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(54) Title: PROCESS FOR PRODUCING A NOBLE METAL CATALYST SUPPORTED ON CARBON AND ITS USE WITH A TITANOSILICATE FOR THE OXIDATION OF OLEFINS TO ALKYLENE OXIDES

(57) Abstract: The present invention relates to a process for producing a noble metal catalyst, comprising the steps of: 1) mixing a carbon material with a resin in a solvent to prepare a mixture; 2) taking out a carrier from the mixture prepared in the step 1; and 3) supporting a noble metal on the carrier obtained in the step 2. According to the present process, a catalyst capable of producing an alkylene oxide in a high yield can be provided.



DESCRIPTION

PROCESS FOR PRODUCING A NOBLE METAL CATALYST SUPPORTED ON CARBON AND ITS USE
WITH A TITANOSILICATE FOR THE OXIDATION OF OLEFINS TO ALKYLENE OXIDES

5 TECHNICAL FIELD

[0001]

The present application is filed, claiming the priority
based on the Japanese Patent Application No. 2011-078749 (filed
on March 31, 2011), the entire content of which is incorporated
10 herein by reference.

The present invention relates to a process for producing
a noble metal catalyst. The present invention also relates to
a process for producing an alkylene oxide in which the noble
metal catalyst is used.

15

BACKGROUND ART

[0002]

A noble metal catalyst and a titanosilicate catalyst are
used in a process in which hydrogen, oxygen and propylene are
20 reacted to produce propylene oxide. As such a noble metal
catalyst, a catalyst obtained by supporting palladium on
activated carbon, and then calcining the resultant, is known
from JP 2010-168358 A, for example.

25 SUMMARY OF INVENTION

PROBLEM TO BE SOLVED BY THE INVENTION

[0003]

There has been a demand for a catalyst capable of producing an alkylene oxide in a high yield.

5

MEANS FOR SOLVING THE PROBLEM

[0004]

The present invention provides the followings:

[1] A process for producing a noble metal catalyst, comprising the steps of:

10

1) mixing a carbon material with a resin in a solvent to prepare a mixture;

2) taking out a carrier from the mixture prepared in the step 1; and

15

3) supporting a noble metal on the carrier obtained in the step 2.

[2] The process according to the above item [1], wherein the resin is at least one resin selected from the group consisting of polyvinyl alcohol, polyvinyl acetate,

20

polymethylmethacrylate and polystyrene.

[3] The process according to the above item [1] or [2], wherein the noble metal is at least one metal selected from the group consisting of palladium, platinum, ruthenium, rhodium, iridium, osmium and gold.

25

[4] A process for producing an alkylene oxide, comprising

reacting hydrogen, oxygen and an olefin in the presence of a titanosilicate catalyst and a noble metal catalyst produced by the process according to any one of the above items [1] to [3].

[5] The process according to the above item [4], wherein the
5 olefin is propylene.

[6] The process according to the above item [4] or [5], wherein the titanosilicate catalyst is at least one catalyst selected from the group consisting of a titanosilicate having an MWW structure and a precursor thereof.

10

EFFECT OF THE INVENTION

[0005]

According to the present invention, a catalyst capable of producing an alkylene oxide in a high yield can be provided.

15

MODES FOR CARRYING OUT THE INVENTION

[0006]

The process of the present invention is a process for producing a noble metal catalyst, comprising the steps of:

20 1) mixing a carbon material with a resin in a solvent to prepare a mixture;

2) taking out a carrier from the mixture prepared in the step 1; and

3) supporting a noble metal on the carrier obtained in the step

25 2.

The noble metal catalyst produced by the present process is capable of generating hydrogen peroxide from oxygen and hydrogen. In addition, by using the noble metal catalyst in combination with a titanosilicate catalyst, the noble metal catalyst becomes useful as a catalyst to be used in the production of an alkylene oxide (hereinafter, the production of an alkylene oxide is sometimes referred to as "the present production").

[0007]

10 The step 1 is a step in which a carbon material and a resin are mixed in a solvent to prepare a mixture.

[0008]

The carbon material is a material which consists mainly of carbon. Examples of the carbon material include activated carbon, carbon black, graphite and carbon nanotube. Among them, activated carbon is preferable because it has a larger surface area.

The raw materials of the activated carbon and the activation method thereof are not particularly limited, and the activated carbon having a large pore volume is preferable. Examples of the raw materials of the activated carbon include wood, sawdust, palm shell, coal and petroleum materials. Activated carbon obtained by a method in which charcoal obtained from the aforementioned raw materials is activated by being subjected to a high-temperature treatment using water vapor,

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carbon dioxide, air or the like, or a method in which charcoal is activated by using chemicals such as zinc chloride, is preferable. Among them, the activated carbon obtained by the latter is more preferable. The activated carbons which are
5 activated by the aforementioned methods are preferable because their pore volume and average pore size become larger. The form of the activated carbon is not particularly limited, and powdery activated carbon, granular activated carbon, crushed activated carbon, fibrous activated carbon, honeycomb activated carbon
10 or the like may be used.

[0009]

The resin used in the process of the present invention is not particularly limited and any known resin may be used. It is preferable to use a resin soluble in a solvent used in
15 the step 1.

Examples of the resin include polyethylene, polypropylene, polybutadiene, polystyrene, polymethylmethacrylate, polyacrylonitrile, polyacrylic acid, polyethylene glycol, polyvinylpyrrolidone, polyurea,
20 polyester, polyurethane, polyimide, polyethyleneimine, polyvinyl alcohol, polyvinyl chloride, polyvinyl acetate, polyvinylidene fluoride, polycarbonate, Nylon 6, Nylon 66 and a silicone resin. Among them, polyvinyl alcohol, polyvinyl acetate, polymethylmethacrylate and polystyrene are
25 preferable, and polymethylmethacrylate and polystyrene are

more preferable. These resins are readily available. When the noble metal catalyst produced using such a resin is used in the present production, yield of an alkylene oxide tends to increase. In particular, it is preferable to use a hydrophobic resin in the present process. This is because yield of an alkylene oxide tends to further increase and generation of an alkane as a by-product tends to reduce.

[0010]

As a solvent used in the process of the present invention, a solvent capable of dissolving the aforementioned resin is preferable. The solvent can be properly selected depending on the kind of a resin to be used. Examples of such a solvent include water, alcohol solvents, ketone solvents, nitrile solvents, ether solvents, aliphatic hydrocarbon solvents, aromatic hydrocarbon solvents, halogenated hydrocarbon solvents, ester solvents, glycol solvents, and amide solvents.

[0011]

Examples of the alcohol solvent include methanol, ethanol, isopropanol, tert-butanol, 1-hexanol, cyclohexanol, and 2-ethylhexanol.

Examples of the ketone solvent include acetone, 2-butanone, 2-heptanone, and cyclohexanone.

Examples of the nitrile solvent include acetonitrile and benzonitrile.

Examples of the ether solvent include diethyl ether,

tetrahydrofuran, and anisole.

Examples of the aliphatic hydrocarbon solvent include pentane, hexane, heptane, heptane, and cyclohexane.

Examples of the aromatic hydrocarbon solvent include
5 benzene, toluene, and xylene.

Examples of the halogenated hydrocarbon solvent include dichloromethane, chloroform, carbon tetrachloride, and dichloroethane.

Examples of the ester solvent include ethyl acetate,
10 propyl acetate, butyl acetate, ethyl propionate, ethyl lactate, and ethyl pyruvate.

Examples of the glycol solvent include ethylene glycol, diethylene glycol, and propylene glycol.

Examples of the amide solvent include formamide,
15 acetamide, N,N-dimethylformamide, N,N-dimethylacetamide.

These solvents may be used alone or as a mixture of two or more kinds thereof.

[0012]

In the step 1, a carbon material and a resin are mixed
20 in a solvent to prepare a mixture.

In the mixture, the amount of the carbon material in the mixture is preferably from 1 to 10,000 parts by mass, more preferably from 2 to 1,000 parts by mass, based on one part by mass of the resin. The amount of the resin in the mixture is
25 preferably from 0.001 to 50% by mass, more preferably from 0.01

to 20% by mass, based on the total amount of the resin and the solvent.

[0013]

The temperature for mixing the carbon material with the resin is preferably from 10°C to 200°C, more preferably from 20°C to 150°C. The time of mixing is preferably from 10 minutes to 30 hours, more preferably from 1 hour to 24 hours. The order of mixing is not particularly limited, but it is preferable that the resin is dissolved in the solvent and then the carbon material is added thereto. The mixing may be carried out under a nitrogen atmosphere or an air.

[0014]

The step 2 is a step in which a carrier is taken out from the mixture prepared in the step 1.

Preferably, the mixture prepared in the step 1 is cooled (i.e., a cooling process is employed). Cooling the mixture tends to increase an adhesion of the carbon material to the resin, even where an affinity between the carbon material and the resin is low.

When the mixture prepared in the step 1 is cooled, the mixture is preferably cooled to a temperature of from 0°C to 50°C, more preferably from 0°C to 30°C. In addition, the mixture is preferably cooled to a temperature which is lower by preferably 10°C to 200°C, more preferably 20°C to 150°C, and still more preferably 30°C to 120°C than the mixing temperature of

the step 1. The time of cooling the mixture is preferably from 30 minutes to 36 hours, more preferably from 1 hour to 24 hours. The cooling may be carried out under a nitrogen atmosphere or an air.

5 [0015]

In the step 2, a carrier can be taken out from the mixture by filtration, for example.

The obtained carrier may be dried as necessary. When the carrier is dried, the temperature is preferably from 30°C to 10 200°C. It is preferable to dry the mixture under a reduced pressure or under an atmosphere of an inert gas.

[0016]

The step 3 is a step in which a noble metal is supported on the carrier obtained in the step 2 (hereinafter, the carrier 15 obtained in the step 2 is sometimes referred to as "carrier (A)").

[0017]

As the noble metal, for example, palladium, platinum, ruthenium, osmium, rhodium, iridium and gold may be used. The 20 noble metal may be used alone, or as an alloy or mixture of two or more kinds thereof. In particular, the noble metal is preferably palladium, platinum, gold and an alloy or mixture thereof, more preferably palladium, an alloy or mixture of palladium and gold, or an alloy or mixture of palladium and 25 platinum, still more preferably palladium. When the noble

metal catalyst produced using such a noble metal is used in the present production, generation of hydrogen peroxide in the system tends to increase and yield of an alkylene oxide tends to increase in the present production.

5 [0018]

Examples of the method for supporting a noble metal on the carrier (A) include a method of supporting a noble metal compound on the carrier (A) and then reducing the noble metal, and a method of mixing a noble metal colloid and the carrier
10 (A).

[0019]

In the method of supporting a noble metal compound on the carrier (A) and then reducing the noble metal compound, for example, a noble metal compound is firstly supported on the
15 carrier (A) by an impregnation method, and then, the noble metal compound is reduced to form zero valent noble metal.

Examples of the noble metal compound include noble metal chlorides. When palladium is used as the noble metal compound, examples of the palladium compound include tetravalent
20 palladium compounds such as sodium hexachloropalladate (IV) tetrahydrate and potassium hexachloropalladate (IV); and divalent palladium compounds such as palladium (II) chloride, palladium (II) bromide, palladium (II) acetate, palladium (II) acetylacetonate, dichlorobis(benzonitrile)palladium (II),
25 dichlorobis(acetonitrile)palladium (II),

dichloro(bis(diphenylphosphino)ethane)palladium (II),
dichlorobis(triphenylphosphine)palladium (II),
dichlorotetraamminepalladium (II),
dibromotetraamminepalladium (II),
5 dichloro(cycloocta-1,5-diene)palladium (II), and palladium
(II) trifluoroacetate.

[0020]

The impregnation method may be performed, for example,
by impregnating a solution of the noble metal compound (e.g.,
10 an aqueous solution of the aforementioned noble metal compound)
with the carrier (A) at room temperature for 10 minutes to 30
hours.

[0021]

A noble metal catalyst can be obtained by reducing the
15 noble metal compound which the carrier (A) supporting the noble
metal contains. For example, the noble metal compound may be
reduced by a method of reduction using a reductant in a liquid
phase or a gas phase. As a gas-phase reduction, a method in
which hydrogen is used as the reductant and the reduction is
20 carried out at a temperature of from 0°C to 500°C may be used.

When a noble metal compound which generates ammonia gas
at the time of thermal decomposition under an atmosphere of an
inert gas is used as the noble metal compound, the noble metal
compound which has been supported on a carrier may be subjected
25 to thermal treatment under an atmosphere of an inert gas. In

this case, ammonia gas generated from the noble metal compound serves as a reductant. The temperature of the thermal treatment may vary depending on the kind of the noble metal compound used, and the like. When dichlorotetraamminepalladium (II) is used
5 as the noble metal compound, the temperature is preferably from 100°C to 500°C, more preferably from 200°C to 350°C.

[0022]

When the reduction is performed in a liquid phase (liquid-phase reduction), hydrogen, hydrazine monohydrate,
10 formaldehyde and sodium borohydride may be used as a reductant. When hydrazine monohydrate or formaldehyde is used, it may be used in combination with an alkali. Conditions of the liquid-phase reduction may be appropriately adjusted depending on the kind and amount of the noble metal compound, the carrier
15 and the reductant to be used.

[0023]

When the noble metal catalyst is prepared by a process in which a noble metal colloid and the carrier (A) are mixed, for example, the noble metal colloid and the carrier (A) are mixed
20 in a solvent, and then, the mixture is filtrated to obtain a solid. As the solvent, a dispersion media of the noble metal colloid may be used as it is.

Examples of the solvent used in mixing of the noble metal colloid and the carrier (A) include water, methanol, ethanol,
25 and acetonitrile. These solvents may be used alone or as a

mixture of two or more kinds thereof. Among them, a solvent comprising acetonitrile is preferable. When the noble metal catalyst obtained by mixing a noble metal colloid and the carrier (A) in the above-mentioned solvent is used in the present production, yield of an alkylene oxide tends to increase.

The temperature of mixing is not particularly limited, and it is preferably from 0°C to 100°C, more preferably from 15°C to 40°C. The time of mixing is not particularly limited, and it is preferably from 10 minutes to 30 hours, more preferably from 30 minutes to 18 hours.

As the noble metal colloid, a commercially available product may be used, and also, a noble metal colloid prepared by dispersing noble metal particles with a dispersant such as citric acid, polyvinyl alcohol, polyvinylpyrrolidone and sodium hexametaphosphate may be used.

[0024]

In the noble metal catalyst prepared by the present process, the content of the noble metal is preferably 0.01 to 20% by mass, more preferably 0.1 to 10% by mass, based on the mass of the carbon material supporting the noble metal.

[0025]

An alkylene oxide can be produced by reacting hydrogen, oxygen and an olefin in the presence of a titanosilicate catalyst and the noble metal catalyst prepared by the process

of the present invention.

[0026]

The titanosilicate catalyst is a catalyst which consists mainly of titanosilicate and has an ability of olefin
5 epoxidation.

Hereinafter, the titanosilicate of which the titanosilicate catalyst is composed will be described in detail.

[0027]

10 Titanosilicate is a generic name for a silicate having tetra-coordinated Ti (titanium atom), and has a porous configuration. The titanosilicate of which the titanosilicate catalyst is composed refers to a titanosilicate substantially having tetra-coordinated Ti, in which a maximum absorption peak
15 of an ultraviolet-visible absorption spectrum in a wavelength range of 200 nm to 400 nm appears in a wavelength range of 210 nm to 230 nm (see, for example, "Chemical Communications" 1026-1027, (2002), Figs. 2(d) and (e)). The ultraviolet-visible absorption spectrum can be measured by
20 using an ultraviolet-visible spectrophotometer equipped with a diffuse reflector in accordance with a diffuse reflection method.

[0028]

As the titanosilicate of which the titanosilicate
25 catalyst is composed, titanosilicate having fine pores of not

less than 10-membered oxygen ring is preferable, because such titanasilicate has a high olefin epoxidation ability. When the fine pores are too small, a contact between olefins which have entered into the fine pores and active points in the fine pores may be inhibited, or mass transfer of olefins in the fine pores may be restricted. The fine pore herein refers to a pore formed with a Si-O bond and/or a Ti-O bond. The fine pore may be in the state of a half cup called as a side pocket, and does not have to penetrate through the primary particle of

titanasilicate. The term "not less than 10-membered oxygen ring" means that the number of oxygen atoms is 10 or more in either (a) a cross-section of the narrowest part of the fine pore or (b) a ring structure at the fine pore entrance. The fact that a titanasilicate catalyst has fine pores of not less than 10-membered oxygen ring is generally confirmed by an analysis of an X-ray diffraction pattern. In addition, if the catalyst has a known structure, the structure can be easily confirmed by comparison of its X-ray diffraction pattern with the known one.

[0029]

Examples of the titanasilicate of which the titanasilicate catalyst is composed include titanosilicates [1] to [7] described below.

[1] Crystalline titanasilicate having fine pores with a 10-membered oxygen ring:

TS-1 having the MFI structure (for example, US 4,410,501),
TS-2 having the MEL structure (for example, Journal of Catalysis
130, 440-446, (1991)), Ti-ZSM-48 having the MRE structure (for
example, Zeolites 15, 164-170, (1995)), Ti-FER having the FER
5 structure (for example, Journal of Materials Chemistry 8,
1685-1686 (1998)), and the like, in terms of the IZA
(International Zeolite Association) structure code.

[0030]

[2] Crystalline titanosilicate having fine pores with a
10 12-membered oxygen ring:

Ti-Beta having a BEA structure (for example, Journal of
Catalysis 199, 41-47, (2001)), Ti-ZSM-12 having an MTW
structure (for example, Zeolites 15, 236-242, (1995)), Ti-MOR
having an MOR structure (for example, The Journal of Physical
15 Chemistry B 102, 9297-9303, (1998)), Ti-ITQ-7 having an ISV
structure (for example, Chemical Communications
761-762, (2000)), Ti-MCM-68 having an MSE structure (for example,
Chemical Communications 6224-6226, (2008)), Ti-MWW having an
MWW structure (for example, Chemistry Letters 774-775, (2000)),
20 and the like.

[0031]

[3] Crystalline titanosilicate having fine pores with a
14-membered oxygen ring:

Ti-UTD-1 having a DON structure (for example, Studies in
25 Surface Science and Catalysis 15, 519-525, (1995)), and the

like.

[4] Layered titanasilicate having fine pores with a 10-membered oxygen ring:

Ti-ITQ-6 (for example, Angewandte Chemie International Edition 39, 1499-1501, (2000)), and the like.

[5] Layered titanasilicate having fine pores with a 12-membered oxygen ring:

A Ti-MWW precursor (for example, EP-1731515-A1), Ti-YNU-1 (for example, Angewandte Chemie International Edition 43, 236-240, (2004)), Ti-MCM-36 (for example, Catalysis Letters 113, 160-164, (2007)), Ti-MCM-56 (for example, Microporous and Mesoporous Materials 113, 435-444, (2008)), and the like.

[0032]

[6] Mesoporous titanasilicate:

Ti-MCM-41 (for example, Microporous Materials 10, 259-271, (1997)), Ti-MCM-48 (for example, Chemical Communications 145-146, (1996)), Ti-SBA-15 (for example, Chemistry of Materials 14, 1657-1664, (2002)), and the like.

[7] Silylated titanasilicate:

Compounds obtained by silylating the titanosilicates [1] to [4] described above, such as silylated Ti-MWW.

[0033]

The term "12-membered oxygen ring" means a ring structure having 12 oxygen atoms in either region (a) or (b) mentioned in the description regarding "10-membered oxygen ring".

Likewise, the term "14-membered oxygen ring" means a ring structure having 14 oxygen atoms in either region (a) or (b) mentioned above.

[0034]

5 The titanosilicate may be a titanosilicate having a layered structure, such as a layered precursor of a crystalline titanosilicate, a titanosilicate in which spaces between layers in a crystalline titanosilicate are expanded. Whether a titanosilicate has a layered structure or not can be confirmed
10 by electron microscopy or measurement of an X-ray diffraction pattern. The layered precursor refers to a titanosilicate which forms a crystalline titanosilicate by a treatment such as dehydration condensation. It can be easily determined from the structure of a corresponding crystalline titanosilicate
15 that a layered titanosilicate has fine pores of not less than 12-membered oxygen ring.

 The Ti-MWW precursor refers to a titanosilicate having a layered structure, which forms a Ti-MWW by a dehydration-condensation. The dehydration-condensation may
20 be carried out by heating the Ti-MWW precursor usually at a temperature of greater than 200°C to 1000°C or less, preferably at a temperature within the range of 300°C to 650°C.

[0035]

 The titanosilicates of [1] to [5] and [7] have fine pores
25 with a pore size of 0.5 to 1.0 nm. The pore size refers to the

longest distance of in (a) a cross-section of the narrowest part of the fine pore and (b) a fine pore entrance. Preferably, the pore size refers to a diameter in the above-mentioned regions (a) and (b). The pore size can be determined by an analysis of an X-ray diffraction pattern.

[0036]

Among the aforementioned titanosilicates, a mesoporous titanosilicate which has regular mesofine pores is preferable. The regular mesofine pore refers to a structure in which mesopores are regularly and repeatedly arranged. When the titanosilicate is a mesoporous titanosilicate, the mesoporous titanosilicate which has mesofine pores having an average pore size of 2 nm to 10 nm is more preferable.

[0037]

Silylating of the titanosilicates can be carried out by a method in which the titanosilicate is brought into contact with a silylating agent or a method described in EP 1488853 A1. Examples of the silylating agent include 1,1,1,3,3,3-hexamethyl disilazane and trimethylchlorosilane.

[0038]

Among the aforementioned titanosilicates of [1] to [7], Ti-MWW and Ti-MWW precursor are preferably used, and Ti-MWW precursor is more preferably used as a titanosilicate of which the titanosilicate catalyst is composed. The silylated Ti-MWW or Ti-MWW precursor may be used for a titanosilicate catalyst.

The Ti-MWW or Ti-MWW precursor shaped by using a known method may be used for a titanosilicate catalyst.

[0039]

In the titanosilicate catalyst used in the present
5 production, the content of titanium atom is preferably from 0.001 to 0.1 mol, more preferably from 0.005 to 0.05 mol, based on one mol of silicon atoms contained.

[0040]

In the present production, the noble metal catalyst
10 obtained by the process of the present invention is preferably used in an amount of 0.01 to 100 parts by mass, more preferably 0.1 to 100 parts by mass, based on one part by mass of the titanosilicate catalyst used.

[0041]

15 The present production is preferably carried out in a solvent. As the solvent, water, an organic solvent and mixtures thereof are preferable. Examples of the organic solvent include alcohol solvents, ketone solvents, nitrile solvents, ether solvents, aliphatic hydrocarbon solvents, aromatic
20 hydrocarbon solvents, halogenated hydrocarbon solvents, ester solvents, glycol solvents and mixtures thereof. Among them, nitrile solvents are preferable.

[0042]

Examples of the nitrile solvent include linear or
25 branched saturated aliphatic nitriles and aromatic nitriles.

The specific examples of the nitrile solvent include acetonitrile, propionitrile, isobutyronitrile and benzonitrile. Acetonitrile is preferable.

The solvent is preferably a mixed solvent of water and nitrile. In the mixed solvent, a mass ratio of water and nitrile (water : nitrile) is preferably from 90 : 10 to 0.01 : 99.99, more preferably from 50 : 50 to 0.1 : 99.9, still more preferably 40 : 60 to 5 : 95.

[0043]

In the present production, oxygen may be a molecular oxygen such as an oxygen gas. The oxygen gas may be an oxygen gas produced by a pressure swing method or an oxygen gas having a high purity produced by cryogenic separation. Alternatively, air may be used as oxygen.

[0044]

In the present production, a hydrogen gas is usually used as hydrogen.

The oxygen gas and/or the hydrogen gas used in the present production may be diluted with an inert gas which does not obstruct the progress of the present production. Examples of the inert gas include nitrogen, argon, carbon dioxide, methane, ethane, and propane.

The amounts of the oxygen gas and the hydrogen gas supplied to the present production and the concentration of the inert gas used for diluting the gases may be appropriately

adjusted according to an amount of the olefin to be used, the scale of the reaction and the like.

The molar ratio of oxygen and hydrogen supplied to the reactor (oxygen : hydrogen) is, for example, preferably from 1 : 50 to 50 : 1, more preferably from 1 : 5 to 5 : 1.

[0045]

Examples of an olefin used in the present production include linear or branched olefins having 2 to 10 carbon atoms and cyclic olefins having 4 to 10 carbon atoms.

10 Examples of the linear or branched olefin having 2 to 10 carbon atoms include ethylene, propylene, butene, pentene, hexene, heptene, octene, nonene, decene, 2-butene, isobutene, 2-pentene, 3-pentene, 2-hexene, 3-hexene, 4-methyl-1-pentene, 2-heptene, 3-heptene, 2-octene, 3-octene, 2-nonene, 3-nonene,
15 2-decene, and 3-decene.

Examples of the cyclic olefin having 4 to 10 carbon atoms include cyclobutene, cyclopentene, cyclohexene, cycloheptene, cyclooctene, cyclononene, and cyclodecene.

A preferable olefin is a linear or branched olefin having 20 2 to 6 carbon atoms, and more preferable olefin is propylene.

[0046]

In the present production, the olefin is preferably used in an amount of 0.2 to 5 mol based on one mole of oxygen. When the present production is performed in the continuous manner,
25 the olefin is preferably used in an amount of 0.01 to 1000 g,

based on 1 kg of the solvent used in the present production.
[0047]

Examples of the reactor used in the present production include a flow-through fixed bed reactor and a flow-through
5 slurry complete mixing apparatus.

The reaction temperature of the present production is preferably from 0°C to 150°C, more preferably from 40°C to 90°C.

In the present production, the pressure is preferably 0.1 MPa to 20 MPa, more preferably 1 MPa to 10 MPa as a gauge pressure.

10 After completion of the present production, the alkylene oxide may be brought out by distillation to separate a substance from the liquid phase or gas phase taken out of the reactor.
[0048]

It is preferable to carry out the present production in
15 the presence of a polycyclic compound as an additive. It is preferable to use the polycyclic compound in the present production because generation of propane as a by-product tends to be suppressed and hydrogen efficiency tends to be improved. The hydrogen efficiency herein refers to a product amount of
20 propylene oxide relative to the amount of hydrogen consumed.

The specific examples of the polycyclic compound include anthracene, tetracene, 9-methylantracene, naphthalene, diphenyl ether, anthraquinone, 9,10-phenanthraquinone, benzoquinone, 2-ethylanthraquinone, as well as the compounds
25 described in JP 2009-23998 A and JP 2008-106030 A. Among them,

a condensed polycyclic aromatic compound such as anthracene, tetracene, 9-methylanthracene, naphthalene, anthraquinone, 9,10-phenanthraquinone and 2-ethylanthraquinone are preferable, and anthraquinone is more preferable.

5 [0049]

In the present production, the polycyclic compound is preferably used in an amount of 0.001 to 500 mmol, more preferably 0.01 to 50 mmol, based on 1 kg of the solvent used in the present production.

10 [0050]

In the present production, a salt with an ammonium ion, an alkylammonium ion or an alkylarylammonium ion (hereinafter, the salt is sometimes collectively referred to as "ammonium salt") may be used as an additive. When the ammonium salt is
15 used in the present production, the hydrogen efficiency tends to be improved.

Examples of the ammonium salt include ammonium salts of an inorganic acid, such as ammonium sulfate, ammonium hydrogen sulfate, ammonium hydrogen carbonate, ammonium phosphate,
20 ammonium hydrogen phosphate, diammonium hydrogen phosphate, ammonium dihydrogen phosphate, ammonium hydrogen pyrophosphate, ammonium pyrophosphate, ammonium halides and ammonium nitrate; and ammonium salts of an organic acid, such as ammonium acetate. Among them, diammonium hydrogen
25 phosphate is preferable.

In the present production, the ammonium salt is preferably used in amount of 0.001 to 100 mmol based on 1 kg of the solvent used in the present production.

[0051]

5 The reaction mixture obtained by reacting hydrogen, oxygen and an olefin in the presence of a noble metal catalyst prepared by the process of the present invention and a titanasilicate catalyst contains an objective alkylene oxide, an unreacted olefin and an alkane as a by-product. The
10 objective alkylene oxide can be taken out from the reaction mixture by a known purifying means such as separation by distillation.

EXAMPLES

15 [0052]

Hereinafter, the present invention will be described in more detail by way of Examples. Analyzers and analysis methods used in the following examples are as follows.

[0053]

20 (Elemental Analysis)

(1) Content of Pd (palladium atoms) in the activated carbon supporting Pd or the noble metal catalyst was measured by the microwave decomposition/ICP emission spectrometry (the detection limit is 0.01 % by mass or less).

25 (2) Contents of Ti (titanium atoms) and Si (silicon atoms)

in the titanosilicate catalyst were measured by the alkali fusion/dissolution in nitric acid/ ICP emission spectrometry.

[0054]

(Powder X-ray diffractometry)

5 A powder X-ray diffraction pattern of the sample was determined by using the following device under the following conditions.

Device: RINT 2500 V manufactured by Rigaku Denki Co., Ltd.

Radiation Source: Cu K- α radiation

10 Output 40 kV-300 mA

Scanning Field: $2\theta = 0.75^\circ$ to 30°

Scanning Speed: $1^\circ/\text{minute}$

When the measured X-ray diffraction pattern was equal to that disclosed in Fig.1 of EP 1731515, it was concluded that
15 the sample measured was Ti-MWW precursor. When the measured X-ray diffraction pattern was equal to that disclosed in Fig.2 of EP 1731515, it was concluded that the sample measured was Ti-MWW.

[0055]

20 (Ultraviolet-Visible Absorption Spectrum)

The sample was thoroughly pulverized in an agate mortar, and formed into pellets (7 mm ϕ) to prepare a sample for measurement. An ultraviolet-visible absorption spectrum of the sample was determined by using the following device under
25 the following conditions.

Device: a diffusion reflector (Praying Mantis manufactured by HARRICK)

Device Accessory: an ultraviolet-visible spectrophotometer (V-7100 manufactured by JASCO Corporation)

5 Pressure: atmospheric pressure

Measured Value: reflectance

Data Acquisition Time: 0.1 second

Band Width: 2 nm

Measurement Wavelength: 200 to 900 nm

10 Height of Slit: semi-open

Data Acquisition Interval: 1 nm

Baseline Correction (Reference): BaSO₄ pellets (7 mmφ)

When the maximum absorption in a wavelength range of 200 nm to 400 nm appeared in a wavelength range of 210 nm to 230
15 nm, it was concluded that the sample measured was titanosilicate.

[0056]

Example 1

(Production of carrier)

20 A 1 L eggplant flask was charged with 1.8 g of polyvinyl alcohol (manufactured by Wako Pure Chemical Industries, Ltd., degree of polymerization: 500) and 600 mL of water under a nitrogen atmosphere, and the temperature of the mixture was elevated to 90°C with stirring. After the mixture was kept at
25 that temperature for 1 hour, 9.0 g of activated carbon

(manufactured by Japan Enviro Chemicals, Ltd., Special Order Shirasagi) and 50 mL of water were added thereto to obtain a suspension, and then the suspension was kept at that temperature for 4 hours. Then, the heat was removed and the suspension was cooled to a room temperature. After the suspension was filtered, the obtained solid was washed with 200 mL of water, and then was dried in vacuum at 80°C for 10 hours to obtain 10.3 g of Carrier A.

[0057]

10 (Production of noble metal catalyst)

A 500 mL eggplant flask was charged with 3.0 g of Carrier A and 300 mL of water under a nitrogen atmosphere, and the mixture was stirred at room temperature. After that, 50 mL of aqueous dispersion containing 0.29 mmol of palladium (Pd) colloid (manufactured by JGC Catalysts and Chemicals Ltd.) was slowly added dropwise to the obtained suspension at room temperature under a nitrogen atmosphere. After the completion of the dropwise addition, the suspension was stirred at room temperature for further 6 hours under a nitrogen atmosphere. After that, water was removed from the suspension by using a rotary evaporator and the residue was dried in vacuum at 80°C for 10 hours to obtain 3.0 g of Noble Metal Catalyst A. The palladium (Pd) content in the Noble Metal Catalyst A, measured by ICP emission spectrometry, was 0.91% by mass.

25 [0058]

Example 2

(Production of carrier)

A 1 L eggplant flask was charged with 1.8 g of methyl methacrylate polymer (manufactured by Wako Pure Chemical Industries, Ltd.) and 600 mL of water/ethanol solution (volume ratio = 1/4) under a nitrogen atmosphere, and the temperature of the mixture was elevated to 80°C with stirring. After the mixture was kept at that temperature for 1 hour, 9.0 g of activated carbon (manufactured by Japan Enviro Chemicals, Ltd., Special Order Shirasagi) and 50 mL of water/ethanol solution (volume ratio = 1/4) were added thereto to obtain a suspension, and then the suspension was kept at that temperature for 4 hours. Then, the heat was removed and the suspension was cooled to a room temperature. After the suspension was filtered, the obtained solid was washed with 200 mL of water/ethanol solution (volume ratio = 1/4), and then was dried in vacuum at 80°C for 10 hours to obtain 10.8 g of Carrier B.

[0059]

(Production of noble metal catalyst)

A 500 mL eggplant flask was charged with 3.0 g of Carrier B and 300 mL of water under a nitrogen atmosphere, and the mixture was stirred at room temperature. After that, 50 mL of aqueous dispersion containing 0.29 mmol of palladium (Pd) colloid (manufactured by JGC Catalysts and Chemicals Ltd.) was slowly added dropwise to the obtained suspension at room temperature

under a nitrogen atmosphere. After the completion of the dropwise addition, the suspension was stirred at room temperature for further 6 hours under a nitrogen atmosphere. After that, the solvent was removed from the suspension by using a rotary evaporator and the residue was dried in vacuum at 80°C for 10 hours to obtain 2.9 g of Noble Metal Catalyst B. The palladium (Pd) content in the Noble Metal Catalyst B, measured by ICP emission spectrometry, was 0.91% by mass.

[0060]

10 Example 3

(Production of noble metal catalyst)

A 500 mL eggplant flask was charged with 2.7 g of Carrier B and 270 mL of acetonitrile under a nitrogen atmosphere, and the mixture was stirred at room temperature. After that, 50 mL of aqueous dispersion containing 0.27 mmol of palladium (Pd) colloid (manufactured by JGC Catalysts and Chemicals Ltd.) was slowly added dropwise to the obtained suspension at room temperature under a nitrogen atmosphere. After the completion of the dropwise addition, the suspension was stirred at room temperature for further 6 hours under a nitrogen atmosphere. After that, the solvent was removed from the suspension by using a rotary evaporator and the residue was dried in vacuum at 80°C for 10 hours to obtain 2.5 g of Noble Metal Catalyst C. The palladium (Pd) content in the Noble Metal Catalyst C, measured by ICP emission spectrometry, was 0.92% by mass.

[0061]

Example 4

(Production of carrier)

A 1 L eggplant flask was charged with 1.8 g of polystyrene
5 (manufactured by Wako Pure Chemical Industries, Ltd., degree
of polymerization: about 2000) and 600 mL of cyclohexane under
a nitrogen atmosphere, and the temperature of the mixture was
elevated to 80°C with stirring. After the mixture was kept at
that temperature for 1 hour, 9.0 g of activated carbon
10 (manufactured by Japan Enviro Chemicals, Ltd., Special Order
Shirasagi) and 50 mL of cyclohexane were added thereto to obtain
a suspension, and then the suspension was kept at that
temperature for 4 hours. Then, the heat was removed and the
suspension was cooled to a room temperature. After the
15 suspension was filtered, the obtained solid was washed with 200
mL of cyclohexane, and then was dried in vacuum at 80°C for 10
hours to obtain 11.2 g of Carrier C.

[0062]

(Production of noble metal catalyst)

20 A 500 mL eggplant flask was charged with 3.0 g of Carrier
C and 300 mL of water/ethanol solution (volume ratio = 1/1) under
a nitrogen atmosphere, and the mixture was stirred at room
temperature. After that, 50 mL of aqueous dispersion
containing 0.29 mmol of palladium (Pd) colloid (manufactured
25 by JGC Catalysts and Chemicals Ltd.) was slowly added dropwise

to the obtained suspension at room temperature under a nitrogen atmosphere. After the completion of the dropwise addition, the suspension was stirred at room temperature for further 6 hours under a nitrogen atmosphere. After that, the solvent was removed from the suspension by using a rotary evaporator and the residue was dried in vacuum at 80°C for 10 hours to obtain 2.7 g of Noble Metal Catalyst D. The palladium (Pd) content in the Noble Metal Catalyst D, measured by ICP emission spectrometry, was 1.02% by mass.

10 [0063]

Example 5

(Production of noble metal catalyst)

A 500 ml eggplant flask was charged with 2.7 g of Carrier C and 270 mL of acetonitrile under a nitrogen atmosphere, and the mixture was stirred at room temperature. After that, 50 mL of aqueous dispersion containing 0.27 mmol of palladium (Pd) colloid (manufactured by JGC Catalysts and Chemicals Ltd.) was slowly added dropwise to the obtained suspension at room temperature under a nitrogen atmosphere. After the completion of the dropwise addition, the suspension was stirred at room temperature for further 6 hours under a nitrogen atmosphere. After that, the solvent was removed from the suspension by using a rotary evaporator and the residue was dried in vacuum at 80°C for 10 hours to obtain 2.6 g of Noble Metal Catalyst E. The palladium (Pd) content in the Noble Metal Catalyst E, measured

by ICP emission spectrometry, was 0.94% by mass.

[0064]

Preparation Example 1

(Preparation of Pd/AC catalyst)

5 A 1 L eggplant flask was charged with 9.5 g of activated carbon (manufactured by Japan Enviro Chemicals, Ltd., Special Order Shirasagi) and 900 mL of water under an air atmosphere, and the mixture was stirred at room temperature to obtain a suspension. Then, 80 mL of aqueous dispersion containing 0.90
10 mmol of palladium (Pd) colloid (manufactured by JGC Catalysts and Chemicals Ltd.) was slowly added dropwise to the obtained suspension at room temperature under an air atmosphere. After the completion of the dropwise addition, the suspension was stirred at room temperature for further 6 hours under an air
15 atmosphere. After that, the water was removed from the suspension by using a rotary evaporator and the residue was dried in vacuum at 80°C for 10 hours to obtain 9.5 g of Pd/AC Catalyst. The palladium (Pd) content in the Pd/AC Catalyst, measured by ICP emission spectrometry, was 0.95% by mass.

20 [0065]

Preparation Example 2

(Preparation of calcined Pd/AC catalyst)

 Under a nitrogen atmosphere, 2.4 g of the Pd/AC Catalyst obtained in Preparation Example 1 was calcined at 300°C for 6
25 hours to obtain 2.4 g of Calcined Pd/AC Catalyst. The palladium

(Pd) content in the Calcined Pd/AC Catalyst, measured by ICP emission spectrometry, was 1.03% by mass.

[0066]

Preparation Example 3

5 (Preparation of titanosilicate catalyst)

In an autoclave, 899 g of piperidine, 2402 g of pure water, 112 g of tetra-n-butyl orthotitanate, 565 g of boric acid, and 410 g of fumed silica (cab-o-sil M7D) were stirred under an air atmosphere to obtain a gel. After the obtained gel was aged
10 for 1.5 hours, the autoclave was sealed. Subsequently, the temperature of the gel was elevated to 160°C over 8 hours with stirring, and the gel was kept at that temperature for 120 hours to obtain a suspension.

After the obtained suspension was filtered, the filtrate
15 was washed with water until its pH reached about 10. The obtained solid was dried at 50°C until weight loss thereof was no longer observed to obtain 515 g of Solid (a). To 75 g of the obtained solid (a) was added 3750 mL of 2 M nitric acid to obtain a mixture, and then the mixture was refluxed for 20 hours.

20 Subsequently, the mixture was filtered, and the obtained solid was washed with water until its pH reached near-neutral, and then the obtained product was dried in vacuum at 150°C until weight loss thereof was no longer observed to obtain 61 g of a White Powder (a). The X-ray diffraction pattern and the
25 ultraviolet-visible absorption spectrum of the White Powder (a)

were measured. As a result, it was confirmed that the White Powder (a) was a Ti-MWW precursor.

60 g of the obtained White Powder (a) was calcined at 530°C for 6 hours to obtain 54 g of Powder (t). It was confirmed that the obtained Powder (t) was a Ti-MWW from the X-ray diffraction pattern, and that the Powder (t) was titanosilicate having tetra-coordinated Ti from the ultraviolet-visible absorption spectrum. The same manner was repeated two times to obtain a total of 162 g of Powder (t).

An autoclave was charged with 135 g of the obtained Powder (t) at room temperature under an air atmosphere, and 300 g of piperidine and 600 g of pure water were added thereto, and then the mixture was stirred to obtain a gel. After the obtained gel was aged for 1.5 hours, the autoclave was sealed.

Subsequently, the temperature of the gel was elevated to 160°C over 4 hours with stirring, and the gel was kept at that temperature for 24 hours to obtain a suspension.

After the obtained suspension was filtered, the filtrate was washed with water until its pH reached about 9. The obtained solid was dried at 150°C until weight loss thereof was no longer observed to obtain 141 g of White Powder (b). The X-ray diffraction pattern and the ultraviolet-visible absorption spectrum of the White Powder (b) were measured. As a result, the X-ray diffraction pattern of Powder (b) showed a similar pattern to that of Ti-MWW precursor, and it was confirmed that

the White Powder (b) had a structure having fine pores of 12-membered oxygen ring. Furthermore, it was confirmed, from the ultraviolet-visible absorption spectrum, that the White Powder (b) was titanosilicate. The titanium (Ti) content
5 measured by ICP emission spectrometry was 1.61% by mass.

The obtained White Powder (b) was stirred in 80 g of a mixed solvent of water/acetonitrile (mass ratio = 20/80) containing 0.1% by mass of hydrogen peroxide for 1 hour, and then the mixture was filtered and the filtrate was washed with
10 80 g of water to obtain Titanosilicate Catalyst A.

[0067]

Example 6

(Production of propylene oxide)

A 0.3 L autoclave was used as a reactor. The reactor was
15 charged with 2.28 g of Titanosilicate Catalyst A and 0.63 g of Noble Metal Catalyst A, and then the autoclave was sealed. To the autoclave were supplied 339 L/Hr of a mixed gas of oxygen/hydrogen/nitrogen (volume ratio = 3.4/3.8/92.8), 135 g/Hr of solution of water/acetonitrile (mass ratio = 30/70)
20 containing 0.7 mmol/kg of anthraquinone, 3.0 mmol/kg of diammonium hydrogen phosphate, and 54 g/Hr of propylene, and the continuous reaction (retention time: 40 min), in which a solution containing a reaction product (i.e., liquid phase) and a produced gas (i.e., gas phase) were extracted from the
25 reaction mixture and taken out from the reactor through a filter,

was carried out. During the reaction, the temperature of the mixture was adjusted to 50°C, and the internal pressure of the reactor was adjusted to 6.0 MPa (gauge pressure).

The liquid phase and the gas phase taken out after four hours from the start of the reaction were analyzed by a gas chromatography. As a result, propylene oxide was produced in an amount of 200.9 mmol/Hr, and selectivity of by-product propane was 8.3%.

[0068]

10 Example 7

(Production of propylene oxide)

The procedure of Example 6 was repeated except that 0.63 g of Noble Metal Catalyst B was used instead of 0.63 g of Noble Metal Catalyst A. A product amount of propylene oxide and selectivity of by-product propane were analyzed in the same manner as in Example 6. Results are given in Table 1 below.

[0069]

Example 8

(Production of propylene oxide)

20 The procedure of Example 6 was repeated except that 0.63 g of Noble Metal Catalyst C was used instead of 0.63 g of Noble Metal Catalyst A. A product amount of propylene oxide and selectivity of by-product propane were analyzed in the same manner as in Example 6. Results are given in Table 1 below.

25 [0070]

Example 9

(Production of propylene oxide)

The procedure of Example 6 was repeated except that 0.63 g of Noble Metal Catalyst D was used instead of 0.63 g of Noble Metal Catalyst A. A product amount of propylene oxide and selectivity of by-product propane were analyzed in the same manner as in Example 6. Results are given in Table 1 below.

[0071]

Example 10

(Production of propylene oxide)

The procedure of Example 6 was repeated except that 0.63 g of Noble Metal Catalyst E was used instead of 0.63 g of Noble Metal Catalyst A. A product amount of propylene oxide and selectivity of by-product propane were analyzed in the same manner as in Example 6. Results are given in Table 1 below.

[0072]

Comparative Example 1

The procedure of Example 6 was repeated except that 0.63 g of Pd/AC Catalyst was used instead of 0.63 g of Noble Metal Catalyst A. A product amount of propylene oxide and selectivity of by-product propane were analyzed in the same manner as in Example 6. Results are given in Table 1 below.

[0073]

Comparative Example 2

The procedure of Example 6 was repeated except that 0.63

g of Calcined Pd/AC Catalyst obtained in Preparation Example 2 was used instead of 0.63 g of Noble Metal Catalyst A. A product amount of propylene oxide and selectivity of by-product propane were analyzed in the same manner as in Example 6. Results are given in Table 1 below.

[0074]

Table 1

	Example					Comparative Example	
	6	7	8	9	10	1	2
Product amount of propylene oxide (mmol/Hr)	200.9	185.8	189.0	209.3	227.4	137.1	139.7
Selectivity of by-product propane (%)	8.3	6.6	4.4	4.3	3.2	9.5	18.5

[0075]

It was confirmed that a high product amount of propylene oxide was attained by using the noble metal catalysts of Examples 1 to 5, which were produced by the present process.

[0076]

Comparative Example 3

A 0.3 L autoclave was used as a reactor. The reactor was charged with 2.28 g of Titanosilicate Catalyst A and 1.06 g of Calcined Pd/AC Catalyst obtained in Preparation Example 2, and

then the autoclave was sealed. To the autoclave were supplied 281 L/Hr of a mixed gas of oxygen/hydrogen/nitrogen (volume ratio = 3.3/3.6/93.1), 90 g/Hr of solution of water/acetonitrile (mass ratio = 30/70) containing 0.7 mmol/kg of anthraquinone, 3.0 mmol/kg of diammonium hydrogen phosphate, and 36 g/Hr of propylene, and the continuous reaction (retention time: 60 min), in which a solution containing a reaction product (i.e., liquid phase) and a produced gas (i.e., gas phase) were extracted from the reaction mixture and taken out from the reactor through a filter, was carried out. During the reaction, the temperature of the mixture was adjusted to 50°C, and the internal pressure of the reactor was adjusted to 4.0 MPa (gauge pressure).

The liquid phase and the gas phase taken out after 6 hours from the start of the reaction were analyzed by a gas chromatography. As a result, propylene oxide was produced in an amount of 167.7 mmol/Hr. On the other hand, all of the product amounts (mmol/Hr) of propylene oxide in the Examples 6-10 of the present inventions, which are shown in Table 1, were greater than 167.7 mmol/Hr.

INDUSTRIAL APPLICABILITY

[0077]

According to the present process, a catalyst capable of producing an alkylene oxide in a high yield can be provided.

CLAIMS

1. A process for producing a noble metal catalyst,
comprising the steps of:

- 5 1) mixing a carbon material with a resin in a solvent to prepare
a mixture;
2) taking out a carrier from the mixture prepared in the step
1; and
3) supporting a noble metal on the carrier obtained in the step
10 2.

2. The process according to claim 1, wherein the resin is
at least one resin selected from the group consisting of
polyvinyl alcohol, polyvinyl acetate, polymethylmethacrylate
15 and polystyrene.

3. The process according to claim 1 or 2, wherein the noble
metal is at least one metal selected from the group consisting
of palladium, platinum, ruthenium, rhodium, iridium, osmium and
20 gold.

4. A process for producing an alkylene oxide, comprising
reacting hydrogen, oxygen and an olefin in the presence of a
titanosilicate catalyst and a noble metal catalyst produced by
25 the process according to any one of claims 1 to 3.

5. The process according to claim 4, wherein the olefin is propylene.

5 6. The process according to claim 4 or 5, wherein the titanosilicate catalyst is at least one catalyst selected from the group consisting of a titanosilicate having an MWW structure and a precursor thereof.

INTERNATIONAL SEARCH REPORT

International application No
PCT/JP2012/059297

A. CLASSIFICATION OF SUBJECT MATTER INV. B01J21/18 B01J23/38 B01J23/44 B01J29/89 B01J37/02 B01J37/04 B01J37/08 C07D301/00 ADD.		
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) B01J C07D		
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) 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.
X	WO 97/43116 A1 (HYPERION CATALYSIS INT [US]) 20 November 1997 (1997-11-20) abstract page 34, line 20 - page 36, line 11 examples 6-8, 10, 12, 14 -----	1-6
X	EP 1 967 518 A1 (SUMITOMO CHEMICAL CO [JP]) 10 September 2008 (2008-09-10) abstract paragraphs [0007] - [0010], [0022] example 1 -----	1-6
X	US 2005/014636 A1 (ZHOU BING [US] ET AL) 20 January 2005 (2005-01-20) abstract paragraphs [0016] - [0019], [0130], [0187] example 1 -----	1-3
☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* 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 5 July 2012		Date of mailing of the international search report 16/07/2012
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Fischbach, Malaika

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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