

DESCRIPTION

PROCESS FOR PRODUCING TITANIUM-CONTAINING SILICON
OXIDE CATALYST, SAID CATALYST AND PROCESS FOR PRODUCING
5 OXIRANE COMPOUND USING THE SAME

TECHNICAL FIELD

The present invention relates to a process for
10 producing oxirane compounds. More particularly, the
invention relates to a process for producing oxirane
compounds such as propylene oxide by subjecting an
olefin type compound such as propylene to reaction with
a hydroperoxide by applying a titanium-containing
15 silicon oxide catalyst prepared by non-hydrolytic
condensation in the absence of water.

BACKGROUND ART

Methods are known by those skilled in the art that
20 oxirane compounds such as propylene oxide are produced
by subjecting olefin type compounds such as propylene
to reaction with a hydroperoxide in the presence of a
catalyst. As catalysts used for such methods, for
example, a specific titanium-containing silicon oxide
25 catalyst is disclosed in U.S. Patent No. 4,367,342, but
this catalyst is insufficient in view of the yield of
the objective product. In Journal of Molecular Catalysis

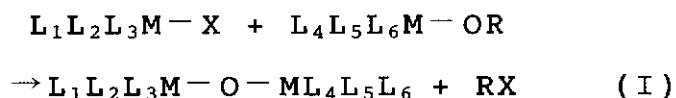
A: Chemical 182-183 (2002) 81-88, a method of epoxidating cyclohexene by using a catalyst prepared by non-hydrolytic condensation in a liquid phase is disclosed, but this disclosure has no description about
5 epoxidating another olefin type compounds other than cyclohexene and the catalyst performance disclosed is unsatisfied in view of abilities exerting high activity and selectivity as an epoxidation catalyst.

10 **DISCLOSURE OF THE INVENTION**

 An object of the present invention is to provide a process for producing oxirane compounds that can produce oxirane compounds in high yield by subjecting an olefin type compound to reaction with a hydroperoxide
15 with using a catalyst which is provided by silylation of a titanium-containing silicon oxide prepared by non-hydrolytic condensation in a liquid phase in the absence of water.

 Namely, the present invention provides a process
20 for producing a titanium-containing silicon oxide catalyst, which comprises subjecting a titanium-containing silicon oxide prepared by non-hydrolytic condensation represented by the following formula (I) in a liquid phase in the absence
25 of water, to silylation, and also a process for producing an oxirane compound, which comprises subjecting an olefin type compound to reaction with a hydroperoxide

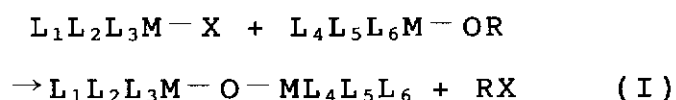
in the presence of said catalyst.



wherein M represents Si or Ti, X represents a halogen
5 group or carboxy group, R represents a hydrogen atom
or hydrocarbon group, and L_1 to L_6 independently
represent an alkoxy group, halogen group, carboxy group,
hydrogen atom or hydrocarbon group.

Another object of the present invention is to
10 provide a process for producing propylene oxide that
can produce propylene oxide in high yield by subjecting
propylene to reaction with a hydroperoxide with using
a titanium-containing silicon oxide catalyst prepared
by non-hydrolytic condensation in a liquid phase in the
15 absence of water.

Namely, the present invention provides a process
for producing propylene oxide, which comprises
subjecting propylene to reaction with a hydroperoxide
in the presence of a titanium-containing silicon oxide
20 catalyst prepared by non-hydrolytic condensation
represented by the following formula (I) in a liquid
phase in the absence of water.

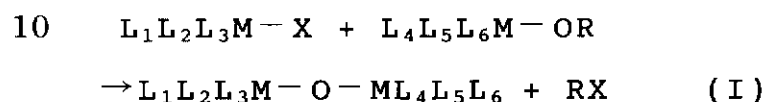


25 wherein M represents Si or Ti, X represents a halogen
group or carboxy group, R represents a hydrogen atom
or hydrocarbon group, and L_1 to L_6 independently

represent an alkoxy group, halogen group, carboxy group, hydrogen atom or hydrocarbon group.

BEST MODE FOR CARRYING OUT THE INVENTION

5 In the present invention, the catalyst can be obtained by silylation of a titanium-containing silicon oxide prepared by non-hydrolytic condensation represented by the following formula (I) in a liquid phase in the absence of water.

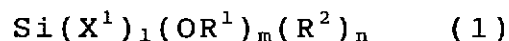


wherein M represents Si or Ti, X represents a halogen group or carboxy group, R represents a hydrogen atom or hydrocarbon group, and L_1 to L_6 independently
15 represent an alkoxy group, halogeno group, carboxy group, hydrogen atom or hydrocarbon group.

An example of the process for preparing the catalyst of the present invention, is explained as follows.

20 As starting, a wet gel of titanium-containing silicon oxide is prepared by gelating a silica source and titanium source by the non-hydrolytic condensation represented by the formula (I) described above in a liquid phase.

25 The silica source used in this reaction may preferably include silicon compounds represented by the following formula (1)



wherein X^1 represents a halogen group or carboxy group,
 R^1 and R^2 independently represents a hydrogen atom or
 hydrocarbon group, and l , m and n are integers of 0 to
 5 4 respectively, $l+m+n=4$ and l or m is 1 or more.

Examples of X^1 include a halogen group such as a
 fluorine, chlorine, bromine and iodine atom and a
 carboxy group such as an acetoxy group; of these,
 chlorine atom is preferable.

10 Examples of R^1 include a hydrocarbon group (which
 may contain a heteroatom such as an oxygen and nitrogen
 atom) such as a methyl group, ethyl group, propyl group,
 isopropyl group and butyl group; preferable is isopropyl
 group in view of gelation rate.

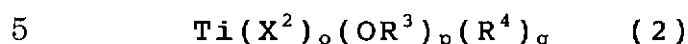
15 R^2 includes, for example, a hydrocarbon group
 (which may contain a heteroatom such as an oxygen and
 nitrogen atom) such as a methyl group, ethyl group,
 propyl group, isopropyl group, butyl group, phenyl group
 and benzyl group.

20 Specific silicon compounds are exemplified by
 silicon tetrachloride, tetraisopropoxysilane,
 methyltrichlorosilane, dimethyldichlorosilane and
 trimethylchlorosilane.

Of these silicon compounds described above, it is
 25 preferable to prepare the gel using as a main component,
 a tetrahalogeno-silane and/or a tetraalkoxy-silane in
 view of stabilization of a gel structure through

strengthening thereof.

The titanium source used may preferably include titanium compounds represented by the following formula (2)



wherein X^2 represents halogen group, R^3 and R^4 independently represents a hydrocarbon group, and o , p and q are integers of 0 to 4 respectively with being $o+p+q=4$.

10 Examples of X^2 includes a halogen group such as a fluorine, chlorine, bromine and iodine atom; of these, chlorine atom is preferable.

Examples of R^3 and R^4 include a hydrocarbon group having 1 to 18 of carbon atoms (which may contain a
15 heteroatom such as an oxygen and nitrogen atom) such as a methyl group, ethyl group, propyl group, isopropyl group, butyl group and phenyl group.

Specific titanium compounds are exemplified by halogeno-titanium compounds such as titanium
20 tetrachloride, titanium alkoxide compounds such as titanium ethoxide, titanium isopropoxide, titanium isobutoxide and titanium t-butoxide, and titanium diisopropoxide (bis-2,4-pentanedionate).

The gel is prepared by mixing the silica source
25 and titanium source described above. The silica source and titanium source may be used alone or in 2 or more kinds thereof, respectively.

In the non-hydrolytic condensation a non-aqueous solvent may be used or not. It is essential that the non-aqueous solvent is substantially free from water, it specifically includes alcohols, ethers, hydrocarbons, halogenated hydrocarbons and the like; and a mixture thereof. The non-aqueous solvent added may react with the silica source or titanium source described above.

A structure-determining agent such as primary to tertiary amines, quaternary ammonium ions and surfactants may be used or not in preparation of the gel.

An amount of titanium source to silica source is usually 10^{-5} to 1 in terms of molar ratio, preferably 0.00008 to 0.4; and more preferably 0.01 to 0.1.

A gelation temperature is usually -30 to 200°C , and the gelation will be accelerated by heating. When being subjected to heating, the gelation is preferably carried out in a sealed pressure-resistant vessel to avoid vaporization of the silica source, titanium source and non-aqueous solvents.

Since the wet gel obtained by the process described above contains the RX represented in the formula (I) described above and/or the non-aqueous solvents, a titanium-containing silicon oxide is obtained by eliminating them with drying. The drying can be carried out at 0 to 200°C under reduced pressure or flow of

a gas such as nitrogen.

A wet gel obtained by subjecting an alkoxide to hydrolytic condensation in the presence of water has a drawback of shrinkage thereof due to the strong
5 capillary force of water being generated during drying, resulting in reduction of surface area and pore volume thereof. To overcome this drawback, a drying with supercritical carbon dioxide is used but this causes other drawback such as requirement of high-pressure
10 equipment.

On the other hand, a wet gel obtained by non-hydrolytic condensation can provide titanium-containing silicon oxide having large surface area and pore volume with a conventional drying facility,
15 because a weak capillary force is permitted by the RX represented in the formula (I) described above and/or non-aqueous solvents while being eliminated by drying.

To use the titanium-containing silicon oxide obtained as a catalyst, the specific surface area
20 thereof is preferably $200 \text{ m}^2/\text{g}$ or more, and more preferably $400 \text{ m}^2/\text{g}$ or more. The specific pore volume is preferably 0.2 ml/g or more.

Propylene oxide can be obtained in high yield by reacting propylene with a hydroperoxide using the
25 titanium-containing silicon oxide obtained by the above-mentioned process as a catalyst.

But, in order to enhance the performance of

catalyst applied to production of an oxirane compound by reacting an olefin type compound such as propylene with a hydroperoxide, it is preferable to subject the titanium-containing silicon oxide to silylation.

5 The silylation is carried out by subjecting a silylating agent to contact with the titanium-containing silicon oxide obtained by non-hydrolytic condensation, followed by conversion of a halogen group and an alkoxy group remaining on the catalyst surface into a silyl group. The silylating agent includes, for example, halogen organic silanes, organic silyl amines and organic silyl amides and derivatives thereof, and organic silazanes. Specifically included are chlorotrimethylsilane, 10 methoxytrimethylsilane, hexamethyldisilazane and the like. The silylation may be carried out in a gas phase or liquid phase. In addition, a solvent may be used or not. The treatment temperature is not particularly limited, but is preferably in the range of 0 °C to 200 °C. 20 The contacting time is also not particularly limited, but is preferably 10 minutes to 10 hours.

The silylation may be carried out after or before drying the wet gel or simultaneously with the gel preparation.

25 The catalyst obtained by the method mentioned above can be particularly suitably used for production of an oxirane compound by subjecting an olefin type compound

to reaction with a hydroperoxide.

The olefin type compound may be a noncyclic-, monocyclic- or polycyclic-olefin type compound as well as a mono-olefin, di-olefin or poly-olefin compound
5 having 3 or more of double bonds. When there exists 2 or more of olefin bonds in a compound, these may be conjugated bond or non-conjugated bond. Commonly preferable are olefin type compounds having 2 to 60 of carbon atoms. The olefin type compounds may have a
10 substituent group, and the substituent group is preferably a one being relatively stable. Examples of the mono-olefin type hydrocarbon include ethylene, propylene, 1-butene, isobutylene, 1-hexene, 2-hexene, 3-hexene, 1-octene, 1-decene, styrene and cyclohexene.
15 Appropriate examples of the di-olefin type compound include butadiene and isoprene. When having substituent group, it is exemplified by a halogen atom, furthermore may be various substituent groups having an oxygen, sulfur or nitrogen atom together with a hydrogen atom
20 and/or a carbon atom. The particularly preferable substituted olefin type compound includes olefin type unsaturated alcohols and olefin type unsaturated hydrocarbons substituted with a halogen, and examples thereof include allyl alcohol, crotyl alcohol and
25 allyl chloride. Particularly suitable olefin type compound is an alkene having 3 to 40 carbon atoms which may be substituted with a hydroxyl group or a halogen

atom.

The hydroperoxide used for converting an olefin type compound into an oxirane compound may includes organic hydroperoxides and hydrogen peroxide, and
5 preferable are organic hydroperoxides.

The organic hydroperoxides are exemplified by cumene hydroperoxide, ethylbenzene hydroperoxide, t-butyl hydroperoxide and the like; most preferable is cumene hydroperoxide.

10 The organic hydroperoxide or hydrogen peroxide to be used may be a diluted or concentrated purified or non-purified product.

The reaction may be carried out in a liquid phase in the presence or absence of a solvent. The solvent
15 is preferably a one present in a liquid state at a temperature and under a pressure of the reaction as well as substantially inactive to reactants and products. The solvent may be a substance present in a hydroperoxide solution used. For example, when a cumene hydroperoxide
20 solution is constituted with a mixture of cumene hydroperoxide and cumene as a raw material therefor, it can be used as the solvent without addition of any other solvent.

The reaction temperature is usually 0 to 200 °C,
25 and preferably 25 to 200 °C. The pressure may be a level enough to maintain the reaction mixture in a liquid state. Commonly advantageous pressure is 100 to 10000 kPa.

The amount of the olefin type compound (by mole) to that of hydroperoxide (by mole) in the reaction is not limited, but is usually 1 or more in terms of molar ratio, and preferably 1 to 50 times by mole.

5 The process of the present invention can be performed in the form of a slurry or fixed bed. The reaction can be carried out by a batch-wise, semi-continuous or continuous method.

10 **EXAMPLE**

The invention is specifically explained with reference to the following Examples.

Example 1

Preparation of catalyst

15 In a pressure-proof ampoule under an inert gas
atmosphere titanium isopropoxide,
tetraisopropoxysilane and silicon tetrachloride were
added in the molar ratio of 1.0 : 4.5 : 5.5 to mix and
then sealed. The weight of the content was 17.6 g. This
20 was subjected to gelation by heating in an oven at 110 °C
for 4 days. After breaking the sealing, a wet gel was
dried under vacuum condition at 150 °C for 4 hours to
obtain 6.1 g of a dry gel. The reddish brown dry gel
obtained was crushed in a mortar to obtain a
25 titanium-containing silicon oxide (powder). This was
used as a catalyst.

Synthesis of propylene oxide

Using the catalyst obtained by the manner described above, a cumene solution of 25 % by weight of cumene hydroperoxide (CHPO) and propylene were subjected to reaction in a reactor (autoclave) to synthesize propylene oxide and the reaction result was evaluated. After charging 1 g of catalyst, 30 g of the cumene solution of CHPO and 17 g of propylene into an autoclave, the reaction was carried out under an autogenous pressure at a reaction temperature of 85 °C for 1.5 hours of reaction time (including the time required for heating up). The reaction result is shown in Table 1.

Example 2

Preparation of catalyst

After putting 3 g of powder obtained in the catalyst preparation of Example 1 in a flask, 2 g of hexamethyldisilazane and 30 g of toluene were mixed therewith, followed by heating at 110 °C for 1.5 hours. After collecting the resulting powder with filtration, it was dried at 110 °C under a reduced pressure of 10 mmHg for 2 hours to obtain a silylated catalyst.

Synthesis of propylene oxide

By using this catalyst obtained, CHPO and propylene were subjected to reaction to synthesize propylene oxide in the same manner as in the propylene oxide synthesis of Example 1. The reaction result is shown in Table 1.

Table 1

Catalyst	Example 1	Example 2
Silylation	No	Yes
Reaction Results		
CHPO Conversion Ratio (%)	48.0	49.1
PO/C3' Selectivity* (%)	93.6	97.9

*: PO/C3' Selectivity = moles of propylene oxide produced / moles of reacted propylene $\times$ 100

5 Example 3

Preparation of catalyst

In a pressure-proof ampoule under an inert gas atmosphere titanium isopropoxide, tetraisopropoxysilane, silicon tetrachloride and trimethylchlorosilane were added in the molar ratio of 1.0 : 8.0 : 7.1 : 7.5, followed by addition of 12 ml of dichloromethane as a solvent to mix and then being sealed. The weight of the content was 26.0 g. This was subjected to gelation by heating in an oven at 110 °C for 4 days. After breaking the sealing, a wet gel was dried under vacuum at 150 °C for 4 hours to obtain 5.1 g of a dry gel. The light red dry gel obtained was crushed in a mortar to obtain a titanium-containing silicon oxide (powder).

Synthesis of propylene oxide

By using the powder obtained by the manner described above as a catalyst, CHPO and propylene were subjected to reaction in a reactor (autoclave) to synthesize propylene oxide and the reaction result was evaluated. After charging 1 g of catalyst, 30 g of a cumene solution containing 25 % by weight of CHPO and 17 g of propylene into the autoclave, the reaction was carried out under an autogenous pressure at a reaction temperature of 85 °C for 1.5 hours of reaction time (including the time required for heating up). Consequently, CHPO conversion was 74.1 % and PO/C3' selectivity was 92.8 %.

Example 4

Preparation of catalyst

After putting 3 g of powder obtained in the same manner as in the catalyst preparation of Example 3 into a flask, 2 g of hexamethyldisilazane and 30 g of toluene were mixed therewith, followed by heating at 110 °C for 1.5 hours. After collecting the powder with filtration, it was dried at 110 °C under a reduced pressure of 10 mmHg for 2 hours to obtain a silylated catalyst.

Synthesis of propylene oxide

Propylene oxide was produced in the same manner as in the synthesis of propylene oxide of Example 3

except using the catalyst obtained in the above catalyst preparation. Consequently, CHPO conversion was 89.0 % and PO/C3' selectivity was 99.2 %.

5 Example 5

Preparation of catalyst

In a pressure-proof ampoule under an inert gas atmosphere titanium tetrachloride, silicon tetrachloride, trimethylchlorosilane, trimethylchlorosilane and diisopropyl ether were added in the molar ratio of 1.0 : 6.0 : 2.0 : 2.0 : 18.0, followed by addition of 15 ml of dichloromethane as a solvent to mix and then being sealed. The weight of the content was 44.4 g. This was subjected to gelation by heating in an oven at 110 °C. After breaking the sealing, a wet gel was dried under vacuum at 150 °C for 4 hours to obtain 5.9 g of a dry gel. The yellowish brown dry gel obtained was crushed in a mortar to obtain a titanium-containing silicon oxide (powder).

20

Synthesis of propylene oxide

Propylene oxide was produced in the same manner as in the synthesis of propylene oxide of Example 3 except using the catalyst obtained in the above catalyst preparation. Consequently, CHPO conversion was 43.6 % and PO/C3' selectivity was 92.4 %.

25

Example 6**Preparation of catalyst**

After putting 3.3 g of powder obtained by the manner same as applied to the catalyst preparation of Example 5 in a flask, 2.3 g of hexamethyldisilazane and 34 g of toluene were mixed therewith, followed by heating at 110 °C for 1.5 hours. After collecting the powder with filtration, it was dried at 110 °C under a reduced pressure of 10 mmHg for 2 hours to obtain a silylated catalyst.

Synthesis of propylene oxide

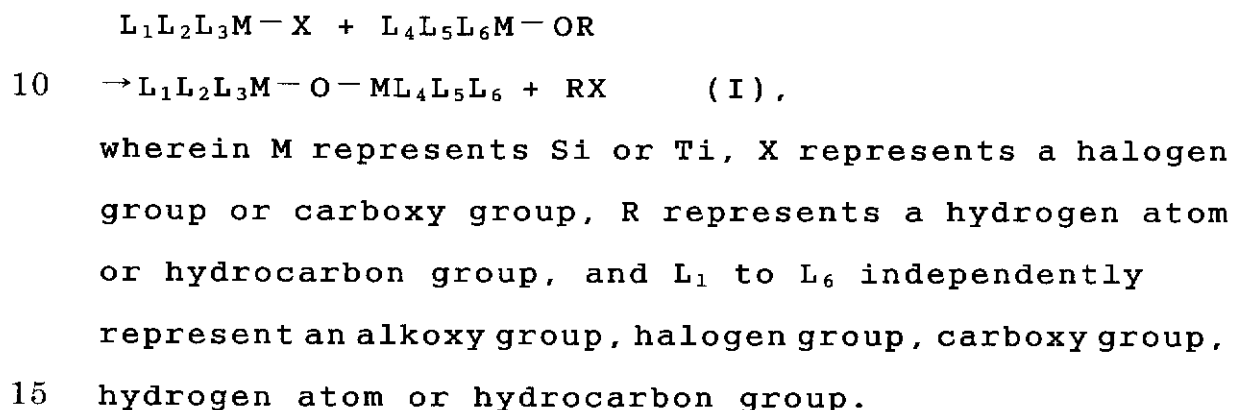
Propylene oxide was produced in the same manner as in the synthesis of propylene oxide in Example 3 except using the catalyst obtained in the above catalyst preparation. Consequently, CHPO conversion was 72.8 % and PO/C3' selectivity was 99.6 %.

INDUSTRIAL APPLICABILITY

As explained above, the present invention can provide a process for producing a titanium-containing silicon oxide catalyst which can apply to a reaction for obtaining an oxirane compound in high production yield from an olefin type compound such as propylene and a hydroperoxide, and a process for efficiently producing an oxirane compound by using said catalyst.

CLAIMS

1. A process for producing a titanium-containing silicon oxide catalyst, comprising subjecting a titanium-containing silicon oxide prepared by non-hydrolytic condensation represented by the following formula (I) in a liquid phase in the absence of water to silylation.



2. A titanium-containing silicon oxide catalyst obtained by the process according to Claim 1.

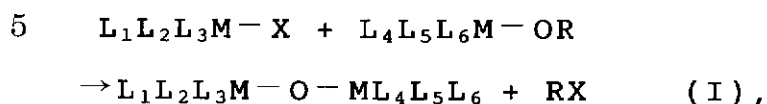
3. A process for producing an oxirane compound, comprising subjecting an olefin type compound to reaction with a hydroperoxide in the presence of the titanium-containing silicon oxide catalyst of Claim 2.

4. The process according to Claim 3, wherein the olefin type compound is propylene.

5. The process according to Claim 3, wherein the hydroperoxide is an organic hydroperoxide.

6. A process for producing propylene oxide, comprising subjecting propylene to reaction with a

hydroperoxide in the presence of a titanium-containing silicon oxide catalyst prepared by non-hydrolytic condensation represented by the following formula (I) in a liquid phase in the absence of water



wherein M represents Si or Ti, X represents a halogen group or carboxy group, R represents a hydrogen atom or hydrocarbon group, and L_1 to L_6 independently
 10 represent an alkoxy group, halogen group, carboxy group, hydrogen atom or hydrocarbon group.

7. The process according to Claim 6, wherein the hydroperoxide is cumene hydroperoxide.