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

(57) **Abstract:** A process for producing an olefin oxide comprising: a first step of contacting a catalyst comprising a copper oxide, and one or both of ruthenium oxide and one metal oxide other than a copper oxide and a ruthenium oxide, with water and a second step of reacting an olefin with oxygen in the presence of the catalyst obtained in the first step.



DESCRIPTION

PROCESS FOR PRODUCING OLEFIN OXIDE

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims the benefit U.S. Provisional
5 Application No. 61/550,850 filed on October 24, 2011, the
contents of which are hereby incorporated by reference in their
entirety into the present disclosure.

FIELD OF THE INVENTION

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

BACKGROUND ART

Olefin oxides, such as propylene oxide, are important and
15 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.

20 SUMMARY OF THE INVENTION

The present invention provides:

[1] A process for producing an olefin oxide comprising:

a first step of contacting a catalyst comprising a copper
oxide, and one or both of a ruthenium oxide and one metal oxide
25 other than a copper oxide and a ruthenium oxide, with water and

a second step of reacting an olefin with oxygen in the
presence of the catalyst obtained in the first step;

[2] The process according to [1], wherein the catalyst is
contacted with water and an alkaline metal compound or an
30 alkaline earth metal compound;

[3] The process according to [1], wherein the catalyst is

contacted with water and an inorganic acid;

[4] The process according to any one of [1] to [3], wherein the first step further comprises calcining the catalyst at a temperature from 350°C to 650°C after contacting;

5 [5] The process according to any one of [1] to [4], wherein the catalyst comprises a copper oxide and a ruthenium oxide;

[6] The process according to any one of [1] to [5], wherein the catalyst further comprises an alkaline metal component or an alkaline earth metal component;

10 [7] The process according to any one of [1] to [6], wherein the catalyst further comprises a halogen component.

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides a process for producing
15 an olefin oxide comprising:

a first step of contacting a catalyst comprising a copper oxide, and one or both of a ruthenium oxide and one metal oxide other than a copper oxide and a ruthenium oxide, with water and

a second step of reacting an olefin with oxygen in the
20 presence of the catalyst obtained in the first step.

The catalyst comprises a copper oxide, and one or both of a ruthenium oxide and one metal oxide other than a copper oxide and a ruthenium oxide. The catalyst preferably comprises
25 a copper oxide and one metal oxide other than copper oxide, and more preferably comprises a copper oxide and a ruthenium oxide and one metal oxide other than copper oxide and ruthenium oxide.

The copper oxide is generally composed of an oxygen atom and copper, and examples thereof include Cu_2O and CuO , and CuO
30 is preferable.

The ruthenium oxide is generally composed of an oxygen atom and ruthenium, and examples thereof include RuO_4 and RuO_2 , and RuO_2 is preferable.

5 Examples of the metal oxides other than copper oxide and ruthenium oxide include manganese oxides, tellurium oxides, bismuth oxides, antimony oxides, chromium oxides, rhenium oxides, cobalt oxides, nickel oxides, osmium oxides, cerium oxides, germanium oxides, tin oxides, tungsten oxides, thallium
10 oxides, indium oxides, iridium oxides, lanthanum oxides, iron oxides, molybdenum oxides, selenium oxides, vanadium oxides and niobium oxides.

 The tellurium oxide is generally composed of an oxygen atom and tellurium, and examples thereof include TeO , TeO_2 and
15 TeO_3 , and TeO_2 is preferable.

 The manganese oxide is generally composed of an oxygen atom and manganese, and examples thereof include MnO , MnO_2 , Mn_2O_3 and Mn_3O_4 , and Mn_2O_3 is preferable.

 The bismuth oxide is generally composed of an oxygen atom
20 and bismuth, and examples thereof include BiO , BiO_2 , Bi_2O and Bi_2O_3 .

 The antimony oxide is generally composed of an oxygen atom and antimony, and examples thereof include SbO_2 , Sb_2O_3 , Sb_2O_4 and Sb_2O_5 , and SbO_2 and Sb_2O_3 are preferable.

25 The chromium oxide is generally composed of an oxygen atom and chromium, and examples thereof include CrO_3 and Cr_2O_3 , and Cr_2O_3 is preferable.

 The rhenium oxide is generally composed of an oxygen atom and rhenium, and examples thereof include ReO_2 , ReO_3 and Re_2O_7 ,
30 and ReO_2 and ReO_3 are preferable.

 The cobalt oxide is generally composed of an oxygen atom and cobalt, and examples thereof include CoO , Co_3O_4 and Co_2O_3 ,

and Co_3O_4 is preferable.

The nickel oxide is generally composed of an oxygen atom and nickel, and examples thereof include NiO .

5 The osmium oxide is generally composed of an oxygen atom and osmium, and examples thereof include OsO_2 and OsO_4 , and OsO_2 is preferable.

The cerium oxide is generally composed of an oxygen atom and cerium, and examples thereof include Ce_2O_3 and CeO_2 , and CeO_2 is preferable.

10 The germanium oxide is generally composed of an oxygen atom and germanium, and examples thereof include GeO and GeO_2 , and GeO_2 is preferable.

The tin oxide is generally composed of an oxygen atom and tin, and examples thereof include SnO_2 , SnO , Sn_2O_3 and Sn_3O_4 , and
15 SnO_2 and SnO are preferable.

The tungsten oxide is generally composed of an oxygen atom and tungsten, and examples thereof include W_3O , $\text{W}_{17}\text{O}_{47}$, W_5O_{14} , WO_2 and WO_3 , and WO_2 and WO_3 are preferable.

The thallium oxide is generally composed of an oxygen atom and thallium, and examples thereof include Tl_2O , Tl_2O_3 and Tl_4O_3 ,
20 and Tl_4O_3 is preferable.

The indium oxide is generally composed of an oxygen atom and indium, and examples thereof include In_2O_3 .

The iridium oxide is generally composed of an oxygen atom and iridium, and examples thereof include IrO_2 .
25

The lanthanum oxide is generally composed of an oxygen atom and lanthanum, and examples thereof include La_2O_3 .

The iron oxide is generally composed of an oxygen atom and lanthanum, and examples thereof include FeO , Fe_2O_3 and Fe_3O_4 ,
30 and Fe_2O_3 is preferable.

The molybdenum oxide is generally composed of an oxygen atom and molybdenum, and examples thereof include MoO_2 or MoO_3 .

The selenium oxide is generally composed of an oxygen atom and selenium, and examples thereof include SeO_2 and SeO_3 , and SeO_2 is preferable.

5 The vanadium oxide is generally composed of an oxygen atom and vanadium, and examples thereof include VO , VO_2 , V_2O_3 , V_6O_{13} and V_2O_5 , and V_2O_5 is preferable.

The niobium oxide is generally composed of an oxygen atom and niobium, and examples thereof include NbO , NbO_2 and Nb_2O_5 .

10 The catalyst preferably consists of copper oxide and one or two metal oxides selected from the group consisting of ruthenium oxide, manganese oxide, tellurium oxide, bismuth oxide, antimony oxide, chromium oxide, rhenium oxide, cobalt oxide, nickel oxide, osmium oxide, cerium oxide, germanium oxide, 15 tin oxide, tungsten oxide, thallium oxide, indium oxide, iridium oxide, lanthanum oxide, iron oxide, molybdenum oxide, selenium oxide, vanadium oxide and niobium oxide. The catalyst more preferably consists of copper oxide and one or two metal oxides selected from the group consisting of ruthenium oxide, tellurium 20 oxide, manganese oxide, bismuth oxide, antimony oxide, cerium oxide, germanium oxide and tin oxide. The catalyst still more preferably consists of copper oxide and one or two metal oxides selected from the group consisting of ruthenium oxide, tellurium oxide, manganese oxide and tin oxide. The catalyst especially 25 preferably consists of copper oxide and one or both of ruthenium oxide and tellurium oxide.

The catalyst may comprise a composite metal oxide. Examples of the composite metal oxide include those composed 30 of copper, ruthenium and oxygen; those composed of copper, sodium and oxygen; those composed of sodium, ruthenium and oxygen; those composed of copper, ruthenium, sodium and any other metals and

oxygen; those composed of copper, any other metals and oxygen; and those composed of ruthenium, any other metals and oxygen; those composed of sodium and any other metals and oxygen. If the catalyst comprises the composite metal oxide, it may be supported on the support or any of the other components.

The catalyst preferably contains a support, such as a porous support and a non-porous support. One or both of a copper oxide and a ruthenium oxide are preferably supported on a support, more preferably supported on a porous support. Examples of the non-porous support include a non-porous support comprising SiO_2 such as CAB-O-SIL (registered trademark). The catalyst containing a support is valuable for production of olefin oxides, which is one aspect of the present invention.

The porous support has pores capable of supporting one or both of a copper oxide and a ruthenium oxide. The porous support preferably comprises 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 porous supports may also comprise zeolites.

The support may be in form of powder, or shaped to a desired structure as necessary.

The catalyst preferably comprises one or more selected from the group consisting of an alkaline metal component and an alkaline earth metal component.

The alkaline metal component may be an alkaline metal-containing compound, and may be an alkaline metal ion. The alkaline earth metal component may be an alkaline earth metal-containing compound, and may be 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. The alkaline metal component may be an alkaline metal oxide. Example of the alkaline metal oxide include Na₂O, Na₂O₂,
5 K₂O, KO₂, K₂O₂, Rb₂O, Rb₂O₂, Cs₂O, Cs₂O₂, CsO₂, CsO₃, Cs₂O₃, Cs₁₁O₃, Cs₄O and Cs₇O. Examples of the alkaline metal ion include Na⁺, K⁺, Rb⁺ and Cs⁺.

Examples of the alkaline earth metal-containing compound include compounds containing an alkaline earth metal such as
10 Ca, Mg, Sr and Ba. The alkaline earth metal component may be an alkaline metal earth oxide. Examples of the alkaline earth metal oxide include CaO, CaO₂, MgO, MgO₂, SrO, SrO₂, BaO and BaO₂. Examples of the alkaline earth metal ion include Ca²⁺, Mg²⁺, Sr²⁺ and Ba²⁺.

15 The alkaline metal-containing compound is preferable, and a sodium-containing compound is more preferable.

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
20 alkaline metal salt comprises the alkaline metal ion as mentioned above and an anion. The alkaline earth metal salt comprises the alkaline earth metal ion as mentioned above and an anion. Examples of anions in such salts include F⁻, Cl⁻, Br⁻, I⁻, OH⁻, NO₃⁻, SO₄²⁻, CO₃²⁻, HCO₃⁻ and SO₃²⁻. Such salt is preferably an
25 alkaline metal salt containing a halogen such as an alkaline metal halide, or an alkaline earth metal-containing salt containing a halogen such as an alkaline earth metal halide, and an alkaline metal salt containing a halogen is more preferable, and an alkaline metal chloride is still more
30 preferable.

The alkaline metal component or the alkaline earth metal component may be supported on the support as mentioned above.

The catalyst may contain a halogen component. The halogen component is generally a halogen-containing compound. Examples of the halogen include chlorine, fluorine, iodine and bromine.

5 Examples of the halogen-containing compound include halides of copper, ruthenium or any other metals of metal oxides and oxyhalides of copper, ruthenium or any other metals of metal oxides. If the catalyst comprises the halogen component, the component may be supported on the porous support as mentioned
10 above.

When a copper oxide, and one or both of a ruthenium oxide and one metal oxide other than a copper oxide and a ruthenium oxide, and optionally any of the components are supported on a porous support in the catalyst, the total content of these
15 components is preferably 0.01 to 80 parts by weight relative to 100 parts of support. 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 part by weight, still more preferably 0.1 part
20 by weight relative to 100 parts by weight of a support. The upper limit of the total content is more preferably 50 parts by weight, still more preferably 30 parts by weight relative to 100 parts by weight of a support.

When both of a copper oxide and a ruthenium oxide are
25 included, the ruthenium/copper molar ratio in the catalyst is preferably 0.01/1 to 50/1 based on their atoms. 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 0.1/1, still more preferably 0.2/1.
30 The upper limit of the molar ratio is more preferably 5/1, still more preferably 1/1.

When a copper oxide and alkaline metal or alkaline earth metal are included, alkaline metal or alkaline earth metal/copper molar ratio in the catalyst is preferably 0.001/1 to 50/1 based on their atoms. 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 0.01/1, still more preferably 0.1/1. The upper limit of the molar ratio is more preferably 10/1, still more preferably 5/1.

When a copper oxide and other oxide except ruthenium oxide are included, the other component/copper molar ratio in the catalyst is preferably 0.001/1 to 50/1 based on their atoms. 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 0.01/1, still more preferably 0.05/1. The upper limit of the molar ratio is more preferably 10/1, still more preferably 5/1.

The catalyst can be produced according to the conventional methods.

When each of the metal oxides is supported on a support, the catalyst can be obtained by impregnating a support with a solution containing a copper ion and one or both of a ruthenium ion and other metal ion other than a copper ion and a ruthenium ion to prepare a composition, followed by calcining the composition.

If the catalyst comprises an alkaline metal or alkaline earth metal component or any other components as mentioned above, the catalyst can be obtained in the same procedure as mentioned above except that solution further contains an alkaline metal or alkaline earth metal-containing ion, a halogen ion or an metal ion of any other metal which forms any of the metal oxides as

mentioned above.

The solution containing a copper ion and one of both of a ruthenium ion and one metal ion other than a copper ion and a ruthenium ion can be prepared by dissolving a copper metal salt and one or both of a ruthenium metal salt and one metal salt other than a copper metal salt and a ruthenium metal salt in a solvent. Examples of the copper metal salt include copper acetate, copper ammonium chloride, copper bromide, copper carbonate, copper ethoxide, copper hydroxide, copper iodide, copper isobutyrate, copper isopropoxide, copper oxalate, copper oxychloride, copper nitrates, and copper chlorides. Examples of the ruthenium metal salt include, for example, a halide such as ruthenium bromide, ruthenium chloride, ruthenium iodide, an oxyhalide such as Ru_2OCl_4 , Ru_2OCl_5 and Ru_2OCl_6 , a halogeno complex such as $[\text{RuCl}_2(\text{H}_2\text{O})_4]\text{Cl}$, an ammine complex such as $[\text{Ru}(\text{NH}_3)_5\text{H}_2\text{O}]\text{Cl}_2$, $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$, $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_2$ and $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$, a carbonyl complex such as $\text{Ru}(\text{CO})_5$ and $\text{Ru}_3(\text{CO})_{12}$, a carboxylate complex such as $[\text{Ru}_3\text{O}(\text{OCOCH}_3)_6(\text{H}_2\text{O})_3]$, ruthenium nitrosylchloride, and $[\text{Ru}_2(\text{OCOR})_4]\text{Cl}$ (R=alkyl group having 1 to 3 carbon atoms), a nitrosyl complex such as $[\text{Ru}(\text{NH}_3)_5(\text{NO})]\text{Cl}_3$, $[\text{Ru}(\text{OH})(\text{NH}_3)_4(\text{NO})](\text{NO}_3)_2$ and $[\text{Ru}(\text{NO})](\text{NO}_3)_3$, an amine complex, an acetylacetonate complex, and ammonium salt such as $(\text{NH}_4)_2\text{RuCl}_6$.

Examples of the tellurium salt or compound include, for example, a halide such as TeF_6 , TeBr_4 , TeCl_4 and TeI_4 , an oxyhalide, oxide such as TeO , TeO_2 and TeO_3 , an alkoxide such as $\text{Te}(\text{OC}_2\text{H}_5)_4$, ammonium tellurate, a tellurate such as H_2TeO_3 , H_6TeO_6 , Na_2TeO_3 and Na_2TeO_4 , preferably halide and oxide, more preferably oxide, still more preferably TeO_2 .

Examples of the manganese metal salt include manganese carbonate, manganese nitrate, manganese sulfate, manganese bromide, manganese chloride, manganese iodide, manganese

perchlorate, manganese acetate, and manganese acetylacetonate.

Examples of the bismuth metal salt include bismuth carbonate, bismuth nitrate, bismuth sulfate, bismuth bromide, bismuth chloride, bismuth iodide, bismuth oxychloride and
5 bismuth acetate.

Examples of the rhenium metal salt such as rhenium carbonyl, rhenium chloride, rhenium pentacarbonyl bromide, and rhenium pentacarbonyl chloride.

Examples of the chromium metal salt such as chromium
10 nitrate, chromium bromide, chromium chloride, chromium perchlorate, chromium sulfate, chromium acetate, and chromium acetylacetonate.

Examples of the iron metal salt such as $\text{FeO}(\text{OH})$, $\text{Fe}(\text{NO}_3)_3$, FeSO_4 , $\text{Fe}_2(\text{SO}_4)_3$, FeC_2O_4 , FeI_2 , FeBr_2 , FeBr_3 , FeCl_2 , FeCl_3 ,
15 $\text{Fe}(\text{ClO}_4)_2$, $\text{Fe}(\text{ClO}_4)_3$, $\text{Fe}(\text{OC}_2\text{H}_5)_3$ and $\text{C}_4\text{H}_6\text{FeO}_4$.

Examples of the molybdenum metal salt such as MoCl_3 , MoCl_5 , MoF_6 , $\text{Mo}(\text{CO})_6$ and $(\text{NH}_4)_2\text{MoO}_4$.

Examples of the tungsten metal salt such as tungsten chloride, tungsten dichloride, tungsten dioxide, and tungsten
20 ethoxide.

Examples of the selenium metal salt such as SeOCl_2 , HeSeO_3 , Se_2Cl_2 and SeCl_4 .

Examples of the antimony metal salt such as antimony bromide, antimony chloride, antimony iodide, antimony ethoxide,
25 and antimony acetate.

Examples of the vanadium metal salt such as VCl_3 , VF_3 , VF_4 , VBr_3 , VOSO_4 , VOCl_3 , VOC_2O_4 and $\text{V}(\text{CH}_3\text{COCHCOCH}_3)_3$.

Examples of the nickel metal salt such as nickel sulfate, nickel nitrate, nickel bromide, nickel chloride, nickel iodide,
30 nickel perchlorate, nickel carbonate, nickel oxalate, and nickel hydroxide.

Examples of the cobalt metal salt such as cobalt sulfate, cobalt nitrate, cobalt bromide, cobalt chloride, cobalt iodide, cobalt perchlorate, cobalt acetylacetonate, cobalt acetate, cobalt carbonate, cobalt carbonyl, and cobalt hydroxide.

5 Examples of the tin metal salt such as tin sulfate, tin bromide, tin chloride, tin iodide, tin acetylacetonate, tin acetate, tin methoxide, tin butoxide, tin ethoxide, tin oxalate and tin tartrate.

10 Examples of the niobium metal salt include NbCl_5 , F_5Nb , NbI_5 and $\text{Nb}(\text{OC}_2\text{H}_5)_5$.

Examples of the germanium metal salt such as germanium bromide, germanium chloride, germanium iodide, germanium isopropoxide, germanium ethoxide, and germanium methoxide.

15 Examples of the thallium metal salt such as thallium sulfate, thallium nitrate, thallium bromide, thallium chloride, thallium iodide, thallium acetate, thallium carbonate, and thallium oxalate.

20 Examples of the indium metal salt include halides such as InBr , InBr_3 , InCl , InCl_3 , InI , InI_3 , InF_3 , $\text{In}(\text{OH})_3$, $\text{In}(\text{OCH}(\text{CH}_3)_2)_3$, $\text{In}(\text{NO}_3)_3$, $\text{In}(\text{ClO}_4)_3$, $\text{In}_2(\text{SO}_4)_3$, and $\text{In}(\text{OOCCH}_3)_3$.

Examples of the iridium metal salt includes IrBr_3 , IrBr_4 , IrCl_3 , IrCl_4 and IrI_4 .

25 Examples of the lanthanum metal salt include $\text{La}(\text{NO}_3)_3$, $\text{La}(\text{OH})_3$, $\text{La}_2(\text{CO}_3)_3$, $\text{La}_2(\text{SO}_4)_3$, LaBr_3 , LaCl_3 , LaF_3 , LaI_3 , $\text{La}(\text{ClO}_4)_3$, $\text{La}_2(\text{C}_2\text{O}_4)_3$, $\text{La}(\text{OC}_3\text{H}_7)_3$ and $\text{La}(\text{C}_2\text{H}_5\text{O})_3$,

Examples of the cerium metal salt include $\text{Ce}(\text{NO}_3)_3$, $\text{Ce}_2(\text{CO}_3)_3$, $\text{Ce}(\text{SO}_4)_2$, $\text{Ce}_2(\text{SO}_4)_3$, CeBr , CeCl_3 , CeF_3 , CeI_2 , $\text{Ce}(\text{ClO}_4)_3$, $(\text{CH}_3\text{COO})_3\text{Ce}$ and $\text{Ce}_3(\text{C}_2\text{O}_4)_3$.

30 Examples of the osmium metal salts include osmium halides such as osmium chloride.

If the solvent contains an alkaline metal or alkaline earth metal ion, it can be prepared by adding an alkaline metal or

alkaline earth metal salt to a solvent.

The alkaline metal or alkaline earth metal salt for the solution may be the same as or different from the alkaline metal component or the alkaline earth metal component. Examples of the alkaline metal salt and the 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 alkaline metal or alkaline earth metal component such as NaCl and the halogen component such as halides and oxyhalides of Cu or Ru. 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 composition as prepared by the impregnation is usually dried, and the drying method thereof is not limited. The
5 composition as prepared by the impregnation is preferably dried at a temperature of 40°C to 200°C before calcining the composition. Drying may be performed under an atmosphere of oxygen containing gas such as air or also under an inert gas atmosphere (for example, Ar, N₂, He) at standard pressure or reduced pressure. A drying
10 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
15 gas atmosphere containing oxygen. Examples of such a gas include air, an oxygen gas, 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
20 depending on the kind of the gases and the compositions, however, a too high temperature may cause agglomeration of ruthenium oxide and copper oxide. Accordingly, the calcination temperature is typically 200°C to 800°C, preferably 400°C to 600°C. The calcining time is preferably in the range from 0.5 hour to 24
25 hours.

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,
30 tableting. The calcination is normally performed after shaping into the desired structures, but it can also be performed before shaping them.

In the first step, the catalyst is contacted with water.

The catalyst is preferably contacted with water and an alkaline metal compound or an alkaline earth metal compound. The catalyst is also preferably contacted with water and an inorganic acid.

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

The alkaline metal compound or alkaline earth metal compound is preferably an alkaline metal compound, more preferably a sodium-containing compound or a potassium-containing compound, still more preferably a sodium-containing compound.

Examples of the alkaline metal compound and the alkaline earth metal compound 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. Among them, preferred are alkaline metal halides and alkaline metal nitrates, and more preferred are NaNO_3 and NaCl .

Examples of the inorganic acid include hydrogen chloride,
5 hydrogen bromide, hydrogen fluoride, hydrogen iodide, sulfurous acid, sulfuric acid, phosphorous acid, phosphoric acid, borous acid, boric acid, nitrous acid and nitric acid. Among them, preferred are hydrogen chloride, sulfuric acid, phosphoric acid, boric acid and nitric acid, and more preferred is hydrogen
10 chloride.

The amount of water used is not limited, and it is preferably 0.01 to 10000 parts by weight relative to 1 part of catalyst, more preferably 0.1 to 2000 parts by weight, and still more preferably 0.5 to 100 parts by weight relative to 1 part
15 of catalyst.

The alkaline metal or alkaline earth metal/copper molar ratio in the catalyst is preferably 0.001/1 to 50/1 based on their atoms. When the alkaline metal or alkaline earth metal/copper molar ratio falls within such a range, the
20 selectivity of the olefin oxide can be further improved. The lower limit of the alkaline metal or alkaline earth metal/copper molar ratio is more preferably 0.01/1, and still more preferably 0.1/1. The upper limit of the alkaline metal or alkaline earth metal/copper molar ratio is more preferably 10/1, and still more
25 preferably 5/1.

The inorganic acid/copper molar ratio is usually 0.01 to 100, more preferably 0.05 to 90, and still more preferably 0.1 to 80.

30 The contacting is usually carried out at a temperature from 0°C to 120°C , and preferably from 5°C to 100°C .

The contacting time is not limited, and is usually 1 minute to 48 hours, and preferably 5 minutes to 24 hours.

The catalyst obtained by contacting is preferably dried to remove water. The mixture obtained by contacting may be dried as it is or may be dried after filtration. Herein, when the filtration is carried out, the mixture obtained after the filtration can be washed with water, or both of water and inorganic acid.

The drying method is not limited. The mixture obtained by contacting is preferably dried at a temperature of 15°C to 200°C before calcining the composition. Drying may be performed under an atmosphere of oxygen containing gas such as air or also under an inert gas atmosphere (for example, Ar, N₂, He) at standard pressure or reduced pressure. A drying time is preferably in the range from 0.5 to 24 hours. The catalyst obtained can be calcined at a temperature from 200°C to 800°C, and preferably from 400°C to 600°C after contacting. The calcining time is usually 10 minutes to 48 hours, preferably 20 minutes to 24 hours, more preferably 30 minutes to 20 hours.

The method of calcining the catalyst is not limited, and the calcination of the catalyst is preferably performed under a gas atmosphere containing oxygen. Examples of such a gas include air, an oxygen gas, 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.

The second step is a step of reacting an olefin with oxygen in the presence of the catalyst obtained in the first step.

The olefin may have a linear or branched structure. The

olefin usually contains 2 to 10 carbon atoms, and preferably contains 2 to 8 carbon atoms. Examples of the olefin include ethylene, propylene, butene, pentene, hexene, heptene, octene, and butadiene, ethylene, propylene and butane are preferable, and propylene is more preferable.

The reaction is generally performed in the gas phase. In the reaction, the olefin and oxygen may be fed in the form of a gas, respectively. 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, 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 kind of catalyst, the reaction temperature or the like. The amount of oxygen is typically 0.01 mole to 100 mole, and preferably 0.03 mole to 30 mole, and more preferably 0.05 mole to 10 mole, and especially preferably 0.25 mole to 10 mole, with respect to 1 mol of the olefin.

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

The reaction is usually 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 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 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 the increased pressure.

The reactor type is not limited. Examples of the reactor type 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 reactor can be used. If the number of reactors is large, small reactors as for example microreactors, can be used, which can have multiple channels. Adiabatic type or heat exchange type may also be used.

In the second step, the olefin oxide can be produced. The olefin oxide may have a linear or branched structure. The olefin oxide usually contains 2 to 10 carbon atoms, and preferably contains 2 to 8 carbon atoms. Examples of the olefin oxides include ethylene oxide, propylene oxide, butene oxide, pentene oxide, hexene oxide, heptene oxide, octene oxide, and 3,4-epoxy-1-butene, and ethylene oxide, propylene oxide and butene oxide are preferable, and propylene oxide is more preferable.

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

The catalyst used in the above-mentioned reaction may be

used in the above-mentioned first step.

EXAMPLES

In Examples 1 and 2 and Comparative Examples 1 and 2, each measurement 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 an ice bath. The two methanol solutions were mixed together and added to anisole as an external standard, and then analyzed with two FID-GCs equipped with different columns, PoraBOND U (25 m) and PoraBOND Q (25 m).

The detected products were propylene oxide (PO), acetone (AT), CO₂, CO, propanal (PaL) and acrolein (AC).

Propylene selectivities (S_{PO}) were 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 catalyst.

Example 1

Amorphous silica powder (3.9 g; SiO₂, Japan Aerosil, 380 m²/g) was added to an aqueous solution mixture containing 0.43 g of (NH₄)₂RuCl₆ (Alfa), 0.60 g of Cu(NO₃)₂ (Wako), 0.20 g of NaCl (Wako), 0.05 g of TeO₂ (Wako) and 40g of H₂O. The obtained mixture was stirred for 24 hours in air, at room temperature. The resulting material was then heated at 100°C until dried, and calcined at 500°C for 12 hours in air to obtain the metal oxide composition having the following composition.

The molar ratio of Ru/Cu/Na/Te: 0.5/1/1.4/0.1

The total amount of Ru, Cu, Na and Te: 10.4 parts by weight relative to 100 parts by weight of SiO₂.

Then, 1.0 g of the metal oxide composition was contacted with 10 g of H₂O, and the resultant mixture was filtrated and washed with 2 L of H₂O. The solid obtained was dried at room temperature for 24h and calcined at 500°C for 2h to obtain the catalyst.

The catalyst was evaluated by using a fixed-bed reactor. Filling a 0.6 inch OD reaction tube made of quartz glass with 1 mL of the prepared catalyst, the reaction tube was supplied with 7.5 mL/min. of propylene, 15 mL/min. of the air, and 16.5 mL/min. of a nitrogen gas to carry out the reaction, at the reaction temperature of 250°C under atmospheric pressure. The feed ratio of propylene to oxygen was 2.4 (molar ratio, propylene/oxygen). Gas hourly space velocity (GHSV) =2340 (h⁻¹). The result of Example 1 is shown in Table 1.

Comparative Example 1

Amorphous silica powder (3.9 g; SiO₂, Japan Aerosil, 380 m²/g) was added to an aqueous solution mixture containing 0.43 g of (NH₄)₂RuCl₆ (Alfa), 0.60 g of Cu(NO₃)₂ (Wako), 0.20 g of NaCl (Wako), 0.05g of TeO₂ (Wako) and 40g of H₂O. The obtained mixture was stirred for 24 hours in air, at room temperature. The resulting material was then heated at 100°C until dried, and calcined at 500°C for 12 hours in air to obtain the metal oxide composition having the following composition.

The molar ratio of Ru/Cu/Na/Te: 0.5/1/1.4/0.1

The total amount of Ru, Cu, Na and Te: 10.4 parts by weight relative to 100 parts by weight of SiO₂.

The catalyst was evaluated in the same manners as Example 1 and the result of Comparative Example 1 is shown in Table 1.

Table 1

	PO selectivity (%)
Example 1	66
Comparative Example 1	61

Example 2

Amorphous silica powder (1.9 g; SiO₂, Japan Aerosil, 380 m²/g) was added to an aqueous solution mixture containing 0.55 g of (NH₄)₂RuCl₆ (Alfa), 0.30 g of Cu(NO₃)₂ (Wako) and 40 g of H₂O. The obtained mixture was stirred for 24 hours in air at 25°C.

The resulting material was then heated at 100°C until dried, and calcined at 500°C for 12 hours in air to obtain the metal oxide composition.

Two point two (2.2) g of the metal oxide composition and 0.1 g of NaCl (Wako) was added to 5 g of H₂O and mixed them at 25°C for 24 hours. Then, the obtained mixture was heated at 100°C until dried followed by calcining at 500°C for 12 hours in air to obtain the catalyst having the following composition.

The molar ratio of Ru/Cu/Na: 1.3/1/1.4

The total amount of Ru, Cu, Na: 14.3 parts by weight relative to 100 parts by weight of SiO₂.

The catalyst was evaluated in the same manners as Example 1 except the reaction temperature of 270°C and the result is shown in Table 2.

Comparative Example 2

Amorphous silica powder (1.9 g; SiO₂, Japan Aerosil, 380 m²/g) was added to an aqueous solution mixture containing 0.55 g of (NH₄)₂RuCl₆ (Alfa), 0.30 g of Cu(NO₃)₂ (Wako), 0.10 g of NaCl (Wako) and 40g of H₂O. The obtained mixture was stirred for 24 hours in air, at 25°C.

The resulting material was then heated at 100°C until dried, and calcined at 500°C for 12 hours in air to obtain the catalyst having the following composition.

The molar ratio of Ru/Cu/Na: 1.3/1/1.4.

The total amount of Ru, Cu and Na: 14.3 parts by weight relative to 100 parts by weight of SiO₂.

The catalyst was evaluated in the same manners as Example 1 except the reaction temperature of 270°C and the result is shown in Table 2.

Table 2

	PO selectivity (%)
Example 2	16
Comparative Example 2	4

Example 3

Amorphous silica powder (44mg; SiO₂, Alfa, 85-115 m²/g) was added to an aqueous solution mixture containing 3.6 mg of (NH₄)₂RuCl₆ (Aldrich), 1.8 mg of Cu(NO₃)₂ (Alfa), 0.90 mg of NaCl (Alfa) and 950 mg of H₂O. The obtained mixture was stirred for 1 hour in air, at room temperature.

The resulting material was then heated at 165°C until dried, and calcined at 480°C for 6 hours in air to obtain the metal oxide composition having the following composition.

The molar ratio of Ru/Cu/Na: 1.3/1/1.4.

The total amount of Ru, Cu and Na: 14.3 parts by weight relative to 100 parts by weight of SiO₂.

Next, 10 mg of the metal oxide composition was added to 400 µL of 1.0 M HCl (Ru/Cu/Na/HCl=1.3/1/1.4/71 molar ratio), and stirred at room temperature for 1 hour. The slurry was dried at 165°C, and calcined at 480°C for 2 hours.

The catalyst was evaluated by using a micro-reactor. The catalyst (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 at a gas hourly space velocity (GSHV) of $20,000\ h^{-1}$ with a mass flow controller (MKS, Andover, MA), at a reactor temperature of $250^\circ C$. Gas sampling was accomplished by withdrawing reactor exit gases using the passivated 200 micron ID capillary sampling probe. The data analysis 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), CO_2 , CO, and propanal (PaL) and acrolein (AC).

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 catalyst.

The result is shown in Table 3.

Comparative Example 3

Amorphous silica powder (44 mg; SiO_2 , Alfa, 85-115 m^2/g) was added to an aqueous solution mixture containing 3.6 mg of $(NH_4)_2RuCl_6$ (Aldrich), 1.8 mg of $Cu(NO_3)_2$ (Alfa), 0.90 mg of NaCl (Alfa) and 950 mg of H_2O . The obtained mixture was stirred for 1 hour in air, at room temperature.

The resulting material was then heated at $100^\circ C$ until dried, and calcined at $480^\circ C$ for 6 hours in air to obtain the metal oxide composition having the following composition.

The molar ratio of Ru/Cu/Na: 1.3/1/1.4.

The total amount of Ru, Cu and Na: 14.3 parts by weight relative to 100 parts by weight of SiO₂.

The catalyst was evaluated in the same manner as Example 3, and the result is shown in Table 3.

Table 3

	PO selectivity (%)
Example 3	63
Comparative Example 3	45

Example 4

The catalyst prepared in Comparative Example 3 was evaluated for 12 hours in the same condition as Example 3. Then, 10 mg of the used catalyst in the above-mentioned evaluation was added to 400 μ L of 1.0 M HCl (Ru/Cu/Na/HCl=1.3/1/1.4/71 molar ratio), and stirred at room temperature for 1 hour. The slurry was dried at 165°C, and calcined at 480°C for 2 hours.

The catalyst was evaluated in the same manner as Example 3, and the result is shown in Table 4.

Table 4

	PO selectivity (%)
Example 4	64

WHAT WE CLAIM ARE:

1. A process for producing an olefin oxide comprising:
a first step of contacting a catalyst comprising a copper oxide, and one or both of ruthenium oxide and one metal oxide
5 other than a copper oxide and a ruthenium oxide, with water and
a second step of reacting an olefin with oxygen in the presence of the catalyst obtained in the first step.
2. The process according to claim 1, wherein the
catalyst is contacted with water and an alkaline metal compound
10 or an alkaline earth metal compound.
3. The process according to claim 1, wherein the catalyst is contacted with water and an inorganic acid.
4. The process according to claim 1, wherein the first
step further comprises calcining the catalyst at a temperature
15 from 350°C to 650°C after contacting.
5. The process according to claim 1, wherein the catalyst comprises a copper oxide and a ruthenium oxide.
6. The process according to claim 1, wherein the catalyst further comprises an alkaline metal component or an
20 alkaline earth metal component.
7. The process according to claim 1, wherein the catalyst further comprises a halogen component.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 12/59945

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - B01J 23/00 (2012.01)

USPC - 502/318

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)
USPC: 502/318

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 practicable, search terms used)
Electronic Database Searched PUBWEST (PGPB,USPT,USOC,EPAB,JPAB), Totalpatent; Google. Search Terms Used olefin oxide, ethylene oxide, copper oxide, CuO, ruthenium oxide, RuO, metal oxide

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2011/0152547 A1 (Senkan et al.) 23 June 2011 (23.06.2011) entire document especially	1-7
A	US 2011/0152547 A1 (Senkan et al.) 23 June 2011 (23.06.2011) entire document	1-7
A	US 7,507,845 B1 (Gueckel) 24 March 2009 (24.03.2009) entire document	1-7
A	US 7,348,444 B2 (Evans et al.) 25 March 2008 (25.03.2008) entire document	1-7

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

* Special categories of cited documents:

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"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

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

"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

21 November 2012 (12.11.2012)

Date of mailing of the international search report

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