 24 hours in the air to impregnate the support with the metal salts. The resulting material was then heated at 100°C until dried, and calcined at 500°C for 12 hours in air to give the catalyst.

The catalyst was evaluated by using a fixed-bed reactor. Filling a 1/2-inch OD reaction tube made of stainless steel with 1 mL of the thus obtained catalyst, the reaction tube was supplied with 450 NmL/h of propylene, 900 NmL/h of air, and 990 NmL/h of a nitrogen gas to carry out the reaction at the reaction temperature of 200, 250 and 270°C under increased pressure (equivalent to 0.3 MPa in the absolute pressure).

The result is shown in Table 1.

Table 1

Example	1		
Total metal loading (wt%)	12.5		
W/Cu/Na (weight ratio of metal)	4/2/1		
Reaction temperature (°C)	200	250	270
Propylene conversion (%)	0.04	0.1	0.2
Propylene oxide selectivity (%)	24	5	4

Example 2

The catalyst obtained in Example 1 (5.0 mg) was placed in a well of a reactor as mentioned in Angew. Chem. Int. Ed. 38 (1999) 2794, equipped with array microreactors, wells along each reactor channel and a passivated 200 micron ID capillary sampling probe within the reactor channel. The mixture gas consisting of 1 vol% propylene (C_3H_6), 4 vol% O_2, and 95 vol% He was fed to the well containing the catalyst, at a gas hourly space velocity (GHSV) of 20,000 h^{-1}, at a reactor temperature of 250°C.

Gas sampling was accomplished by withdrawing reactor exit gases using the passivated 200 micron ID capillary sampling probe.

Data analysis for sample gases was conducted by an on-line Micro-Gas Chromatograph (Varian, CP-4900) equipped with a thermal conductivity detector (TCD), PoraPLOT U (10M) and Molecular sieve 13X (10M).

The detected products were propylene oxide (PO), acetone (AT), acetaldehyde (AD), CO_x (CO_2 and CO), and propanal +

acrolein (PaL+AC).

The propylene conversion, product selectivity, and yield (calculated as selectivity of product × propylene conversion) of products were calculated on the basis of carbon balance. Propylene conversions (X_{PR}) were determined from the following:

$$X_{PR} = \{[PO+AC+AT+2AD/3+CO_2/3]_{out}/[C_3H_6]_{in}\} \times 100\%;$$

and PO selectivities (S_{PO}) were then calculated using the following expression:

$$S_{PO} = \{[PO] / [PO+AC+AT+2AD/3+CO_2/3]\} \times 100\%$$

Note: PaL+AC are reported together since the two compounds appear at the same retention time, although the PaL is typically only found in trace amounts.

The result is shown in Table 2.

Table 2

Example	2
Reaction temperature (°C)	250
Propylene conversion (%)	0.1
Propylene oxide selectivity (%)	25

CLAIMS

1. A process for producing an olefin oxide which comprises reacting an olefin with oxygen in the presence of a catalyst comprising (a) copper oxide, (b) tungsten oxide and (c) alkaline metal component or alkaline earth metal component.

2. The process according to claim 1, wherein the catalyst comprises (d) halogen component.

3. The process according to claim 1 or 2, wherein the catalyst comprises (e) composite oxide.

4. The process according to claim 1, wherein (a) copper oxide, (b) tungsten oxide and (c) alkaline metal component or alkaline earth metal component are supported on a porous support.

5. The process according to claim 2, wherein (a) copper oxide, (b) tungsten oxide, (c) alkaline metal component or alkaline earth metal component and (d) halogen component are supported on a porous support.

6. The process according to claim 4 or 5, wherein the porous support comprises Al_2O_3, SiO_2, TiO_2 or ZrO_2.

7. The process according to claim 4 or 5, wherein the porous support comprises SiO_2.

8. The process according to claim 1 or 2, wherein the total amount of (a) copper oxide, (b) tungsten oxide and (c) alkaline metal component or alkaline earth metal component is

0.01 to 80% by weight of the amount of the catalyst.

9. The process according to claim 1 or 2, wherein the copper/tungsten metal molar ratio in the catalyst is 1/99 to 99/1.

10. The process according to claim 1 or 2, wherein the copper/(c) component metal molar ratio in the catalyst is 1/99 to 99/1.

11. The process according to claim 1 or 2, wherein (a) copper oxide is CuO.

12. The process according to claim 1 or 2, wherein (b) tungsten oxide is WO_2 or WO_3.

13. The process according to claim 1 or 2, wherein (c) alkaline metal component or alkaline earth metal component is an alkaline metal-containing compound or an alkaline earth metal-containing compound.

14. The process according to claim 1 or 2, wherein (c) alkaline metal component or alkaline earth metal component is a sodium-containing compound.

15. The process according to claim 4, wherein the catalyst is obtained by impregnating a porous support with a solution containing a copper ion, a tungsten ion and an alkaline metal or alkaline earth metal ion to prepare a composition, followed by calcining the composition.

16. The process according to claim 5, wherein the catalyst is obtained by impregnating a porous support with a

solution containing a copper ion, a tungsten ion, an alkaline metal or alkaline earth metal ion and a halogen ion to prepare a composition, followed by calcining the composition.

17. The process according to claim 1 or 2, wherein the olefin is propylene and the olefin oxide is propylene oxide.

18. The process according to claim 1 or 2, which comprises reacting an olefin with oxygen at a temperature of 100 to 350°C.

19. A catalyst for production of an olefin oxide which comprises (a) copper oxide, (b) tungsten oxide and (c) alkaline metal component or alkaline earth metal component.

20. The catalyst according to claim 19 which comprises (d) halogen component.

21. The catalyst according to claim 19 or 20 which comprises (e) composite oxide.

22. The catalyst according to claim 19, wherein (a) copper oxide, (b) tungsten oxide and (c) alkaline metal component or alkaline earth metal component are supported on a porous support.

23. The catalyst according to claim 20, wherein (a) copper oxide, (b) tungsten oxide, (c) alkaline metal component or alkaline earth metal component and (d) halogen component are supported on a porous support.

24. The catalyst according to claim 22, which is obtained by impregnating a porous support with a solution containing a

copper ion, a tungsten ion and an alkaline metal or alkaline earth metal ion to prepare a composition, followed by calcining the composition.

25. The catalyst according to claim 23, which is obtained by impregnating a porous support with a solution containing a copper ion, a tungsten ion, an alkaline metal or alkaline earth metal ion and a halogen ion to prepare a composition, followed by calcining the composition.

26. The catalyst according to claim 19 or 20, wherein (c) alkaline metal component or alkaline earth metal component is an alkaline metal-containing compound or an alkaline earth metal-containing compound.

27. The catalyst according to claim 22 or 23, wherein the porous support comprises Al_2O_3, SiO_2, TiO_2 or ZrO_2.

28. The catalyst according to claim 22 or 23, wherein the porous support comprises SiO_2.

29. The catalyst according to claim 19 or 20, wherein the olefin oxide is propylene oxide.

30. Use of a catalyst for producing an olefin oxide, said catalyst comprising (a) copper oxide, (b) tungsten oxide and (c) alkaline metal component or alkaline earth metal component.

31. The use of a catalyst according to claim 30, wherein the olefin oxide is propylene oxide.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 11/38525

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - B01J 23/00; B01J 23/46 (2011.01)
USPC - 502/317,117
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(8): B01J 23/00; B01J 23/00; B01J 23/46 (2011.01);
USPC: 502/317,117

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC: 502/317-318,113,117,118,165,102; 585/444;549/523

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Google Scholar, Google Patents, PubWEST (PGPB,USPT,EPAB,JPAB) (olefin, oxide, Cu, W, alkaline, earth, catalyst, halogen, porous, support, alumina, silica, titania, zirconia, solution, calcine, propylene, Na, K, Rb, Cs)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 6,498,259 B1 (Grey, et al.) 24 Dec 2002 (24.12.2002) column 2, line 52-56, column 3, line 10-20, line 55-58, column 4, line 19-21, line 31-32, line 60-61, column 5, line 47-67, column 6, line 1-23, column 7, line 38	1-31
Y	US 4,388,225 A (Solomon) 14 Jun 1983 (14.06.1983) column 2, line 12-16, column 3, line 1-11	1-31
Y	US 6,765,101 B1 (Bhasin et al.) 20 July 2004 (20.07.2004) entire document especially col 1, ln 66 to col 2, ln 20; col 3, ln 40- 58; col 3, ln 10-14; col 3, ln 53 -59; col 7, ln 27-35; col 7, ln 36-58	1-31
A	US 5,112,795 A (Minahan et al.) 12 May 1992 (12.05.1992) entire document	1-31
A	US 5,958,824 A (Rizkalla et al.) 28 September 1999 (28.09.1999) entire document	1-31

☐ Further documents are listed in the continuation of Box C. ☐

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"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
"P" document published prior to the international filing date but later than the priority date claimed
"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
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
21 Aug 2011 (21.08.2011)	01 SEP 2011
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

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