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SPECIFICATION

PROCESS FOR PRODUCING PROPYLENE OXIDE

TECHNICAL FIELD

The present invention relates to a process for producing propylene oxide. More particularly, the invention relates to a process for producing propylene oxide, wherein said process for producing propylene oxide has excellent characteristics that propylene is converted to propylene oxide using isopropylbenzene hydroperoxide obtained from isopropylbenzene, as an oxygen carrier, that said isopropylbenzene can be repeatedly used, and that formation of by-products after an epoxidation step can be reduced to a small amount thereby to suppress a loss of isopropylbenzene to small.

BACKGROUND ART

A process in which propylene is oxidized using ethylbenzene hydroperoxide as an oxygen carrier to give propylene oxide and styrene is known as Halcon process. Since, in this process, styrene is inevitably produced together with propylene oxide, it is unsatisfactory from the viewpoint that only propylene oxide is to be selectively produced.

On the other hand, a concept of a process in which propylene is converted to propylene oxide using isopropylbenzene hydroperoxide obtained from isopropylbenzene, as an oxygen carrier, and said isopropylbenzene is repeatedly used, is

described in Czechoslovak Patent No. CS 140,743. The process described in said patent does not contain precise descriptions concerning necessary steps except oxidation step, epoxidation step and hydrogenolysis step. Various problems arise in practical recycling of isopropylbenzene and therefore the patent cannot be said as sufficient for industrial realization.

DISCLOSURE OF THE INVENTION

Under such circumstances, an object of the present invention is to provide a process for producing propylene oxide, wherein said process for producing propylene oxide has excellent characteristics that propylene is converted to propylene oxide using isopropylbenzene hydroperoxide obtained from isopropylbenzene, as an oxygen carrier, that said isopropylbenzene can be repeatedly used, and that formation of by-products after an epoxidation steps can be reduced to a small amount thereby to suppress a loss of isopropyl benzene to small.

Namely, the invention relates to a process for producing propylene oxide, which comprises steps described below, wherein the concentration of isopropylbenzene hydroperoxide in a solution containing cumyl alcohol at completion of the epoxidation step is 5 % by weight or less:

oxidation step; a step in which isopropylbenzene is oxidized to obtain isopropylbenzene hydroperoxide,

epoxidation step; a step in which isopropylbenzene hydroperoxide obtained in the oxidation step is reacted with propylene to obtain propylene oxide and cumyl alcohol, and

hydrogenolysis step; a step in which cumyl alcohol obtained in the epoxidation step is subjected to hydrogenolysis to obtain isopropylbenzene, and said isopropylbenzene is recycled to the oxidation step as a raw material for the oxidation step.

BEST MODE FOR CARRYING OUT THE INVENTION

The oxidation step in the present invention is a step in which isopropylbenzene is oxidized to obtain isopropylbenzene hydroperoxide. The oxidation of isopropylbenzene is usually effected by autoxidation with oxygen-containing gas such as the air, an oxygen-enriched air or the like. The oxidation reaction may be carried out without any additive or with an additive such as an alkali. The reaction temperature is usually 50 to 200°C, and the reaction pressure is usually between the atmospheric pressure and 5 MPa. In the oxidation with an additive, the alkali includes alkali metal compounds such as NaOH, KOH and aqueous solutions thereof; and alkaline earth metal compounds, alkali metal carbonates such as Na_2CO_3, $NaHCO_3$, ammonia, $(NH_4)_2CO_3$, alkali metal ammonium carbonates and the like and aqueous solutions thereof.

The epoxidation step in the present invention is a step in which isopropylbenzene hydroperoxide obtained in the oxidation step is reacted with propylene to obtain propylene oxide and cumyl alcohol. From a viewpoint that the desired product should be obtained in a high yield and under a high selectivity, the epoxidation step is preferably conducted in the presence of a catalyst containing a titanium-containing

silicon oxide. The catalyst is preferably a catalyst containing titanium chemically bound to silicon oxide, so-called titanium-silica catalyst. Examples may include products carrying a titanium compound on a silica carrier, products in which a titanium compound is compounded with a silicon oxide by a co-precipitation or sol-gel method, titanium-containing zeolite compounds and the like.

In the present invention, isopropylbenzene hydroperoxide used as the raw material for the epoxidation step may be a dilute or thick purification or non-purification product.

The epoxidation reaction is carried out by contacting propylene and isopropylbenzene hydroperoxide with a catalyst. The reaction may be conducted in a liquid phase using a solvent. The solvent must be a liquid under the reaction temperature and pressure, and substantially inert to the reactants and the product. The solvent may be composed of a substance existing in a solution of the hydroperoxide used. When, for example, isopropylbenzene hydroperoxide is a mixture with isopropylbenzene as the raw material, it is also possible to use said material, without adding a solvent in particular, as the solvent. Other useful solvents include aromatic single-ring compounds (for example, benzene, toluene, chlorobenzene and o-dichlorobenzene), alkane (for example, octane, decane and dodecane) and the like. The epoxidation temperature is generally 0 to 200°C and preferably 25 to 200°C. The pressure may be any pressure sufficient to keep liquid state of the reaction mixture. Generally, the pressure is

advantageously 100 to 10,000 kPa.

The epoxidation can advantageously be carried out with a catalyst in the form of a slurry or a fixed-bed. The fixed-bed is preferred in the case of a large-scale industrial operation. In addition, the reaction can be carried out by a batch process, a semi-continuous process, a continuous process or the like. When a liquid containing the raw materials for reaction is passed through a fixed-bed, the catalyst is not contained at all or substantially in a liquid mixture discharged from a reaction zone.

The hydrogenolysis step in the present invention is a step in which cumyl alcohol obtained in the epoxidation step is subjected to hydrogenolysis to obtain isopropylbenzene, and said isopropylbenzene is recycled to the oxidation step as the raw material for the oxidation step. In other words, the same product, i.e. isopropylbenzene, used in the oxidation step is recovered. The hydrogenolysis is usually carried out by contacting cumyl alcohol and hydrogen with a catalyst. As a catalyst, any catalyst having a hydrogenation ability can be used. Examples of the catalyst include metal catalysts of metals of the group 8th to 10th such as those of cobalt, nickel, palladium and the like and metal catalysts of metals of the group 11th or 12th metals such as those of copper, zinc and the like. Copper catalysts are preferred from the viewpoint that by-products are suppressed. The copper catalysts include copper, Raney copper, copper-chromium, copper-zinc, copper-chromium-zinc, copper-silica, copper-alumina and the like. The reaction can

be conducted in a liquid phase using a solvent or in a gaseous phase. The solvent must be substantially inert to the reactants and the product. The solvent may contain a substance existing in a solution of the cumyl alcohol used. When, for example, cumyl alcohol is a mixture with isopropylbenzene as the product, it is unnecessary to add a solvent in particularly and said product may act as a solvent. Other useful solvents include alkane (for example, octane, decane and dodecane), aromatic single-ring compounds (for example, benzene, ethylbenzene and toluene), and others. The temperature for the hydrogenolysis reaction is generally 0 to 500°C and preferably 30 to 400°C. Generally, the pressure is advantageously 100 to 10,000 kPa. The hydrogenolysis can advantageously be carried out with a catalyst in the form of a slurry or a fixed-bed. The process of the present invention can be carried out by a batch process, a semi-continuous process or a continuous process. When a solution or a gas containing the raw materials for reaction is passed through a fixed-bed, the catalyst is not contained at all or substantially in a liquid mixture discharged from the reaction zone.

In the present invention, it is essential that the concentration of isopropylbenzene hydroperoxide in a solution containing cumyl alcohol is 5% by weight or less, preferably 3% by weight or less when the epoxidation step is completed. Herein, the solution containing cumyl alcohol indicates a solution composed of components which are liquid under the ordinary temperature and the ordinary pressure, and is a solution mainly composed of isopropylbenzene and cumyl alcohol, and

unreacted propylene is not contained.

Isopropylbenzene hydroperoxide remained after the epoxidation is decomposed in the hydrogenolysis step and converted to acetophenone causing a loss of isopropylbenzene.

Further, a cumene dimer forms also causing a loss of isopropylbenzene and this component causes to a blockage trouble in the system. When a recovery step of unreacted propylene and propylene oxide is set up after the epoxidation step, a loss of isopropylbenzene is also caused in this step.

From these view points, it is necessary to control the concentration of isopropylbenzene hydroperoxide in the solution containing cumyl alcohol, when the epoxidation step is completed, within the range of the present invention.

As a method of controlling the isopropylbenzene hydroperoxide concentration, any method of a method of converting to cumyl alcohol; a method of converting to another compound by a reaction after the epoxidation step; removing all or part of isopropylbenzene hydroperoxide to outside of the system of the steps in the present invention by distillation, extraction or the like; a method of reducing the concentration by absorption or the like; and the like, may be used.

Taking account of convenience of the process, it is preferable to convert most part of isopropylbenzene hydroperoxide.

Further, in the present invention, the concentration of an organic acid of the solution containing isopropylbenzene hydroperoxide to be supplied to the epoxidation step is

preferably 0.5 % by weight or less, more preferably 0.1 % by weight or less.

By specifying within this range, the activity of the catalyst used in the epoxidation step can be maintained at high level and the life of the catalyst can be kept for longer time.

Still further, in the present invention, it is preferable that isopropylbenzene hydroperoxide supplied to an epoxidation step has not undergone a heat history including heating at a temperature not lower than the temperature (t ℃) represented by the following equation(1),

$$t\ (℃) = 150 - 0.8 \times W \qquad (1)$$

W: content (% by weight) of isopropylbenzene hydroperoxide in a solution containing isopropylbenzene hydroperoxide.

By specifying within this range, the activity of the catalyst used in the epoxidation step can be maintained at a high level and the life of the catalyst can be kept for longer time.

Moreover, in the present invention, the concentration of sodium of the solution containing isopropylbenzene hydroperoxide to be supplied to the epoxidation step is preferably 0.1 % by weight or less.

By specifying within this range, the activity of the catalyst used in the epoxidation step can be maintained at high level and the life of the catalyst can be kept for longer time.

Moreover, in the present invention, the concentration of water of the solution containing isopropylbenzene hydroperoxide to be supplied to the epoxidation step is

preferably 1 % by weight or less.

By specifying within this range, the activity of the catalyst used in the epoxidation step can be maintained at a high level, the life of the catalyst can be kept for longer time, and further, the epoxidation yield can be maintained higher.

Example 1

A solution containing cumyl alcohol having a isopropylbenzene hydroperoxide concentration of 1 % by weight is continuously passed through a fixed bed flowing reactor in the presence of a copper-chromium catalyst at a rate of 2 times by mol of hydrogen per 1 mol of cumyl alcohol contained in the solution. The conversion of cumyl alcohol is kept almost 100 % by controlling the inlet temperature. At this case, the reaction temperature is 180℃, and the composition of the hydrogenolysis reaction liquid is as follows:

Hydrogenolysis liquid composition	
Isopropylbenzene hydroperoxide	0 % by weight
Cumyl alcohol	0 % by weight
Isopropylbenzene	97.5 % by weight
Acetophenone	1.1 % by weight
Cumene dimer	0.3 % by weight

Comparative Example 1

When the hydrogenolysis is carried out in the same manner as in Example 1 except that the solution containing cumyl alcohol having a isopropylbenzene hydroperoxide concentration of 11 % by weight, the composition of the hydrogenolysis reaction liquid is as follows:

Isopropylbenzene hydroperoxide	0 % by weight
Cumyl alcohol	0 % by weight
Isopropylbenzene	93.6 % by weight
Acetophenone	5.5 % by weight
Cumene dimer	0.9 % by weight

Compared to Example 1, acetophenone and cumene dimer clearly increase and a loss of isopropylbenzene becomes large.

INDUSTRIAL APPLICABILITY

As described above, according to the present invention, there can be provided a process for producing propylene oxide, wherein said process for producing propylene oxide has excellent characteristics that propylene is converted to propylene oxide using isopropylbenzene hydroperoxide obtained from isopropylbenzene, as an oxygen carrier, that said isopropylbenzene can be repeatedly used, and that formation of by-products after an epoxidation step can be reduced to a small amount thereby to suppress a loss of isopropylbenzene to small.

CLAIMS

1. A process for producing propylene oxide, which comprises steps described below, wherein the concentration of isopropylbenzene hydroperoxide in a solution containing cumyl alcohol is 5 % by weight or less when the epoxidation step is completed:

oxidation step; a step in which isopropylbenzene is oxidized to obtain isopropylbenzene hydroperoxide,

epoxidation step; a step in which isopropylbenzene hydroperoxide obtained in the oxidation step is reacted with propylene to obtain propylene oxide and cumyl alcohol, and

hydrogenolysis step; a step in which cumyl alcohol obtained in the epoxidation step is subjected to hydrogenolysis to obtain isopropylbenzene, and said isopropylbenzene is recycled to the oxidation step as a raw material for the oxidation step.

2. The process according to claim 1, wherein the concentration of isopropylbenzene hydroperoxide is 3% by weight or less.